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Synthesis and catalytic activity of an electron-deficient copper–ethylene triazapentadienyl complex†

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The copper(I) ethylene complex $[N\{(C_3F_7)C(Dipp)N\}_2]Cu(C_2H_4)$ (Dipp = 2,6-diisopropylphenyl) has been synthesized by treating $[N\{(C_3F_7)C(Dipp)N\}_2]Cu(NCCH_3)$ with ethylene at room temperature. $[N\{(C_3F_7)C(Dipp)N\}_2]Cu(C_2H_4)$ is an air stable, yellow solid. X-Ray crystallographic data of $[N\{(C_3F_7)C(Dipp)N\}_2]Cu(C_2H_4)$ show that the 1,3,5-triazapentadienyl ligand coordinates to copper in κ^2-fashion. The copper atom adopts a trigonal-planar geometry. $[N\{(C_3F_7)C(Dipp)N\}_2]Cu(C_2H_4)$ and $[N\{(C_3F_7)C(Dipp)N\}_2]Cu(NCCH_3)$ effectively catalyze carbene and nitrene transfer to a variety of substrates in high efficiencies.

Introduction

There has been a considerable amount of interest in the synthesis and catalytic properties of nitrogen based ligand supported transition metal complexes, in particular those containing fluorinated analogs of the venerable tris(pyrazoyl)borate ligand.[1–7] For example, ligands such as $[HB(3,5\text{-}(CF_3)_2Pz)_3]^-$, in addition to permitting the stabilization of a variety of unusual complexes of the coinage metals, support silver adducts such as $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(THF)$ and $[HB(3,5\text{-}(CF_3)_2Pz)_3]Ag(C_2H_4)$ that have been shown to catalyze a variety of carbene transfer reactions, including the formation and rearrangement of halonium ylides.[1,8–13] As a continuation of this effort, we have recently reported the preparation and some coordination chemistry of highly fluorinated 1,3,5-triazapentadienyl (TAP) ligands,[14–17] a closely related analogs of the popular 1,5-diazapentadienyl (β-diketiminate) systems. While the chemistry of 1,5-diazapentadienyl systems have been widely investigated,[18] the same is not true of the metal adducts of triaza analogs,[1,19–30] and as far as we are aware, there is only one note of the use of fluorinated triazapentadienyl complexes as catalysts.[14] Herein, we report the synthesis and characterization of an easily isolable copper–ethylene complex, and its utility as a group transfer catalyst.

Results and discussion

The copper(I) ethylene complex $[N\{(C_3F_7)C(Dipp)N\}_2]Cu(C_2H_4)$ (**2**) was prepared by treating $[N\{(C_3F_7)C(Dipp)N\}_2]Cu(NCCH_3)$ (**1**)[17] with ethylene at room temperature (Fig. 1). Alternatively, $[N\{(C_3F_7)C(Dipp)N\}_2]Cu(C_2H_4)$ can also be synthesized using the lithium salt of the triazapentadienyl ligand $[N\{(C_3F_7)C(Dipp)N\}_2]Li$ and CuOTf and ethylene. $[N\{(C_3F_7)C(Dipp)N\}_2]Cu(C_2H_4)$ is an air stable, yellow solid. ^1H and ^{13}C NMR signals of copper(I)-coordinated ethylene in $CDCl_3$ appear at 3.37 and 86.0 ppm, respectively (*cf*. for free ethylene ^1H and ^{13}C signals at 5.40 and 123.3 ppm, respectively).

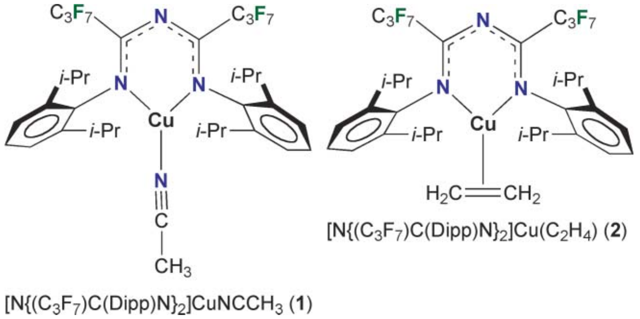

Fig. 1 1,3,5-Triazapentadienyl complexes of copper, $[N\{(C_3F_7)C(Dipp)N\}_2]CuL$ (L = $NCCH_3$ (**1**), C_2H_4 (**2**)).

A number of well authenticated copper(I)–ethylene adducts are known.[9] $[HC\{(Me)C(2,6\text{-}Me_2C_6H_3)N\}_2]Cu(C_2H_4)$ represents a three-coordinate copper–ethylene adduct supported by a 1,5-diazapentadienyl ligand.[31] The ethylene ^{13}C NMR signal in this adduct was observed at δ 74.7 ppm. In general, up-field shift of ethylene carbons in diamagnetic metal adducts has been attributed to the increased shielding caused by the metal-to-ethylene π-back-donation.[32–34] Thus $[N\{(C_3F_7)C(Dipp)N\}_2]Cu(C_2H_4)$, with an ethylene ^{13}C NMR signal at 86.0 ppm, displays relatively less Cu→ethylene π-backbonding. This is not suprising considering the presence of two fluoroalkyl groups and an extra nitrogen atom on the ligand backbone of the $[N\{(C_3F_7)C(Dipp)N\}_2]Cu(C_2H_4)$.

Addition of an excess of ethylene to $CDCl_3$ solutions of $[N\{(C_3F_7)C(Dipp)N\}_2]Cu(C_2H_4)$ yielded two sharp signals at 5.40 ppm (for free ethylene) and 3.37 ppm (coordinated ethylene in $[N\{(C_3F_7)C(Dipp)N\}_2]Cu(C_2H_4)$), indicating no observable ethylene exchange on the NMR time scale at the room temperature. However with $[N\{(C_3F_7)C(2,6\text{-}Cl_2C_6H_3)N\}_2]Cu(C_2H_4)$ and $[N\{(C_3F_7)C(C_6F_5)N\}_2]Cu(C_2H_4)$, a similar experiment led to the coalescence of the bound ethylene signal.[14,15]

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Treatment of $CDCl_3$ solutions of $[N\{(C_3F_7)C(Dipp)N\}_2]Cu(C_2H_4)$ with CO at room temperature led to quantitative formation of $[N\{(C_3F_7)C(Dipp)N\}_2]CuCO$,[17] as evident from the disappearance of the ethylene signal in the ^1H NMR spectrum and the appearance of ^1H NMR signals corresponding to $[N\{(C_3F_7)C(Dipp)N\}_2]CuCO$. The formation of the Cu–CO adduct was further confirmed by IR spectroscopy (ν_{CO} band at 2109 cm^{-1}). This process is reversible. It is possible to obtain $[N\{(C_3F_7)C(Dipp)N\}_2]Cu(C_2H_4)$ by treating a $CDCl_3$ solution of $[N\{(C_3F_7)C(Dipp)N\}_2]CuCO$ with an excess of ethylene.

Crystals of $[N\{(C_3F_7)C(Dipp)N\}_2]Cu(C_2H_4)$ which were subjected to X-ray crystallography, exhibited twinning, but this issue was resolved satisfactorily. The resulting X-ray crystal structure is illustrated in Fig. 2. The basic features are similar to those observed for $[N\{(C_3F_7)C(C_6F_5)N\}_2]Cu(C_2H_4)$ and $[HC\{(Me)C(2,6\text{-}Me_2C_6H_3)N\}_2]Cu(C_2H_4)$.[15,31] The 1,3,5-triazapentadienyl ligand coordinates to copper in κ^2-fashion. The copper atom adopts a trigonal planar geometry. The average Cu–N, average Cu–C and C=C distances of $[HC\{(Me)C(2,6\text{-}Me_2C_6H_3)N\}_2]Cu(C_2H_4)$ and $[N\{(C_3F_7)C(Dipp)N\}_2]Cu(C_2H_4)$ are 1.912(2), 1.989(2), 1.365(3) Å and 1.9404(9), 1.9999(11), 1.3518 (14) Å, respectively.

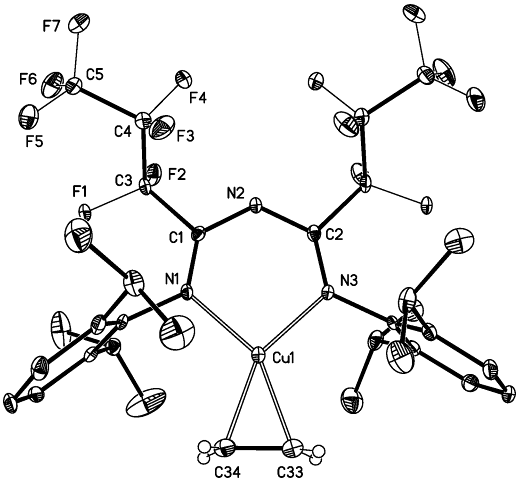
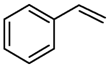
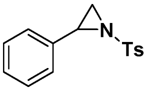
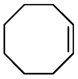
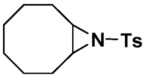
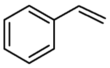
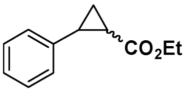
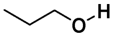
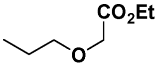
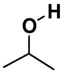
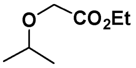
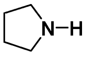
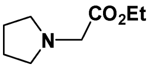
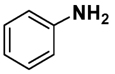
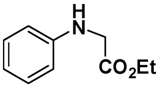
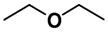
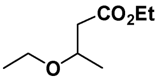
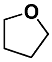
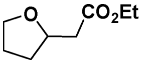


Fig. 2 Molecular structure of $[N\{(C_3F_7)C(Dipp)N\}_2]Cu(C_2H_4)$ (**2**). Selected distances (Å) and angles (°): Cu(1)–N(1) 1.9403(9), Cu(1)–N(3) 1.9406(9), Cu(1)–C(34) 1.9974(11), Cu(1)–C(33) 2.0006(11), C(33)–C(34) 1.3518(14); N(1)–Cu(1)–N(3) 95.55(4), C(34)–Cu(1)–C(33) 39.52(4).

Catalytic properties of metal adducts of fluorinated triazapentadienyl ligands have not been explored in detail. Therefore we wished to establish whether $[N\{(C_3F_7)C(Dipp)N\}_2]Cu(C_2H_4)$ (**2**) would function as an atom transfer catalyst as this would provide a platform for further developments of this unique scaffold. In addition, the corresponding acetonitrile complex $[N\{(C_3F_7)C(Dipp)N\}_2]Cu(NCCH_3)$ (**1**) was investigated for comparative purposes.

Initial experiments were conducted with the nitrene precursor, TsN=IPh, and two alkene substrates styrene and cyclooctene.[35–38] Gratifyingly both complexes effect nitrene transfer, providing the corresponding aziridines in excellent yield (entries 1 and 2, Table 1). It was also found that on reaction of styrene with ethyl diazoacetate (EDA), both complexes serve as carbene transfer agents providing the expected cyclopropane as a diastereomeric mixture (entry 3, Table 1), favoring the *cis*-isomer (1.6 : 1).[39]

Table 1 Products and yields from atom transfer reactions catalyzed by copper complexes **1** and **2** (experimental details given in ESI†)

Entry	Substrate	Product	Product yield[a] (%)	
			1[b]	**2**[b]
1		 N Ts	98	96
2		 N–Ts	76	76
3		 CO_2Et	97 (1.6)[c]	93 (1.6)[c]
4	 O H	 CO_2Et O	85	90
5	 O H	 O CO_2Et	85	91
6	 N–H	 N CO_2Et	80	93
7	 NH_2	 H N CO_2Et	85	~100
8	 O	 CO_2Et O	94	92
9	 O	 O CO_2Et	98	98

[a] The yields correspond to chromatographically purified materials and are the average of at least two independent runs. [b] The reactions shown in entries 1, 2, 3, 8 and 9 are conducted with 5 mol% of **1** or **2** while the others (entries 4–7) were run at 2 mol% of the catalyst. [c] *Cis* : *trans* ratio determined by ^1H NMR spectroscopy.

Similarly, the combination of catalysts **1** or **2** with EDA resulted in carbene insertion into O–H bonds of alcohols (entries 4 and 5, Table 1), N–H bonds of amines (entries 6 and 7, Table 1), and C–H bonds of ethers, all of which proceed in excellent chemical yields (entries 8 and 9, Table 1).[6,36,40–44]

Conclusions

Fluorinated 1,3,5-triazapentadienyl supporting ligand $[N\{(C_3F_7)C(Dipp)N\}_2]^-$ allows the isolation of a thermally stable copper(I) ethylene complex $[N\{(C_3F_7)C(Dipp)N\}_2]Cu(C_2H_4)$ in good yield. $[N\{(C_3F_7)C(Dipp)N\}_2]Cu(C_2H_4)$ and the related acetonitrile analog $[N\{(C_3F_7)C(Dipp)N\}_2]Cu(NCCH_3)$ function as effective carbene and nitrene transfer catalysts on treatment with ethyl diazoacetate or TsN=IPh, respectively. These reactions proceed in excellent yields and in the case of carbene transfer this occurs with *minimal* carbene dimerization, a common by-product in these reactions.

Experimental

General procedures

All manipulations were carried out under an atmosphere of purified nitrogen using standard Schlenk techniques or in a Drybox. Solvents were purchased from commercial sources, purified using Innovative Technology SPS-400 PureSolv solvent drying system or by distilling over conventional drying agents and degassed by the freeze–pump–thaw method prior to use. Glassware was oven-dried at 150 °C overnight. NMR at 25 °C on a JEOL Eclipse 500 and 300 spectrometers (^{1}H: 500.16 MHz or 300.53 MHz; ^{13}C: 125.77 MHz or 75.57 MHz; ^{19}F: 470.62 MHz or 282.78 MHz). Proton and carbon chemical shifts are reported in ppm *vs.* Me_4Si. ^{19}F NMR chemical shifts were referenced relative to external $CFCl_3$. Elemental analyses were performed using a Perkin Elmer Series II CHNS/O analyzer. Melting points were obtained on a Mel-Temp II apparatus and were not corrected. $(CuOTf)_2$·benzene, *n*-butyllithium, ethylene, ethyl diazoacetate and silica gel, 200–400 mesh, 60 Å were purchased from commercial sources. $[N\{(C_3F_7)C(Dipp)N\}_2]H$ (Dipp = 2,6-diisopropylphenyl),[17] $[N\{(C_3F_7)C(Dipp)N\}_2]Cu(NCCH_3)$[17] and *N*-(*p*-toluenesulfonyl)phenyliodinane[45] were synthesized using published procedures.

$[N\{(C_3F_7)C(Dipp)N\}_2]Cu(C_2H_4)$. $[N\{(C_3F_7)C(Dipp)N\}_2]Cu(NCCH_3)$ (0.10 g, 0.12 mmol) was dissolved in *n*-hexane (15 mL) and C_2H_4 was bubbled into the solution for about 3 min. After stirring for 1 h under C_2H_4 atmosphere, the solvent was removed in several steps using reduced pressure and an ethylene stream to assure the removal of acetonitrile from the solution without losing the coordinated ethylene. The resulting residue was then dissolved in CH_2Cl_2–*n*-hexane (1 : 3) (4 mL) and cooled to –20 °C to obtain needle shaped crystals of $[N\{(C_3F_7)C(Dipp)N\}_2]Cu(C_2H_4)$. Yield: 0.084 g (85%). Mp: darkens at 120 °C and melts completely at 155 °C. ^{19}F NMR ($CDCl_3$): δ –80.36 (triplet, 6F, J_{FF} = 10.1 Hz, CF_3), –105.59 (quartet, 4F, J_{FF} = 10.1 Hz, α-CF_2), –121.90 (s, 4F, β-CF_2). ^{1}H NMR ($CDCl_3$): δ 7.09 (s, 6H, *m,p*-Ar), 3.37 (s, 4H, C_2H_4), 2.94 (septet, 4H, J_{HH} = 6.9 Hz, CH), 1.21 (d, 12H, J_{HH} = 6.9 Hz, CH_3), 1.12 (d, 12H, J_{HH} = 6.9 Hz, CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): (selected) δ 86.0 (s, C_2H_4). ^{19}F NMR (C_6D_6): δ –80.34 (t, 6F, J_{FF} = 10.9 Hz, CF_3), –105.16 (quartet, 4F, J_{FF} = 10.9 Hz, α-CF_2), –121.46 (s, 4F, β-CF_2). ^{1}H NMR (C_6D_6): δ 6.98 (s, 6H, *m,p*-Ar), 3.26 (s, 4H, C_2H_4), 3.11 (septet, 4H, J_{HH} = 6.9 Hz, CH), 1.21 (d, 12H, J_{HH} = 6.9 Hz, CH_3), 1.05 (d, 12H, J_{HH} = 6.9 Hz, CH_3). ^{13}C NMR (C_6D_6): (selected) δ 86.1 (t, $^1J_{CH}$ = 158 Hz, C_2H_4). Anal. Calc. for $C_{34}H_{38}N_3F_{14}Cu$: C, 49.91; H, 4.68; N, 5.14. Found: C, 49.54; H, 4.81; N, 5.06%.

$[N\{(C_3F_7)C(Dipp)N\}_2]Cu(C_2H_4)$ can also be synthesized using the lithium salt of the triazapentadiene ligand. *n*-Butyllithium (0.2 mL, 1.6 M in hexanes) was added dropwise to a *n*-hexane (25 mL) solution of $[N\{(C_3F_7)C(Dipp)N\}_2]H$ (0.233 g, 0.32 mmol) at –78 °C. After the addition, the reaction mixture was allowed to warm slowly to room temperature and stirred for further 2 h. The solvent was removed under reduced pressure to obtain a white solid. It was dissolved in CH_2Cl_2 (10 mL) and then transferred *via* a cannula to a flask containing $(CuOTf)_2$·benzene (0.081 g, 0.16 mmol). Ethylene (1 atm) was bubbled into this mixture for about 1 min. The mixture was then stirred at room temperature for 1 h under a C_2H_4 atmosphere. *n*-Hexane (5 mL) was added and the mixture stirred for further 5 min. It was filtered through a bed of Celite, the filtrate was collected and the solvents were removed under reduced pressure to yield $[N\{(C_3F_7)C(Dipp)N\}_2]Cu(C_2H_4)$ as a yellow powder (0.21 g, 80%).

X-Ray crystallographic data

A suitable crystal covered with a layer of cold hydrocarbon oil was selected and mounted with paratone-N oil in a cryo-loop and immediately placed in the low-temperature nitrogen stream. The X-ray intensity data were measured at 100(2) K on a Bruker SMART APEX CCD area detector system equipped with a Oxford Cryosystems 700 Series cooler, a graphite monochromator, and a Mo-Kα fine-focus sealed tube (λ = 0.710 73 Å). The crystals show twinning, but it was resolved satisfactorily using Cell_Now (two cell domains with the second domain rotated from first domain by 180° degrees about the reciprocal axis (–0.093 0.000 1.000) and real axis (0.000 0.000 1.000)). The data frames were integrated with the Bruker SAINT-Plus software package. Data were corrected for absorption effects using the multi-scan technique (SADABS). Structures were solved and refined using the Bruker SHELXTL (Version 6.14) software package. All the non hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at calculated positions and refined riding on the corresponding carbons.

Crystal data: $C_{34}H_{38}CuF_{14}N_3$, monoclinic, $P2_1/n$, 100 K; a = 10.4857(4), b = 23.4593(9), c = 14.9020(6) Å, β = 97.622(1)°, V = 3633.3(2) Å^3, Z = 4; $R1$, $wR2$ ($I > 2\sigma(I)$) = 0.0431, $wR2$ = 0.0643, GOOF = 1.031.

General procedure for nitrene transfer reactions with catalysts $[N\{(C_3F_7)C(Dipp)N\}_2]CuL$ (L = $NCCH_3$ or C_2H_4) and *N*-(*p*-toluenesulfonyl)phenyliodinane

Aziridination of alkenes. A solution of alkene (0.5 mmol of styrene or cyclooctene) and *N*-(*p*-toluensulfonyl)phenyliodinane (0.5 mmol) were stirred in acetonitrile (1 mL) at room temperature for 2 min. The catalyst (5 mol%) was added at once, and the resulting mixture was stirred at room temperature overnight. C_6Me_6 (0.0275 mmol, 4.5 mg) was added as the internal standard. The reaction mixture was diluted with CH_2Cl_2 (25 mL), filtered through a short plug of Celite and concentrated under reduced pressure. The mixture was subjected to flash chromatography (SiO_2, hexanes–ethyl acetate (9 : 1)) and the eluent concentrated to dryness. The yields were estimated using ^{1}H NMR spectroscopy by integration of product resonances relative to the internal standard. The NMR data of the products (*N*-(*p*-toluenesulfonyl)-2-phenylaziridine[46–48] and *N*-(*p*-toluenesulfonyl)-9-azabicyclo[6.1.0]nonane[48,49]) have been reported previously (and are given in the ESI†).

General procedure for carbene transfer reactions with catalysts $[N\{(C_3F_7)C(Dipp)N\}_2]CuL$ (L = $NCCH_3$ or C_2H_4) and ethyl diazoacetate

Cyclopropanation of styrene. The catalyst (0.025 mmol, 5 mol%) and styrene (0.45 mL, ~4 mmol) were dissolved in CH_2Cl_2 (8.5 mL) and stirred for 3 min. Ethyl diazoacetate (0.057 g, 0.5 mmol) in CH_2Cl_2 (5 mL) was added to this mixture solution by automatic syringe over a period of ~2 h. The resulting solution was stirred overnight at room temperature, filtered through a short plug of Celite, the solvent evaporated and the residue was purified by flash chromatography on SiO_2 (hexanes–ethyl ether (9 : 1)) yielding the desired product as a colourless oil. The yield was calculated based on the weight of the isolated and purified product, ethyl 2-phenylcyclopropane-1-carboxylate[50,51] (see ESI† for NMR data).

O–H insertion in alcohols. Ethyl diazoacetate (0.057 g, 0.5 mmol) dissolved in CH_2Cl_2 (5 mL) was added by an automatic syringe over a period of ~2 h to a stirred solution of the catalyst (0.010 mmol, 2 mol%) and alcohol (1 mmol of 1-propanaol or 2-propanol) in CH_2Cl_2 (9 mL). The resulting mixture was stirred overnight at room temperature. C_6Me_6 (0.0275 mmol, 4.5 mg) was added as the internal standard. The mixture was filtered through a short plug of Celite and the solvent evaporated to dryness. The residue was purified by flash chromatography on SiO_2 (hexanes–ethyl acetate (9 : 1)) and the eluent concentrated to dryness. The yields were estimated using ^1H NMR spectroscopy by integration of product resonances relative to the internal standard. The NMR data of the products (ethyl propoxyacetate[42] and ethyl isopropoxyacetate[42]) have been reported previously (and are given in the ESI section).

N–H insertion in amines. Ethyl diazoacetate (0.057 g, 0.5 mmol) dissolved in CH_2Cl_2 (5 mL) was added by an automatic syringe over a period of ~2 h to a stirred solution of the catalyst (0.010 mmol, 2 mol%) and the amine (0.5 mmol of pyrrolidine or aniline) in CH_2Cl_2 (9 mL). The resulting mixture was stirred overnight at room temperature. C_6Me_6 (0.0275 mmol, 4.5 mg) was added as the internal standard. The mixture was filtered through a short plug of Celite, the solvent evaporated and the residue was purified by flash chromatography on SiO_2 (hexanes–ethyl acetate (9 : 1)). The yields were estimated using ^1H NMR spectroscopy by integration of product resonances relative to the internal standard. The NMR data of the products (ethyl *N*-pyrrolidinylacetate[44] and ethyl 2-(phenylamino)acetate[44]) have been reported previously (and are given in the ESI†).

C–H insertion in ethers. Ethyl diazoacetate (0.057 g, 0.5 mmol) dissolved in the ether (5 mL) was added by an automatic syringe over a period of ~2 h to a stirred solution of the catalyst (0.025 mmol, 5 mol%) in the ether (9 mL of diethyl ether or tetrahydrofuran). The resulting mixture was stirred overnight at room temperature, filtered through a short plug of Celite, the solvent evaporated and the residue was purified by flash chromatography on SiO_2 (hexanes–ethyl ether (9 : 1)) yielding the desired products as colourless oils. The yields were calculated based on the weights of isolated and purified products, ethyl 3-ethoxybutanoate[52] and ethyl (tetrahydrofuran-2-yl)acetate[52] (see ESI† for NMR data).

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