Journal of Alloys and Compounds 488 (2009) 518–523

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Insertion reactions of scandium pyridyl complexes supported by a ferrocene diamide ligand

Colin T. Carver, Paula L. Diaconescu*

Department of Chemistry & Biochemistry, University of California, Los Angeles, CA 90095, United States

ARTICLE INFO

Article history:
Received 30 May 2008
Received in revised form
25 September 2008
Accepted 6 October 2008
Available online 25 November 2008

Keywords:
Scandium
Pyridyl
Ferrocene
Ethylene
Alkyne
Butadiene

ABSTRACT

Unlike reported examples of early transition metal η^2(N,C)-pyridyl complexes, scandium η^2(N,C)-pyridyl complexes supported by a ferrocene diamide ligand react further with pyridines to give coupling products. Although most of their insertion reactions with unsaturated substrates are similar to those of previous yttrocene and zirconocene complexes, in the reaction with butadiene, higher reactivity than the one reported for the yttrocene complex was observed. Herein are discussed reactions of η^2(N,C)-pyridyl scandium complexes supported by a 1,1′-ferrocene diamide ligand with ethylene, 2-butyne, and 1,3-butadiene.

1. Introduction

Methods to functionalize heterocycles have been of long standing interest given the ubiquitous presence of these structures in biological compounds [1–8]. Pioneered by Jordan in the early 1990s, [9–12] the functionalization of N-heterocycles using early transition metal alkyl complexes has found numerous applications [13–25]. These reactions usually involve the insertion of an unsaturated substrate into the metal–carbon bond of a strained metallaaziridine and the formation of a new four or five-member ring metallocycle.

We have recently reported on scandium and yttrium alkyl complexes supported by a 1,1′-ferrocene diamide ligand [26] and their reactions with aromatic heterocycles [27]. Unlike Cp^*_2ScMe, [28] these complexes react with pyridines to give C–C coupled products and ring-open imidazole to give an imidazole–imine–amide product. Given this different reactivity behavior, we became interested in isolating an η^2(N,C)-scandium complex analogous to $Cp^*_2Sc(\eta^2$-N,C-pyridyl) and explore its reactions with unsaturated substrates.

2. Experimental

All experiments were performed under a dry nitrogen atmosphere using standard Schlenk techniques or an MBraun inert-gas glovebox. Solvents were purified using a two-column solid-state purification system by the method of Grubbs [29] and transferred to the glovebox without exposure to air. NMR solvents were obtained from Cambridge Isotope Laboratories, degassed, and stored over activated molecular sieves prior to use. Scandium oxide was purchased from Stanford Materials Corporation, 4 Meadowpoint, Aliso Viejo, CA 92656, and used as received. Sc(fc[NSi^{t}BuMe$_2$]$_2$)(CH$_2$Xy-3,5)(THF) (1^{CH_2Ar}-THF), [26] Sc(fc[NSi^{t}BuMe$_2$]$_2$)Me(THF)$_2$ (1^{Me}-THF), [26] and Sc(fc[NSi^{t}BuMe$_2$]$_2$)(η^2-N,C-6-Ph-pyridyl)(THF), 2-py^{Ph}, [27] were prepared following published procedures. The aromatic heterocycles were distilled or recrystallized before use; all other materials were used as received. ^{1}H NMR spectra[1] were recorded on Bruker300 or Bruker500 spectrometers at room temperature in C_6D_6 unless otherwise specified. Chemical shifts are reported with respect to internal solvent, 7.16 ppm (C_6D_6). CHN analyses were performed by UC Berkeley Micro-Mass facility, 8 Lewis Hall, College of Chemistry, University of California, Berkeley, CA 94720.

2.1. Synthesis of Sc(fc[NSi^{t}BuMe$_2$]$_2$)(η^2-N,C-pyridyl)(py), 2-py

1^{Me}-THF (150 mg, 0.232 mmol) was placed in a Schlenk tube in toluene (10 mL), and 4 equiv of pyridine (73.4 mg, 0.928 mmol) was added. The reaction mixture was warmed to 70 °C for 5 h. The solvent was removed and the resulting yellow solid was extracted with hexanes. Yield 79.8 mg, 53.4%, as two crops from hexanes. ^{1}H NMR (300 MHz, C_6D_6): δ, ppm: 9.12 (d, 2H, NC_5H_5), 8.32 (d, 1H, NC_5H_5 or NC_5H_4), 8.02 (d, 1H, NC_5H_5 or NC_5H_4), 7.23 (m, 1H, NC_5H_5 or NC_5H_4), 6.94 (m, 1H, NC_5H_5

* Corresponding author.
E-mail address: pld@chem.ucla.edu (P.L. Diaconescu).

0925-8388/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2008.10.007

[1] This material is based upon work supported by the NSF grant CHE-9974928.

or NC_5H_4), 6.80 (m, 1H, NC_5H_5 or NC_5H_4), 6.71 (m, 2H, NC_5H_5), 4.19 (bs, 4H, fc-C*H*), 3.62 (bs, 4H, fc-C*H*), 0.84 (s, 18H, SiC(CH_3)$_3$), −0.16 (s, 12H, Si(CH_3)$_2$). ^{13}C NMR (126 MHz, C_6D_6): δ, ppm: 144.1, 134.1, 130.4, 122.3, 104.6, 67.6, 27.7, 20.6, −3.0. Anal. for $C_{32}H_{47}FeN_4Si_2Sc$. Calcd.: C, 59.61%; H, 7.35%; N, 8.69%. Found: C, 59.65%; H, 7.51%; N, 8.51%.

2.2. Reaction of Sc(fc[NSi^{t}BuMe$_2$]$_2$)(η^2-N,C-pyridyl)(py), 2-py, with ethylene

2-py (15 mg, 0.0232 mmol) was dissolved in C_6D_6 (1.5 mL); this solution was placed in a J-Young tube and 10 psi of ethylene was introduced. The reaction mixture was allowed to stand at room temperature and monitored by ^{1}H NMR spectroscopy. The reaction is complete in 4 h and quantitative. Alternately, the insertion product can be formed directly from $1^{CH_2{}^{Ar}}$-THF and pyridine under an atmosphere of ethylene. In a 50-mL Schlenk tube, $1^{CH_2{}^{Ar}}$-THF (200 mg, 0.295 mmol) was combined with 2 equiv of pyridine (46.6 mg, 0.589 mmol) in toluene (8 mL) and ethylene (10 psi) was introduced. The reaction mixture was stirred at 70 °C for 18 h. The solvent was removed and the resulting yellow solid was extracted in hexanes and filtered through Celite. Yield 167 mg, 84.3%, as 2 crops from hexanes. ^{1}H NMR (300 MHz, C_6D_6): δ, ppm: 9.30 (bs, 2H, NC_5H_5), 8.59 (d, 1H, NC_5H_5 or NC_5H_4), 6.98 (tr, 1H, NC_5H_5 or NC_5H_4), 6.89 (tr, 1H, NC_5H_5 or NC_5H_4), 6.85 (d, 1H, NC_5H_5 or NC_5H_4), 6.70 (tr, 2H, NC_5H_5), 6.60 (tr, 1H, NC_5H_5 or NC_5H_4), 4.15 (bs, 2H, fc-C*H*), 3.93 (bs, 2H, fc-C*H*), 3.77 (t, 2H, ScCH_2CH_2Py), 3.60 (bs, 2H, fc-C*H*), 2.99 (bs, 2H, fc-C*H*), 0.99 (s, 18H, SiC(CH_3)$_3$), 0.93 (t, 2H, ScCH_2CH_2Py), 0.35 and 0.01 (s, 12H, Si(CH_3)$_2$). ^{13}C NMR (126 MHz, C_6D_6): δ, ppm: 172.9, 150.9, 147.0, 137.9, 124.1, 123.9, 119.9, 102.0, 71.1, 67.9, 67.3, 66.8, 66.0, 28.0, 25.2, 20.8, −2.0. Anal. for $C_{34}H_{51}FeN_4Si_2Sc$. Calcd.: C, 60.70%; H, 7.64%; N, 8.33%. Found: C, 60.70%; H, 7.95%; N, 8.23%.

2.3. Reaction of Sc(fc[NSi^{t}BuMe$_2$]$_2$)(η^2-N,C-6-Ph-pyridyl)(py), 2-py^{Ph}, with ethylene

2-py^{Ph} (100 mg, 0.140 mmol) was dissolved in toluene (10 mL) and placed in a 100-mL Schlenk tube. Ethylene (0.680 atm) was introduced. The reaction mixture was allowed to stir for 3 h at room temperature. The solvent was removed and the resulting yellow solid was extracted in hexanes and filtered through Celite. Yield 78.3 mg, 83.4%. ^{1}H NMR (500 MHz, C_6D_6): δ, ppm: 7.79 (d, 2H, C_6H_5), 7.20 (t, 2H, C_6H_5), 7.09 (t, 1H, NC_5H_3 or C_6H_5), 7.04 (t, 1H, NC_5H_3 or C_6H_5), 6.88 (d, 1H, NC_5H_3 or C_6H_5), 6.78 (d, 1H, NC_5H_3 or C_6H_5), 4.21 (s, 2H, fc-C*H*), 3.88 (s, 2H, fc-C*H*), 3.78 (t, 2H, ScCH_2CH_2Py), 3.61 (s, 2H, fc-C*H*), 3.18 (s, 2H, fc-C*H*), 0.93 (t, 2H, ScCH_2CH_2Py), 0.93 (s, 18H, SiC(CH_3)$_3$), 0.02 and −0.15 (s, 12H, Si(CH_3)$_2$). ^{13}C NMR (126 MHz, C_6D_6): δ, ppm: 173.2, 158.4, 140.1, 138.7, 130.0, 127.2, 123.5, 120.6, 106.7, 70.0, 68.4, 67.1, 66.6, 36.6, 27.8, 20.4, −3.2, −3.4. Anal. $C_{35}H_{50}FeN_3Si_2Sc$. Calcd.: C, 62.77%; H, 7.52%; N, 6.27%. Found: C, 62.72%; H, 7.87%; N, 6.25%.

2.4. Reaction of Sc(fc[NSi^{t}BuMe$_2$]$_2$)(η^2-N,C-6-Ph-pyridyl)(py), 2-py^{Ph}, with 2-butyne

2-py^{Ph} (200 mg, 0.280 mmol) was placed in a J-Young tube with 2-butyne (76 mg, 1.40 mmol) in C_6D_6. The reaction mixture was heated for 48 h at 50 °C. The volatiles were removed and the resulting brownish-yellow solid was washed with 1.5 mL hexanes, giving a yellow solid. Yield 152 mg, 70.6%. ^{1}H NMR (500 MHz, C_6D_6): δ, ppm: 7.78 (d, 2H, C_6H_5), 7.20 (m, 4H, C_6H_5 and NC_5H_4), 7.05 (m, 1H, NC_5H_4), 7.01 (m, 1H, NC_5H_4), 6.74 (d, 1H, NC_5H_4), 4.18 (s, 2H, fc-C*H*), 3.99 (s, 2H, fc-C*H*), 3.54 (s, 2H, fc-C*H*), 3.04 (s, 2H, fc-C*H*), 2.29 (s, 3H, CH_3-CC), 1.98 (s, 3H, CH_3-CC), 0.91 (s, 18H SiC(CH_3)$_3$), 0.04 and −0.10 (s, 12H, Si(CH_3)$_2$). ^{13}C NMR (126 MHz, C_6D_6): δ, ppm: 167.2, 158.0, 141.3, 139.4, 135.2, 131.1, 129.8, 126.5, 118.7, 118.3, 104.3, 69.2, 68.4, 67.6, 67.2, 27.7, 22.1, 20.2, 12.3, −2.9, −3.9. Anal. for $C_{37}H_{52}FeN_3Si_2Sc$. Calcd.: C, 63.87%; H, 7.53%; N, 6.04%. Found: C, 63.63%; H, 7.87%; N, 6.25%.

2.5. Reaction of Sc(fc[NSi^{t}BuMe$_2$]$_2$)(η^2-N,C-6-Ph-pyridyl)(py), 2-py^{Ph}, with 1,3-butadiene

2-py^{Ph} (200 mg, 0.280 mmol) was dissolved in toluene (10 mL) and placed in a 100-mL Schlenk tube. Butadiene was introduced (ca. 3 atm). The reaction was stirred overnight at room temperature. The volatiles were removed and the product was washed with 1.5 mL hexanes. Yield 148 mg, 75.9%. ^{1}H NMR (300 MHz, C_6D_6): δ, ppm: 7.69 (d, 2H, C_6H_5), 7.24 (t, 2H, C_6H_5 and/or NC_5H_4), 7.09 (m, 1H, C_6H_5 and/or NC_5H_4), 6.92 (m, 1H, C_6H_5 and/or NC_5H_4), 6.84 (td, 1H, $CH_2CHCHCH_2$), 6.65 (m, 2H, C_6H_5 and/or NC_5H_4), 4.37 (m, 1H, $CH_2CHCHCH_2$), 4.24 (s, 1H, $CH_2CHCHCH_2$), 4.18 (s, 1H, $CH_2CHCHCH_2$), 3.89 and 3.49 (m, 8H, fc-C*H*), 3.10 (s, 1H, $CH_2CHCHCH_2$), 2.63 (s, 1H, $CH_2CHCHCH_2$), 1.00 and 0.92 (s, 18H SiC(CH_3)$_3$), −0.02, −0.03, −0.18, and −0.22 (s, 12H, Si(CH_3)$_2$). ^{13}C NMR (126 MHz, C_6D_6): δ, ppm: 174.5, 160.8, 149.0, 140.2, 138.7, 129.4, 129.3, 128.9, 128.4, 124.0, 122.5, 103.7, 103.6, 89.5, 73.2, 70.4, 69.7, 69.5, 69.4, 69.0, 67.6, 65.9, 65.8, 40.9, 28.1, 28.0, 21.2, 20.7, −2.8, −3.2, −3.3, −3.6. Anal. for $C_{37}H_{52}FeN_3Si_2Sc$·0.5 toluene (consistent with X-ray crystal structure). Calcd.: C, 65.57%; H, 7.61%; N, 5.66%. Found: C, 65.15%; H, 7.67%; N, 5.68%.

2.6. X-ray crystal structures

X-ray quality crystals were obtained from various concentrated solutions placed in a −35 °C freezer in the glove box. Inside the glove box, the crystals were coated with oil (STP Oil Treatment) on a microscope slide, which was brought outside the glove box. The X-ray data collections were carried out on a Bruker AXS single crystal X-ray diffractometer using Mo Kα radiation and a SMART APEX CCD detector. The data was reduced by SAINTPLUS and an empirical absorption correction was applied using the package SADABS. The structures were solved and refined using SHELXTL (Brucker 1998, SMART, SAINT, XPREP AND SHELXTL, Brucker AXS Inc., Madison, Wiscosin, USA). All atoms were refined anisotropically and hydrogen atoms were placed in calculated positions unless specified otherwise. Tables with atomic coordinates and equivalent isotropic displacement parameters, with all the bond lengths and angles, and with anisotropic displacement parameters are listed in the cif files.

2.6.1. 2-py

X-ray quality crystals were obtained from a concentrated toluene:pentane solution placed in a −35 °C freezer in the glove box. A total of 14784 reflections ($-13 \le h \le 13$, $-14 \le k \le 14$, $-20 \le l \le 20$) were collected at T = 110(2) K with $2\theta_{max}$ = 56.39°, of which 7992 were unique (R_{int} = 0.0203). The residual peak and hole electron density were 1.34 and −0.78 eÅ^{-3}. The least-squares refinement converged normally with residuals of R_1 = 0.0423 and GOF = 1.035. Crystal and refinement data for 2-py: formula $C_{32}H_{47}N_4Si_2ScFe$, space group $P\bar{1}$, a = 10.4265(11), b = 10.7864(11), c = 15.3460(16), α = 88.151(2), β = 84.251(1), γ = 75.721(2)°, V = 1664.1(3) Å^3, Z = 2, μ = 0.739 mm^{-1}, F(0 0 0) = 684, R_1 = 0.00547 and wR_2 = 0.1138 (based on all 7992 data, $I > 2\sigma(I)$).

2.6.2. 3-py^{Ph}

X-ray quality crystals were obtained from a concentrated toluene: pentane solution placed in a −35 °C freezer in the glove box. The data were not very good and only connectivity information could be obtained. Only cell parameters will be included. A total of 34831 reflections ($-46 \le h \le 46$, $-21 \le k \le 21$, $-19 \le l \le 19$) were collected at T = 100(2) K with $2\theta_{max}$ = 60.94°, of which 10233 were unique. Crystal data for 3-py^{Ph}: formula $C_{35}H_{50}N_3Si_2ScFe$, space group $C2/c$, a = 32.9742, b = 15.5417, c = 13.8670, β = 95.891°, V = 7068.96 Å^3, Z = 8, μ = 0.70 mm^{-1}, F(0 0 0) = 2848.

2.6.3. 5-py^{Ph}

X-ray quality crystals were obtained from a concentrated toluene: pentane solution placed in a −35 °C freezer in the glove box. A molecule of toluene was found. The toluene molecule is sitting on a special position and is disordered such that one of the aromatic carbon atoms is also the methyl group of the other half of the molecule. The occupancy for this carbon atom was fixed to 75% and of three other carbons to 50%. One of the solvent atoms was not refined anisotropically; also hydrogen atoms were not added to the solvent carbon atoms. The allyl group (C2 and C3 atoms) is disordered over two positions. This disorder was model such that each position is occupied 50%. The two components of C2 (C2a and C2b) were not refined anisotropically. This atom (C2) is thermally disordered, accounting for the high electron density found next to it. The disorder was not refined. A total of 34875 reflections ($-13 \le h \le 13$, $-21 \le k \le 21$, $-30 \le l \le 30$) were collected at T = 100(2) K with $2\theta_{max}$ = 56.66°, of which 9535 were unique (R_{int} = 0.0904). The residual peak and hole electron density were 2.20 and −0.90 eÅ^{-3}. The least-squares refinement converged normally with residuals of R_1 = 0.0593 and GOF = 1.032. Crystal and refinement data for 5-py^{Ph}: formula $C_{40.25}H_{52}N_3Si_2ScFe$, space group $P2(1)/c$, a = 10.376(3), b = 16.437(5), c = 22.721(7), β = 93.281(3)°, V = 3868.7(19) Å^3, Z = 4, μ = 0.644 mm^{-1}, F(0 0 0) = 1558, R_1 = 0.1111 and wR_2 = 0.1568 (based on all 9535 data, $I > 2\sigma(I)$).

3. Results and discussion

Although the reaction between the ferrocene 1,1′-diamide scandium benzyl complex, Sc(fc[NSi^{t}BuMe$_2$]$_2$)(CH_2Xy-3,5)(THF) ($1^{CH_2{}^{Ar}}$-THF, Xy = xylyl) [26] and pyridine or 2-picoline gave mixtures of compounds, employing Sc(fc[NSi^{t}BuMe$_2$]$_2$)Me(THF)$_2$ (1^{Me}-THF) [26] allowed the isolation of an η^2(N,C)-pyridyl complex, Sc(fc[NSi^{t}BuMe$_2$]$_2$)(η^2-N,C-pyridyl)(py) (2-py, Eq. (1)). Complex 2-py was characterized by X-ray crystallography, which shows the pyridyl and pyridine ligands coplanar and coordinated in a plane perpendicular to the N_{amide}–Fe–N_{amide} one (Fig. 1).

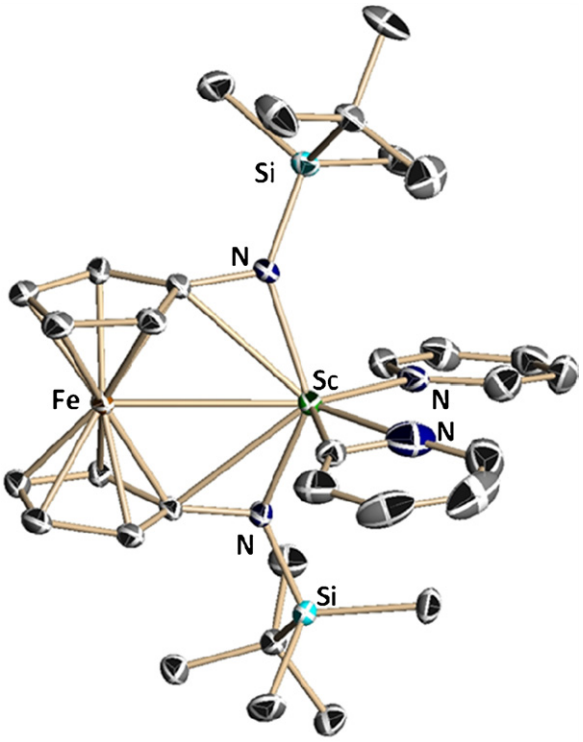
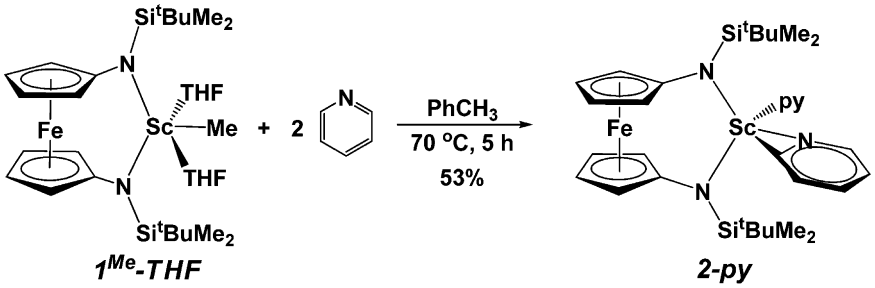
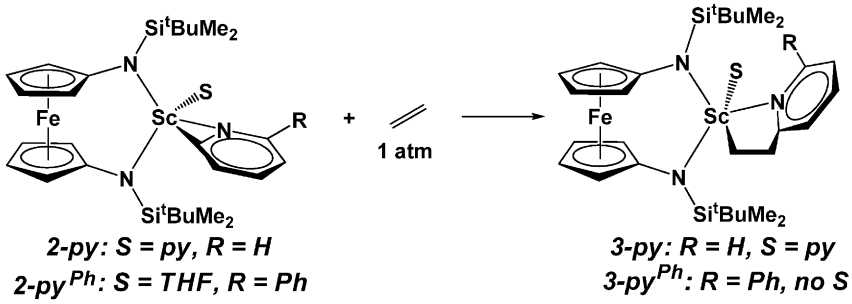


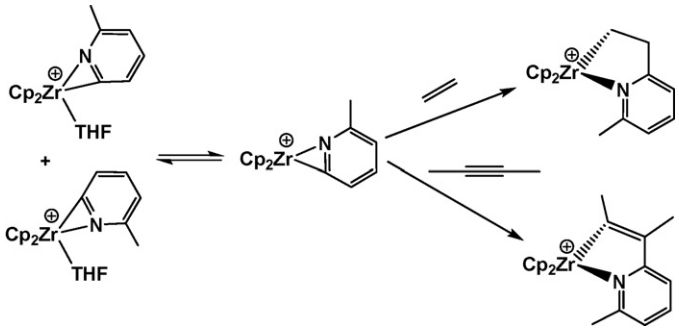
Fig. 1. ORTEP representation of 2-py with thermal ellipsoids at 50% probability (H atoms and solvent molecules were omitted for clarity).



(1)



(2)



Scheme 1. Reaction of a zirconocene pyridyl cation with ethylene and 2-butyne [10,30,31].

The reaction between 2-py and ethylene occurs at room temperature in 4 h to give the insertion product 3-py (Eq. (2)). It was not surprising that the reaction was rather slow since the analogous zirconocene pyridyl cationic complex featuring a pyridine molecule coordinated to the metal center did not react with ethylene [10]. Given the low reactivity of 2-py we decided to focus on a different pyridyl complex. Jordan et al. showed (Scheme 1) that using the steric pressure of a methyl substituent close to the metal center increased the rate of the insertion reactions [10,30,31]. We reasoned that a similar effect would be observed in our system. The phenylpyridyl complex 2-py^{Ph} seemed to be an appropriate choice because it coordinates THF instead of an additional 2-phenylpyridine molecule. Compound 2-py^{Ph} was prepared from 1^{CH_2Ar}-THF in the presence of one equivalent of 2-phenylpyridine. The use of more than one equivalent of 2-phenylpyridine leads to the formation of a product in which the two pyridine rings are coupled in the 2,2′-positions [27].

As expected, the reaction between ethylene and 2-py^{Ph} took place faster than the analogous reaction with 2-py (Eq (2), 0.5 h vs 4 h). Characterization of the insertion product 3-py^{Ph} by X-ray crystallography (Fig. 2) confirms the solution structure indicated by ^{1}H NMR spectroscopy. Inspection of the X-ray crystal structure shows that the pyridine ring is tilted with respect to the ferrocene backbone. This tilting, absent in the case of 2-py, is likely caused by steric factors, since it allows the phenyl ring and the ethylene arm to avoid interactions with the silyl substituents.

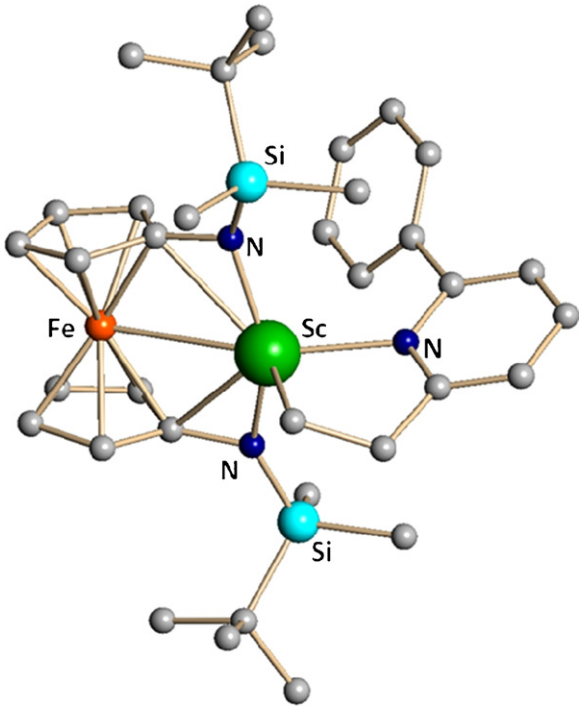
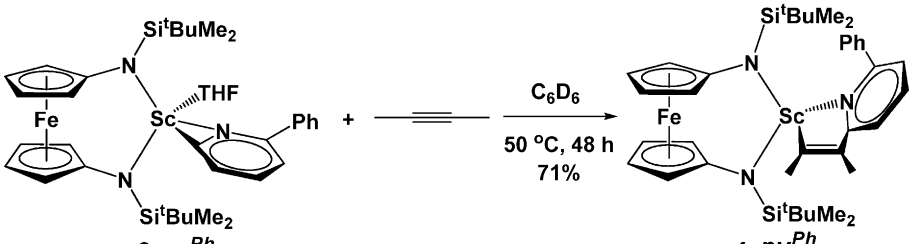
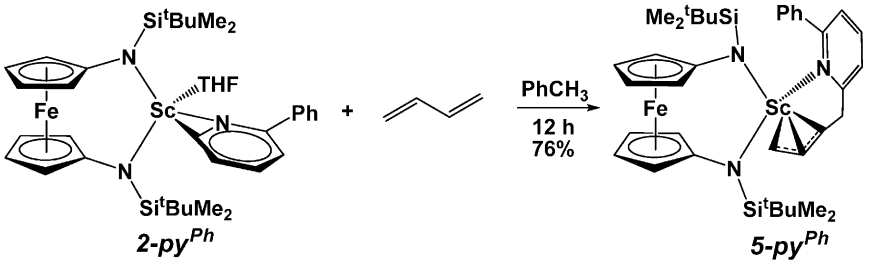


Fig. 2. Molecular structure of 3-py^{Ph} (H atoms and solvent molecules were omitted for clarity).

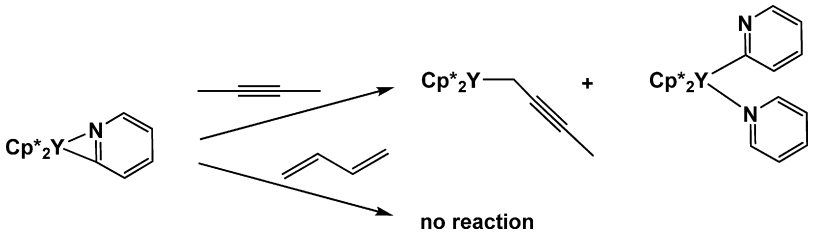
Another reaction of interest with an unsaturated substrate is the reaction between pyridyl complexes and 2-butyne. The zirconocene pyridyl cationic complex reported by Jordan et al. inserted 2-butyne to form a five-member azometallocycle (Scheme 1) [10]. The yttrocene pyridyl complex reported by Teuben et al. showed different reactivity behavior: instead of an insertion reaction, a protonation reaction involving the methyl butyne protons took place (Scheme 2) [32]. The reaction between 2-py^{Ph} and 2-butyne led to the isolation of an insertion product, 4-py^{Ph}, analogous to the one obtained with the zirconocene complex (Eq. (3)). Complex 4-py^{Ph} presented ^{1}H and ^{13}C NMR spectroscopy signatures similar to the values reported for the analogous zirconocene complex.



(3)



(4)



Scheme 2. Reaction of a yttrocene pyridyl complex with 2-butyne and 1,3-butadiene [32].

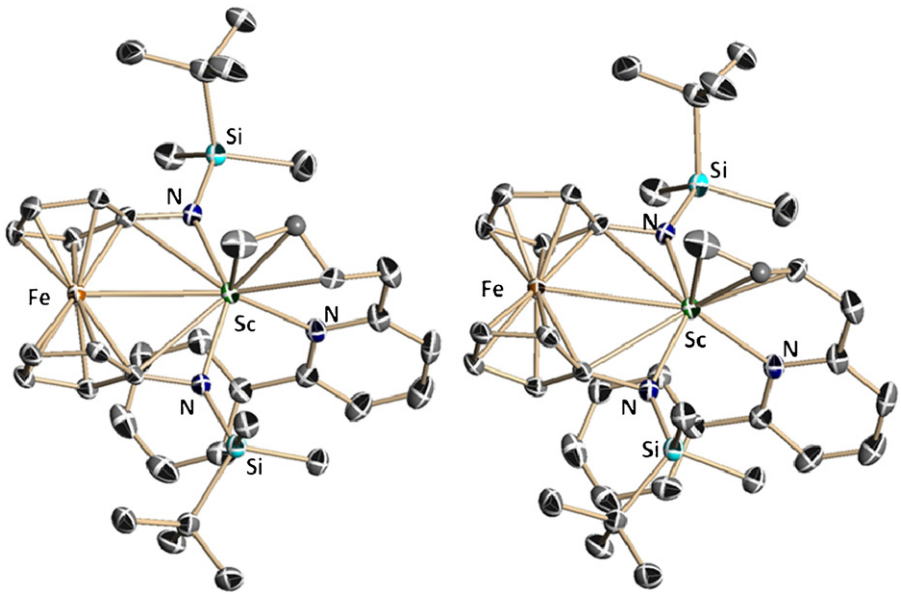


Fig. 3. ORTEP representation of 5-py^{Ph} with thermal ellipsoids at 50% probability (H atoms and solvent molecules were omitted for clarity). Both allyl orientations are shown.

As part of our attempt to compare the reactivity of scandium pyridyl complexes with the reactivity of analogous yttrium and zirconium complexes, we also carried out the reaction with 1,3-butadiene (Eq. (4)). Teuben reported that butadiene did not react with the yttrium complex Cp$^*_2$Y(η^2-*N,C*-pyridyl) [32]. No information related to a reaction of butadiene with the zirconium cationic pyridyl complexes could be found in the reports published by Jordan [10]. When a solution of 2-py^{Ph} was allowed to react with 1 equiv of 1,3-butadiene we observed the formation of one major product, 5-py^{Ph}. Inspection of this product by ^{1}H NMR spectroscopy indicated that the fragment originating in the butadiene molecule is coordinated to the scandium center since all olefinic protons are shifted from the values in butadiene.

Coordination of the allyl moiety to the scandium center was confirmed by X-ray crystallography (Fig. 3), which indicates that the Sc—C bonds to the three carbon atoms are rather similar. We also found that the carbon atoms of the allyl backbone are disordered, analogously to the disorder reported by Bercaw et al. [33] for a non-substituted allyl scandocene complex. The thermal disorder was modeled as a 50:50 population of sites, showing two different orientations for the allyl ligand.

4. Conclusions

The insertion of unsaturated substrates into scandium pyridyl complexes supported by a ferrocene diamide ligand bears similarities and dissimilarities to analogous reactions of zirconocene and yttrocene pyridyl complexes. Although the scandium complexes studied here show heterocycle coupling behavior analogous to the yttrocene complexes, the insertion chemistry is rather different in some aspects. All compounds react with ethylene to form a 5-member ring azometallacycle. However, in the reaction with 2-butyne, the scandium pyridyl complex forms a product analogous to the zirconocene complex, but not to the yttrocene pyridyl complex. The yttrocene pyridyl complex did form a similar insertion product when 2-pentyne was used instead of 2-butyne. Finally, the scandium pyridyl complex reacted with 1,3-butadiene while the yttrocene complex showed no reactivity.

Acknowledgments

The authors thank Dr. Saeed Khan for help with crystallography. This work was supported by UCLA.

References

[1] D.M. D'Souza, T.J.J. Muller, Chem. Soc. Rev. 36 (2007) 1095–1108.
[2] G. Zeni, R.C. Larock, Chem. Rev. 104 (2004) 2285–2310.
[3] I. Nakamura, Y. Yamamoto, Chem. Rev. 104 (2004) 2127–2198.
[4] G. Balme, E. Bossharth, N. Monteiro, Eur. J. Org. Chem. 2003 (2003) 4101–4111.
[5] H.M.L. Davies, S.J. Hedley, Chem. Soc. Rev. 36 (2007) 1109–1119.
[6] S.R. Chemler, P.H. Fuller, Chem. Soc. Rev. 36 (2007) 1153–1160.
[7] M.D. Mihovilovic, P. Stanetty, Angew. Chem. Int. Ed. 46 (2007) 3612–3615.
[8] A. Padwa, S.K. Bur, Tetrahedron 63 (2007) 5341–5378.
[9] R.F. Jordan, A.S. Guram, Organometallics 9 (1990) 2116–2123.
[10] R.F. Jordan, D.F. Taylor, N.C. Baenziger, Organometallics 9 (1990) 1546–1557.
[11] A.S. Guram, R.F. Jordan, Organometallics 10 (1991) 3470–3479.
[12] R.F. Jordan, Adv. Organomet. Chem. 32 (1991) 325–387.
[13] J.C. Lewis, R.G. Bergman, J.A. Ellman, J. Am. Chem. Soc. 129 (2007) 5332–5333.
[14] K.L. Tan, R.G. Bergman, J.A. Ellman, J. Am. Chem. Soc. 123 (2001) 2685–2686.
[15] K.L. Tan, R.G. Bergman, J.A. Ellman, J. Am. Chem. Soc. 124 (2002) 13964–13965.
[16] K.L. Tan, S. Park, J.A. Ellman, R.G. Bergman, J. Org. Chem. 69 (2004) 7329–7335.

[17] S.H. Wiedemann, R.G. Bergman, J.A. Ellman, Org. Lett. 6 (2004) 1685–1687.
[18] S.H. Wiedemann, J.A. Ellman, R.G. Bergman, J. Org. Chem. 71 (2006) 1969–1976.
[19] F. Kakiuchi, S. Murai, Acc. Chem. Res. 35 (2002) 826–834.
[20] N. Fujii, F. Kakiuchi, N. Chatani, S. Murai, Chem. Lett. (1996) 939–940.
[21] N. Fujii, F. Kakiuchi, A. Yamada, N. Chatani, S. Murai, Chem. Lett. (1997) 425–426.
[22] N. Fujii, F. Kakiuchi, A. Yamada, N. Chatani, S. Murai, Bull. Chem. Soc. Jpn. 71 (1998) 285–298.
[23] Z. Zhang, X. Wang, R.A. Widenhoefer, Chem. Commun. (2006) 3717–3719.
[24] C. Liu, X. Han, X. Wang, R.A. Widenhoefer, J. Am. Chem. Soc. 126 (2004) 3700–3701.
[25] X. Han, R.A. Widenhoefer, Org. Lett. 8 (2006) 3801–3804.
[26] C.T. Carver, M.J. Monreal, P.L. Diaconescu, Organometallics 27 (2008) 363–370.
[27] C.T. Carver, P.L. Diaconescu, J. Am. Chem. Soc. (2008), ASAP.
[28] M.E. Thompson, S.M. Baxter, A.R. Bulls, B.J. Burger, M.C. Nolan, B.D. Santarsiero, W.P. Schaefer, J.E. Bercaw, J. Am. Chem. Soc. 109 (1987) 203–219.
[29] A.B. Pangborn, M.A. Giardello, R.H. Grubbs, R.K. Rosen, F.J. Timmers, Organometallics 15 (1996) 1518–1520.
[30] R.F. Jordan, D.F. Taylor, J. Am. Chem. Soc. 111 (1989) 778–779.
[31] A.S. Guram, R.F. Jordan, D.F. Taylor, J. Am. Chem. Soc. 113 (1991) 1833–1835.
[32] B.-J. Deelman, W.M. Stevels, J.H. Teuben, M.T. Lakin, A.L. Spek, Organometallics 13 (1994) 3881–3891.
[33] M.B. Abrams, J.C. Yoder, C. Loeber, M.W. Day, J.E. Bercaw, Organometallics 18 (1999) 1389–1401.