Keywords: azo compounds · bond order · copper · EPR spectroscopy · radical ions

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[5] a) Synthesis of abcp: A solution of lithium hypochlorite (50 g, 0.856 mol) in water (300 mL) was cooled until it began to solidify (external bath temperature −30°C). A solution of 2-aminopyrimidine (5 g, 52.5 mmol) in H_2O (100 mL) was then added slowly and carefully. After completion, the orange-red reaction mixture was warmed to room temperature and extracted several times with dichloromethane. The organic phase was then purified by chromatography on silica gel (CH_2Cl_2/Et_2O, 2/1) to yield the separated red mono- and dichlorinated azo compounds. The ligand abcp was obtained in a yield of 1.20 g (18%). Correct C,H,N analysis; ^1H NMR (250 MHz, 300 K, $CDCl_3$): $\delta = 8.93$ (s). b) Synthesis of **1**-PF_6: The ligand abcp (51 mg, 0.20 mmol) and $[Cu(PPh_3)_4](PF_6)$ (503 mg, 0.40 mmol) were treated for two hours at −70°C in dichloromethane (10 mL). The addition of Et_2O after the mixture had warmed to room temperature precipitated the dark blue product, which was then redissolved in THF (10 mL). Careful addition of Et_2O (about 1 mL) produced a dark blue, partially crystalline material (178 mg, 54%). We attribute the reduction to the presence of excess PPh_3 (see J. W. Hershberger, R. J. Klingler, J. K. Kochi, *J. Am. Chem. Soc.* **1983**, *105*, 61). EPR (CH_2Cl_2, 298 K or 110 K): $g = 2.0077$; UV/Vis (CH_2Cl_2, 300 K): λ_{max} (ε) = 700 (1560), 560 (2350), 403 (6400), 373 (6270) nm ($M^{-1}\,cm^{-1}$); cyclic voltammetry (CH_2Cl_2/0.1 M Bu_4NPF_6): $E_{pa}(ox) = 1.42$ V, $E_{1/2}(red1) = 0.06$ V, $E_{1/2}(red2) = -0.75$ V versus Fc^+/Fc^0 at a scan rate of 100 mV s^{-1}.

[6] Crystal structure analysis of **1**-$(PF_6)\cdot 2THF$: $C_{80}H_{64}Cl_2Cu_2F_6N_6P_5\cdot 2C_4H_8O$, $M_r = 1720.50$ g mol^{-1}, crystal size 0.4 × 0.3 × 0.6 mm, triclinic, space group $P\bar{1}$, $a = 11.5353(9)$, $b = 14.4228(10)$, $c = 14.8086(11)$ Å, $\alpha = 88.040(5)$, $\beta = 70.643(6)$, $\gamma = 66.855(5)°$, $V = 2124.2(3)$ Å^3, $Z = 1$, $\rho_{calcd} = 1.439$ g cm^{-3}, $3.08° < 2\theta < 50°$; 8694 reflections (7472 independent; $h = -14$ to 14, $k = -17$ to 18, $l = -18$ to 19) were collected at −90°C, 7198 reflections were used for the refinement. $R = 0.0578$ [$I > 2\sigma(I)$], $wR_2 = 0.1748$; Siemens P4 diffractometer with graphite monochromator and $Mo_{K\alpha}$ radiation (0.71073 Å). The structure was solved by direct methods (Siemens SHELXS-86) and refined with full-matrix least-square methods (SHELXL-93). Two solvent molecules had to be included, one of which was disordered. Anisotropic thermal parameters were refined for all non-hydrogen atoms. Hydrogen atoms were introduced at calculated positions and refined freely (riding model). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101074. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[12] Note added in proof (July 24, 1998): The molecular structure of Ru complexes of azoaromatic radical anions will be reported by A. Chakravorty et al.

Highly Enantioselective Catalytic Hetero-Diels–Alder Reaction with Inverse Electron Demand[**]

Jacob Thorhauge, Mogens Johannsen, and
Karl Anker Jørgensen[*]

The hetero-Diels–Alder reaction of α,β-unsaturated carbonyl compounds with electron-rich alkenes gives excellent access to substituted 3,4-dihydro-2*H*-pyrans that are very useful precursors for the synthesis of carbohydrates and natural products.[1] The reaction is controlled by the LUMO of the α,β-unsaturated carbonyl compound and the HOMO of the dienophile; electron-withdrawing substituents on the former greatly enhances the reactivity.[1, 2]

Although the reaction usually is highly regioselective, Lewis acids can improve both regioselectivity and reaction rate.[1c] A variety of different achiral Lewis acids, such as $EtAlCl_2$,[3] Me_2AlCl,[3] $ZnCl_2$,[3] $TiCl_4$,[3] Eu(fod)$_3$,[4] Yb(fod)$_3$,[5] $LiClO_4$,[6] $Mg(ClO_4)_2$,[6] and $SnCl_4$[7] have been shown to catalyze inverse hetero-Diels–Alder reactions (fod = 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octadiene).

Although much work has been devoted to the diastereoselective hetero-Diels–Alder reaction with inverse electron demand,[3a, b, 8] the enantioselective addition of electron-rich alkenes to α,β-unsaturated carbonyl compounds with chiral Lewis acids as catalysts is still a relatively unexplored field and only very few reactions have been reported. Examples include the intramolecular cycloaddition of an oxadiene with a diisopropylideneglucose–titanium complex as catalyst (33–88% *ee* for the tetracyclic product),[9] and a reaction catalyzed by *trans*-(4,5-dihydro-4,5-diphenyloxazole)–$Mg(ClO_4)_2$ which yields both ene and hetero-Diels–Alder products in a 89:11 ratio (89% *ee* for the ene product).[1c] Kanemasa has reported an intermolecular hetero-Diels–Alder reaction with inverse electron demand in which the enantioselective addition of (*E*)-oxo-phenylsulfonyl-3-alkenes to enol ethers

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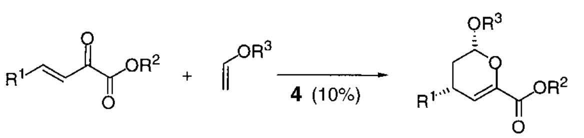
gives dihydropyran adducts in good yields (77–96%) and with enantioselectivities of 59–97% with $TiBr_2$–TADDOLate as the catalyst (TADDOL = tetraphenyl-1,3-dioxolan-4,5-dimethanol).[4b, 10] During the writing of this paper, we became aware of recent work by Evans et al., who have studied the copper(II) bis(dihydrooxazole) catalyzed hetero-Diels–Alder reaction between α,β-unsaturated acylphosphonates and vinyl ethers.[11]

We report here a novel and highly diastereo- and enantioselective catalytic hetero-Diels–Alder reaction of β,γ-unsaturated α-keto esters **1**, substituted in the γ position with alkyl, aryl, and alkoxy substituents, with the electron-rich alkenes **2** to give very attractive dihydropyran adducts **3** [Eq. (1)]. The products thus formed are very useful precursors for the synthesis of carbohydrates and natural products.



(1)

1a: R^1 = Me, R^2 = Et
1b: R^1 = Ph, R^2 = Me
1c: R^1 = OEt, R^2 = Et

2a: R^3 = Et
2b: R^3 = *t*Bu

3a: R^1 = Me, R^2 = Et, R^3 = Et
3b: R^1 = Ph, R^2 = Me, R^3 = Et
3c: R^1 = OEt, R^2 = Et, R^3 = Et
3d: R^1 = OEt, R^2 = Et, R^3 = *t*Bu

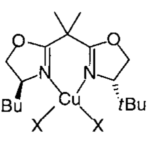
The results of the [4+2] cycloaddition reaction of **1a** with **2a** in the presence of various copper(II) catalysts **4a**, **c**–**f**[12] are presented in Table 1 (OTf = trifluoromethylsulfonate).

Table 1. Results of the reaction **1a** + **2a** → **3a** in the presence of the catalysts **4a**, **c**–**f** (10 mol%).

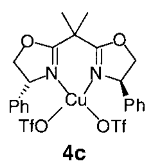
Entry	Catalyst	Solvent	*T* [°C]	Conv. [%]	*ee* [%][a]
1	**4a**	CH_2Cl_2	–45	100	95.6
2	**4a**	CH_2Cl_2	–78	100	97.5
3	**4a**	THF	–45	100	99.0
4	**4a**	THF	–78	100 (89)[b]	99.7
5	**4a**	CH_3NO_2	–20	100	75.8
6	**4c**	CH_2Cl_2	–78	100	63.8
7	**4d**	CH_2Cl_2	–78	95	72.4
8	**4e**	CH_2Cl_2	–78	< 10	< 5
9	**4f**	CH_2Cl_2	–78	10	64.9

[a] Determined by GC on a chiral stationary phase. [b] Yield of isolated product.

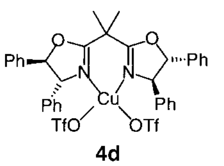
The enantioselectivity induced with **4a** is superior to that induced by **4c**–**f**. The reaction of **1a** and **2a**, catalyzed by **4a** in CH_2Cl_2 at –45 °C, shows complete conversion, and gives the hetero-Diels–Alder product **3a** with 95.6% *ee* (Table 1, entry 1). This is improved to 97.5% when the reaction temperature is reduced to –78 °C (entry 2). The use of THF as solvent leads to a further improvement; **3a** is obtained with 99.0% *ee* at –45 °C, and at –78 °C it is isolated in 89% yield and with 99.7% *ee* (entries 3 and 4). A high conversion is also observed with nitromethane as the solvent, but the *ee* value drops to 75.8% (entry 5). The two phenyl-substituted copper(II) bis(dihydrooxazole)s **4c**, **d** also catalyze the reaction of **1a** with **2a**, but although high conversion is obtained, the *ee* value of **3a** is only moderate (entries 6 and 7). Catalysts **4e**, **f** are much less effective than **4a**, **c**, **d,** and only a low *ee* value of **3a** is observed (entries 8 and 9).



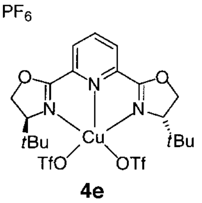
4a: X = OTf
4b: X = PF_6



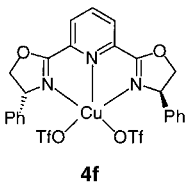
4c



4d



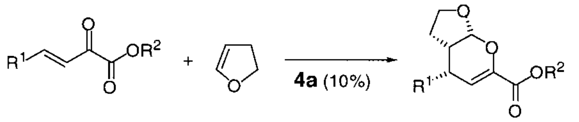
4e



4f

The absolute stereochemistry of the hetero-Diels–Alder product **3a** is dependent on the catalyst; both **4a** and **4c** give the same enantiomer of **3a**—an opposite stereochemistry in the ligand leads to the same absolute stereochemistry in the product.[13] In contrast, **4d** and **4f** give opposite absolute stereochemistries of **3a**.

The scope and the potential of the hetero-Diels–Alder reaction catalyzed by the copper(II) bis(dihydrooxazole)s **4a**, **b** are demonstrated for the reaction of various γ-substituted β,γ-unsaturated α-keto esters **1a**–**c** with the electron-rich alkenes **2a**, **b** [Eq. (1)] and **2c** [Eq. (2)]. The results for the reactions are presented in Table 2.



(2)

1a: R^1 = Me, R^2 = Et
1b: R^1 = Ph, R^2 = Me
1c: R^1 = OEt, R^2 = Et

2c

3f: R^1 = Me, R^2 = Et
3g: R^1 = Ph, R^2 = Me
3h: R^1 = OEt, R^2 = Et

Table 2. Results of the hetero-Diels–Alder reaction of **1a**–**c** with **2a**–**c** in the presence of the catalysts **4a**, **b** (10 mol%) at –78 °C in THF.

Entry	Catalyst	1	2	Product[a]	Yield [%][b]	*ee* [%]
1	**4a**	**1a**	**2a**	**3a**	89	> 99.5[c]
2	**4a**	**1b**	**2a**	**3b**	95	99.5[d]
3	**4a**	**1c**	**2a**	**3c**	93	> 99.5[c]
4	**4b**	**1c**	**2a**	**3c**	88	96.8[c, e]
5	**4a**	**1c**	**2b**	**3d**	61[f]	90.4[c]
6	**4a**	**1a**	**2c**	**3f**	51[14]	> 99.5[c]
7	**4a**	**1b**	**2c**	**3g**	96	99.5[c]
8	**4a**	**1c**	**2c**	**3h**	84	97.5[c, g]

[a] All *de* values are greater than 98%, except for **3g** (95%). [b] Yield of isolated product. [c] Determined by GC on a chiral stationary phase. [d] Determined by HPLC on a chiral stationary phase. [e] CH_2Cl_2 as solvent. [f] Two diastereomers: 4:1, < 10% *ee* for the minor diastereomer. [g] Reaction temperature –45 °C.

The β,γ-unsaturated α-keto esters **1a**–**c** react with **2a** in the presence of **4a** (10 mol%) in THF at –78 °C to give the hetero-Diels–Alder products **3a**–**c** in high yields and with very high enantiomeric excess (≥ 99.5% *ee*; Table 2, entries 1–3). When the anion of the catalyst is changed from OTf^- to PF_6^-, a small decrease in the yield and enantioselectivity of **3c** is observed (88%, 96.8% ee, entry 4). The use of **2b** as the alkene decreases the diastereoselectivity, as now two diastereomers are formed in a ratio of 4:1 (60% *de*). The hetero-Diels–Alder product **3d** is isolated in 61% yield, and the major diastereomer has an *ee* value of 90.4% (entry 5). The drop in the *ee* value is probably due to steric repulsion between the *tert*-butyl substituent and the chiral catalyst in the preferred *endo* transition state for the reaction.

The cyclic enol ether **2c** is also an excellent substrate for the enantioselective reaction catalyzed by **4a**. Reaction of **2c** with **1a** leads to the formation of adduct **3f** in 51% yield,[14] and only one enantiomer can be detected by GC on a chiral stationary phase (*ee* > 99.5%; Table 2, entry 6). The reaction of **1b** is also highly enantioselective, and **3g** is isolated in 96% yield and with 99.5% *ee* (entry 7). The introduction of an ethoxy substituent in the substrate, **1c**, leads likewise to a very selective reaction, as **3h** is obtained in 84% yield and with 97.5% *ee*. The *endo* approach of the alkene was confirmed by an X-ray analysis of the cycloadduct **3h**.

The generality and potential of these highly enantioselective hetero-Diels–Alder reactions with inverse electron demand catalyzed by **4a** are evident from the results presented in Table 2. High yields and very high enantiomeric excess are obtained with alkyl-, aryl-, and alkoxy-substituted oxadienes, and both acyclic and cyclic dienophiles can be used. The reaction thus offers a new and promising method for the synthesis of natural compounds and novel carbohydrates.

Experimental section

3b: Catalyst (*S*)-**4a** was prepared by the addition of $Cu(OTf)_2$ (36 mg, 0.1 mmol) to 2,2′-isopropylidenebis[(4*S*)-4-*tert*-butyl-2-oxazoline] (31 mg, 0.105 mmol) dissolved in dry THF (2 mL) under N_2, followed by stirring for 1 h. Compound **1b** (190 mg, 1.0 mmol) was added to the catalyst solution, which was then cooled to −78 °C. Freshly distilled **2a** (143 µL, 1.5 mmol) was added, and the solution was stirred at this temperature for 50 h. Pentane (2 ml) was then added, and the mixture was filtered through a silica plug with pentane/Et_2O (1/1). The solvent was evaporated, and the crude product was purified by flash chromatography (pentane/Et_2O 90/10) to give **3b** as a pale yellow oil in 95% yield and with 99.5% *ee*, determined by HPLC with a chiral OD column (hexane/*i*PrOH 98/2, 1.0 mL min^{-1}). $[\alpha]^{D}_{20} = +2.1^\circ$ ($c = 1.06$, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.34-7.20$ (m, 5H; C_6H_5), 6.16 (dd, $J = 3.2$, 1.1 Hz, 1H; C=CH), 5.16 (dd, $J = 7.7$, 2.2 Hz, 1H; C-6H), 4.04 (dq, $J = 9.3$, 7.1 Hz, 1H; $OC\mathit{H}HCH_3$), 3.81 (s, 3H; OCH_3), 3.73 (ddd, $J = 9.5$, 7.0, 3.2 Hz, 1H; C-4H), 3.63 (dq, $J = 9.3$, 7.1 Hz, 1H; $OC\mathit{H}HCH_3$), 2.31 (dddd, $J = 13.5$, 7.0, 2.2, 1.1 Hz, 1H; C-5*H*H), 1.97 (ddd, $J = 13.5$, 9.5, 7.7 Hz, 1H; C-5*H*H), 1.23 (t, $J = 7.1$ Hz, 3H; $OCH_2C\mathit{H}_3$); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 163.2$, 142.8, 142.3, 128.6, 127.5, 126.8, 114.5, 100.0, 64.7, 52.2, 37.8, 36.0, 15.1. The reaction has also been run on a gram scale to give **3b** in quantitative yield and with high selectivity (>99% *ee*, >98% *de*).

3h: The catalyst was prepared as described above. Compound **1c** (172 mg, 1 mmol) was added to the catalyst solution, which was then cooled to −78 °C and treated with freshly distilled **2c** (151 µL, 2 mmol). The solution was warmed to −45 °C and stirred for 50 h. Pentane (2 mL) was then added, and the mixture was filtered through a silica plug with pentane/Et_2O (1/1). After evaporation of the solvent, the crude product was purified by flash chromatography (pentane/Et_2O, 75/25) to give **3h** as a highly crystalline, colorless solid in 84% yield and with 97.5% *ee* (determined by GC with a Chrompack Chirasil-DEX CB column). One recrystallization from Et_2O gave the enantiopure product. X-ray spectroscopy confirmed the expected *endo* structure of the product. $[\alpha]^{D}_{20} = -32.1^\circ$ ($c = 1.06$, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 6.01$ (dd, $J = 2.2$, 1.5 Hz, 1H; C=CH), 5.66 (d, $J = 4.0$ Hz, 1H; C-2H), 4.50 (dd, $J = 6.6$, 2.2 Hz, 1H; C-4H), 4.26 (dq, $J = 4.4$, 7.1 Hz, 2H; $OC\mathit{H}_2CH_3$), 4.24 (ddd, $J = 17.9$, 9.2, 3.5 Hz, 1H; C-7a*H*H), 3.97 (dt, $J = 9.2$, 8.1 Hz, 1H; C-7a*H*H), 3.60 (q, $J =$ 7.1 Hz, 2H; $OC\mathit{H}_2CH_3$), 2.75 (m, 1H; C-3H), 2.01 (m, 2H; C-3a*H*H), 1.31 (t, $J = 7.1$ Hz, 3H; $OCH_2C\mathit{H}_3$)1.24 (t, $J = 7.1$ Hz, 3H; $OCH_2C\mathit{H}_3$); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 162.1$, 141.6, 108.6, 102.2, 70.6, 68.4, 64.3, 61.4, 42.5, 23.7, 15.4, 14.2.

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