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High order cycloaddition reactions of $M(CO)_3$-coordinated *N*-cyanoazepine with alkynes; M: Cr, Mo, W

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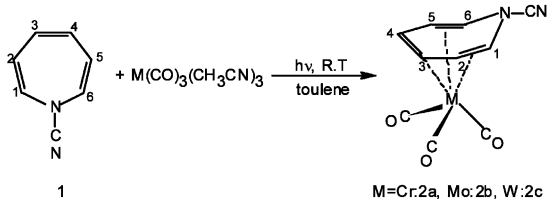
Abstract

Tricarbonyl(*N*-cyanoazepine)metal(0) complexes of chromium (**2a**), molybdenum (**2b**) and tungsten (**2c**) are formed when tricarbonyl-tris(acetonitrile)chromium(0), -molybdenum(0) and -tungsten(0), respectively, are treated photochemically with *N*-cyanoazepine (**1**). The resulting complexes are purified. UV photolysis of $Cr(CO)_3(\eta^6$-*N*-cyanoazepine) (**2a**) and RC≡CR (R: Ph, $SiMe_3$) in toluene gives the [6+2]cycloadducts, tricarbonyl{$\eta^{4:2}$-7,8-diphenyl-9-*N*-cyano-9-azabicyclo[4.2.1]-nona-2,4,7-triene}chromium(0), $[(\eta^{4:2}\text{-}C_8H_6N(CN)Ph_2)Cr(CO)_3]$ (**3a**) and tricarbonyl{$\eta^{4:2}$-7,8-bis(trimethylsilyl)-9-*N*-cyano-9-azabicyclo[4.2.1]-nona-2,4,7-triene}chromium(0), $[(\eta^{4:2}\text{-}C_8H_6N(CN)(SiMe_3)_2)Cr(CO)_3]$ (**3b**). Like **2a**–**c**, these new bicyclic compounds were purified by chromatography, recrystallized and isolated as analytically pure crystalline solids in moderate yields and characterized by mass, IR and NMR spectroscopy. The heterobicyclotrienes (**4a**,**b**) are isolated from (**3a**,**b**) by treatment with cerium(IV) ammonium nitrate (R = $SiMe_3$) or by heating in toluene (R = Ph). © 2002 Published by Elsevier Science B.V.

Keywords: Carbonyl; *N*-Cyanoazepine; Chromium

1. Introduction

Transition metal mediated high order cycloaddition reactions of trienes in [6+4], [6+2] and [4+4] combinations are currently viewed as potentially powerful methodologies for the construction of medium size carbo- and heterocyclic rings [1,2]. They typically display extremely high levels of stereoselectivity and low chemical efficiency [3]. The reactions were first reported by Pettit and co-workers [4] for iron species and later by Kreiter [5–8] using chromium. In addition, other isolated complexes have appeared in the literature over the years [9–12]. More recently, Rigby [1,13] has elegantly applied these and other new metal-promoted cycloadditions to a variety of synthetic problems. The advent of effective photochemically, metal-promoted versions of these transformations has provided convenient access to a range of highly-substituted bicyclo[4.4.1]undecane and bicyclo[4.2.1]nonane carbocyclic systems in diastereomerically pure forms [8,9,14,15]. The chemistry of 1H-azepine and its *N*-substituted complexes has also been known for a long time [16–20]. Even though the cycloadditions of *N*-carbethoxyazepine were successful [21,22], there is no example in literature either for the synthesis of the metal coordinated *N*-cyanoazepine or of cycloaddition reactions with unsaturated species. Therefore, the present work aimed at the photochemical synthesis and isolation of tricarbonyl(η^6-*N*-cyanoazepine)metal(0), M: Cr, Mo, W (**2a**–**c**, Eq. (1)) complexes. The complexes were purified by chromatography and recrystallization, characterized by mass, IR and NMR spectroscopy.



(1)

The second part of the present work is the photochemical [6+2] cycloaddition of tricarbonyl(η^6-*N*-cyanoazepine) (**2a**) with the alkynes of the formula RC≡CR

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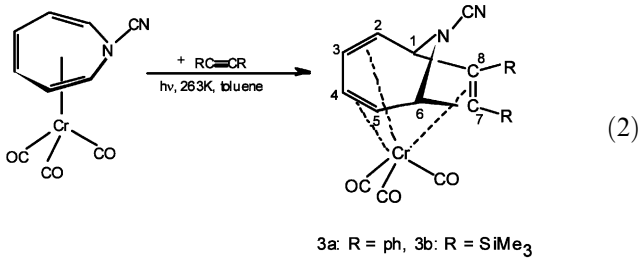
(R: Ph, $SiMe_3$) to produce the bicyclo[4.2.1]nona-2,4,7-triene complexes [($\eta^{4:2}$-$C_8(NCN)H_6R_2$)$Cr(CO)_3$], R: Ph, $SiMe_3$ (**3a**, **3b**, Eq. (2)) and the formation of uncomplex pure ligands (**4a**, **4b**, Eq. (3)).



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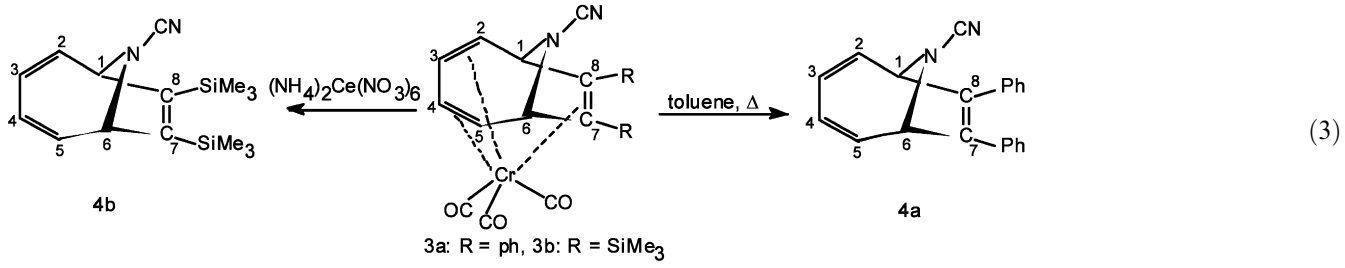


(3)

The resulting complexes were purified by chromatography and recrystallization and characterized by IR, NMR and mass spectroscopy.

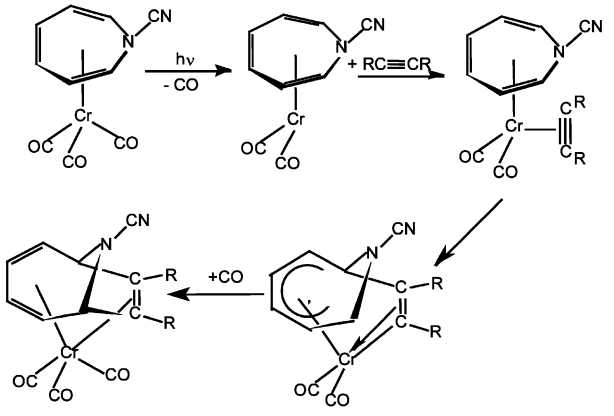
2. Results and discussion

UV irradiation of $M(CO)_3(CH_3CN)_3$ in the presence of *N*-cyanoazepine leads to the formation of the complexes **2a**–**c** (Eq. (1)), and the UV irradiation of tricarbonyl(η^6-*N*-cyanoazepine)chromium(0) (**2a**) in the presence of diphenylacetylene or bis(trimethylsilyl)acetylene leads to the formation of adducts **3a** and **3b**, respectively, as a result of [6+2] cycloadditions of the alkyne to the metal-coordinated *N*-cyanoazepine (Eq. (2)). The composition and the structure of the complexes **2a** [$Cr(CO)_3$(η^6-*N*-cyanoazepine)], **2b** [$Mo(CO)_3$(η^6-*N*-cyanoazepine)], **2c** [$W(CO)_3$(η^6-*N*-cyanoazepine)], **3a** [$Cr(CO)_3$\{$\eta^{4:2}$-7,8-diphenyl-9-*N*-cyano-9-azabicyclo[4.2.1]-nona-2,4,7-triene\}], and **3b** [$Cr(CO)_3$\{$\eta^{4:2}$-7,8-bis(trimethylsilyl)-9-*N*-cyano-9-azabicyclo[4.2.1]-nona-2,4,7-triene\}], are established on the basis of elemental analysis, mass, IR, and NMR spectroscopic data. Moreover, the 9-azabicyclo[4.2.1]nona-2,4,7-triene ligands can also be readily decomposed from the metal (Eq. (3)). Thus if a toluene solution of **3a** is refluxed for 10 min, a ligand exchange occurs forming **4a** and tricarbonyl-(η^6-toluene)chromium(0). Complex **4b** is more robust, and oxidative decomplexation with ammonium cerium nitrate is required to release the organic ligand **4b**. The pure organic compounds **4a**,**b** were isolated (TLC silica) as colorless oils and characterized by NMR and mass spectroscopy. Compounds **4a** and **4b** show no unusual features in their ^{1}H- or $^{13}C\{^1H\}$-NMR spectra and thus provides more compelling evidence of the identity of **3a**,**b**.

The IR spectra of the complexes **2a**–**c** in *n*-hexane solutions exhibit three strong absorption bands in the CO-stretching vibrational region with approximately equal intensities consistent with the expected fac-structure of the $M(CO)_3$ moiety. The spectra show no significant shift of the CN stretching band upon coordination, which can rule out any coordination of the metal atom through the nitrogen lone pair of the azepine ligand. The appearance of three strong CO stretching bands of equal intensities indicates a structure of C_1 or C_s symmetry. In detail, the ^{1}H-NMR spectra of the complexes **2a**–**c** in *d*-chloroform exhibit three multiplets which are assigned for $H_{1,6}$, $H_{2,5}$, $H_{3,4}$ with large, significant shifts from those of the free *N*-cyanoazepine ligand (δ ppm, $H_{1,6} = 5.54$, $H_{2,5} = 5.15$, $H_{3,4} = 6.12$) to higher magnetic field which indicates the $^6\eta$-π-coordination of the *N*-cyanoazepine ligand to the metal atom. The $^{13}C\{^1H\}$-NMR spectra of the complexes **2a**–**c** recorded from their *d*-chloroform solutions show the appearance of a singlet each for $C_{1,6}$, $C_{2,5}$ and $C_{3,4}$. These singlets exhibit a large shift towards higher magnetic field from free *N*-cyanoazepine (δ ppm, $C_{1,6} = 125.16$, $C_{2,5} = 114.95$, $C_{3,4} = 123.26$, NCN = 130.25) upon the coordination to the metal atom indicating the formation of π-complexes, mean while the NCN singlet show no significant shift. In addition, two signals of relative intensities 2:1 are observed in the CO-region. The appearance of a multiplet each for a couple of hydrogen ($H_{1,6}$, $H_{2,5}$, $H_{3,4}$) in the ^{1}H-NMR spectra and a singlet for each couple of carbon atoms

($C_{1,6}$, $C_{2,5}$, $C_{3,4}$) and two singlets for the CO-groups in the ^{13}C-NMR spectra of the complexes **2a**–**c** confirms the formation of η^6-complexes with C_s symmetry.

The IR spectra of the complexes **3a** and **3b** from *n*-C_6H_{14} solutions also show the appearance of three strong stretching bands in the CO-stretching vibrational region with approximately equal intensities consistent with the expected fac-structure of the $M(CO)_3$ moiety indicate a structure with C_1 or C_s symmetry. These bands are shifted towards lower frequency than those of the complexes **2a**–**c**. In detail the ^{1}H-NMR spectra of **3a** and **3b** in *d*-chloroform show multiplets of the protons $H_{1,6}$, $H_{2,5}$, $H_{3,4}$, the most noticeable point being the splitting of the $H_{1,6}$ multiplet into two doublets. This splitting and the small shift of these signals to higher magnetic field compared with **2a** indicate the occurrence of the cycloaddition through the carbon atoms 1 and 6 of the cyanoazepine ring. On the other hand, the $^{13}C\{^1H\}$-NMR of the complexes **3a** and **3b** in *d*-chloroform solutions show eight unique signals for carbon atoms 1 through 8 of the heterobicyclic ring. In addition, three singlets of equal intensities are observed in the CO-region of the spectra. This indicates the structure of C_1 symmetry, mean while the large chemical shift difference in the singlets of C(1) and C(6) confirms the occurrence of cycloaddition of the alkynes to the carbon atoms 1 and 6 of the *N*-cyanoazepine ring. This new bicyclic ligand acts as a chelate through η^4-coordination to C(2)–C(5) and η^2-bonding to C(7)–C(8). The ^{1}H- and ^{13}C-NMR of the free organic ligands **4a** and **4b** are in reasonably good accord with their structures (Eq. (3)). The chemical shifts of some atoms (especially the diene part) are naturally significantly different from those of complexes **3a** and **3b** due to the absence of upfield coordination shifts which are effective in the metal complexes. A comparison of $^{13}C\{^1H\}$-NMR spectra of **4a**,**b** and **3a**,**b** likewise reveals characteristic coordination shifts of the olefinic carbon atoms.



Scheme 1. The proposed mechanism for the formation of complexes **3a** and **3b**.

On the basis of previous works related with [6+4] cycloaddition of heptatriene and derivatives to dienes [5–8], [13a], [15a] and [6+2] addition to olefins [13b], we believe that our cycloaddition reaction to produce adducts **3a**,**b** proceed similarly via the proposed mechanism shown in Scheme 1. As it is shown in the scheme, a vacant coordination site is photogenerated at the metal and the alkyne coordinates to this vacant site prior to C–C bond formation. Stufkens and co-workers [15a] show that in the case of cycloheptatrien additions there are two primary photoprocess, a photoinduced ring slip and photolytic CO loss. These authors concluded that carbonyl loss was the pathway responsible for the cycloaddition process. Rigby and co-workers have suggested a ring slip mechanism based upon the efficiency of the reactions under a constant purge of argon [1,2]. They argued that the purge should reduce the yield if CO ejection and recapture are involved. However, it is possible that the recapture of CO occurs by abstraction of a carbonyl from a molecule of **3a** or **3b**, a process that would be relatively unaffected by a purge since it is potentially autocatalytic. It is clearly shown that, more studies are required to fully elucidate these novel processes. Scheme 1 shows what we believe to be the most likely routes to **3a** and **3b**.

3. Experimental

The preparations and reactions of all complexes were performed under an atmosphere of dry and deoxygenated nitrogen gas using standard Schlenk techniques. Solvents used were purified by refluxing over metallic sodium or anhydrous P_2O_5 under nitrogen atmosphere for a period of 4–5 days prior to use. Reagents and chemicals were purchased from Merck GmbH, Germany and used without further purifications. The photochemical reactions and other treatments were followed by IR spectra taken at appropriate time intervals.

IR spectra were recorded from CH_2Cl_2 or *n*-C_6H_{14} solutions on a JASCO 430 RT-IR spectrophotometer. ^{13}C-NMR spectra were recorded from *d*-$CHCl_3$ or *d*-$C_6H_5CH_3$ solutions on a Bruker AMX 400 FT-NMR spectrometer at 100.62 MHz. ^{1}H-NMR spectra were recorded from *d*-$CHCl_3$ solutions on a Bruker WP 200 at 200 MHz. Tetra methyl silane was used as an internal reference for NMR chemical shifts. Elemental analysis was carried out on a HP 185 C N H analyzer. Mass spectra were taken on a Varian MAT 311 Instrument. Chromatography was performed on silica gel 230–425 mesh. *N*-Cyanoazepine [23] and tricarbonyl-tris(acetonitrile)metal(0) complexes [24] were prepared using the literature procedures.

3.1. Tricarbonyl(η^6-N-cyanoazepine)metal(0)

A solution of 1.0 g of $(CO)_3M(CH_3CN)_3$ [M: Cr (6.65 mmol), Mo (4.52 mmol), W (3.24 mmol)] and 1.0 g of *N*-cyanoazepine (8.46 mmol) in 150 ml of *n*-C_6H_{14} is irradiated [M: Cr (300 min), Mo (250 min), W (210 min)] using a high pressure mercury lamp (Hg-Tauchlampe TQ 150W, Quarzlampen GmbH, Hanau, Germany) which is housed in a water-cooled glass jacket. The resulting dark solution is filtered and then evaporated under high vacuum (0.01 mmHg). The resulting solid is then purified by recrystallization from *n*-C_6H_{14} at −78 °C. The dark orange crystals are best dried under vacuum for 4 h and stored under nitrogen atmosphere for analysis.

3.2. Tricarbonyl(η^6-N-cyanoazepine)chromium(0) (**2a**) pale red solid

Yield: 1.20 g (84% rel. $(CO)_3Cr(CH_3CN)_3$). $C_{10}H_6CrN_2O_3$ (254.17) molar mass by MS 254 g mol^{-1} IR (*n*-C_6H_{14}): $\nu = 1996$ (vs), 1938 (vs), 1912 (s) cm^{-1} (C=O); 2217 (w) cm^{-1} (C≡N).—^{1}H-NMR (200 MHz, $CDCl_3$): $\delta = 3.85$ (m, 2H, $H_{2,5}$), 4.30 (d, 2H, $H_{1,6}$), 6.05 (m, 2H, $H_{3,4}$).—$^{13}C\{^1H\}$-NMR (100.62 MHz, C_7D_8): $\delta = 72.20$ ($C_{1,6}$), 94.30 ($C_{2,5}$), 97.15 ($C_{3,4}$), 128.20 (N–CN), 232.20, 226.05 (C=O).—$C_{10}H_6CrN_2O_3$ (254.17): Anal. Calc.: C, 47.25; H, 2.38; N, 11.02. Found: C, 47.55; H, 2.30; N, 11.20%.

3.3. Tricarbonyl(η^6-N-cyanoazepine)molybdenum(0) (**2b**) pale red solid

Yield: 1.0 g (74% rel. $(CO)_3Mo(CH_3CN)_3$). $C_{10}H_6MoN_2O_3$ (298.11) molar mass by MS 298 g mol^{-1}. IR (*n*-C_6H_{14}): $\nu = 1998$ (vs), 1938 (vs), 1910 (s) cm^{-1} (C=O); 2219 (w) cm^{-1} (C≡N).—^{1}H-NMR (200 MHz, $CDCl_3$): $\delta = 3.85$ (m, 2H, $H_{2,5}$), 4.32 (d, 2H, $H_{1,6}$), 6.03 (m, 2H, $H_{3,4}$).—$^{13}C\{^1H\}$-NMR (100.62 MHz, C_7D_8): $\delta = 73.10$ ($C_{1,6}$), 94.65 ($C_{2,5}$), 97.05 ($C_{3,4}$), 128.35 (N–C≡N), 227.30, 215.45 (C=O).—$C_{10}H_6MoN_2O_3$ (298.11): Anal. Calc.: C, 40.29; H, 2.03; N, 9.40. Found: C, 41.00; H, 2.11; N, 9.45%.

3.4. Tricarbonyl(η^6-N-cyanoazepine)tungsten(0) (**2c**) pale red solid

Yield: 0.75 g (59.9% rel. $(CO)_3W(CH_3CH)_3$). $C_{10}H_6N_2O_3W$ (386.02) molar mass by MS 386 g mol^{-1}. IR (*n*-C_6H_{14}): $\nu = 1995$ (vs), 1934 (vs), 1908 (s) (C=O) cm^{-1}; 2217 (w) cm^{-1} (C≡N).—^{1}H-NMR (200 MHz, $CDCl_3$): $\delta = 3.94$ (m, 2H, $H_{2,5}$), 4.38 (d, 2H, $H_{1,6}$), 6.02 (m, 2H, $H_{3,4}$).—$^{13}C\{^1H\}$-NMR (100.62 MHz, C_7D_8): $\delta = 65.80$ ($C_{1,6}$), 93.20 ($C_{3,4}$), 93.75 ($C_{2,5}$), 128.90 (N–C≡N), 217.15, 206.20 (CO).—$C_{10}H_6N_2O_3W$ (386.02): Anal. Calc.: C, 31.12; H, 1.57; N, 7.26. Found: C, 31.00; H, 1.60; N, 7.30%.

3.5. Tricarbonyl{$\eta^{4:2}$-7,8-diphenyl-9-N-cyano-9-azabicyclo[4.2.1]-nona-2,4,7-triene}-chromium(0) (**3a**)

A solution of **2a** (0.5 g, 1.97 mmol) and diphenyl acetylene (0.5 g, 3.24 mmol) in 150 ml of $C_6H_5CH_3$ was irradiated at 263 K for 540 min using a high-pressure mercury lamp. The residue was then filtered through Celite and the solvent evaporated in high vacuum. Recrystallization from *n*-C_6H_{14}–CH_2Cl_2 (5:1) produced **3a** as a reddish brown crystals.

Yield: 0.60 g (71% rel. **2a**). $C_{24}H_{16}CrN_2O_3$ (432.40) molar mass by MS 432 g mol^{-1}. IR (*n*-C_6H_{14}): $\nu = 1985$ (vs), 1894 (vs), 1720 (m) cm^{-1} (C=O); 2218 (w) cm^{-1} (C≡N).—^{1}H-NMR (200 MHz, $CDCl_3$): $\delta = 4.56$ (m, 2H, $H_{2,5}$), 5.23 (m, 2H, $H_{3,4}$), 5.28 (d, 1H, H_1 or H_6), 5.40 (d, 1H, H_1 or H_6), 7.26 (m, 6H, Ph), 7.60 (m, 4H, Ph).—$^{13}C\{^1H\}$-NMR (100.62 MHz, C_7D_8): $\delta = 58.65$, 59.60 ($C_{1,6}$), 69.16, 69.80 ($C_{2,5}$), 87.25, 88.90 ($C_{7,8}$), 94.80, 95.15 ($C_{3,4}$), 127, 128, 129, 129.4, 130, 130.7 (Ph), 128.95 (C≡N), 228, 228.5, 232.6 (C=O).—$C_{24}H_{16}CrN_2O_3$ (432.40): Anal. Calc.: C, 66.67; H, 3.73; N, 6.48. Found: C, 66.32; H, 3.76; N, 6.42%.

3.6. Tricarbonyl{$\eta^{4:2}$-7,8-bis(trimethylsilyl)-9-N-cyano-9-azabicyclo[4.2.1]-nona-2,4,7-triene}chromium(0) (**3b**)

A solution of **2a** (0.5 g, 1.97 mmol) and bis(trimethylsilyl)acetylene (0.66 g, 0.88 ml, 3.90 mmol) in 150 ml of $C_6H_5CH_3$ was irradiated with UV light at 263 K for 690 min. The resulting solution was then filtered through Celite and the solvent evaporated in high vacuum. The brown residue was then chromatographed on silica gel by using a *n*-C_6H_{14}–CH_2Cl_2–C_3H_6O (10:9:1) mixture. The orange elute was collected and evaporated in vacuum. The resulting residue was recrystallized from *n*-C_6H_{14} at −78 °C for one night. Decantation of the solvent and drying of the residue in vacuum produced **3b** as dark red crystals which were stored under nitrogen atmosphere for analysis.

Yield: 0.55 g (66% rel. **2a**). $C_{24}H_{16}CrN_2O_3$ (424.57) molar mass by MS 424 g mol^{-1}. IR (*n*-C_6H_{14}): $\nu = 1972$ (vs), 1896 (vs), 1722 (m) cm^{-1} (C=O), 2219 (w) cm^{-1} (C≡N).—^{1}H-NMR (200 MHz, $CDCl_3$): $\delta = 0.40$ (s, 18H, $SiMe_3$), 4.58 (m, 2H, $H_{2,5}$), 4.87 (m, 2H, $H_{3,4}$), 4.84 (m, 1H, H_1 or H_6), 5.86 (d, 1H, H_1 or H_6).—$^{13}C\{^1H\}$NMR (100.62 MHz, C_7D_8): $\delta = 1.00$ ($SiMe_3$), 59.20, 59.56 ($C_{1,6}$), 71.80, 72.10 ($C_{2,5}$), 74.30, 75.10 ($C_{7,8}$), 95.80, 96.40 ($C_{3,4}$), 128.42 (C≡N), 229, 229.7, 233.4 (C=O).—$C_{24}H_{16}CrN_2O_3$ (424.57): Anal. Calc.: C, 50.92; H, 5.70; N, 6.60. Found: C, 51.30; H, 5.52; N, 6.48%.

3.7. 7,8-Diphenyl-9-N-cyano-9-azabicyclo[4.2.1]-nona-2,4,7-triene (**4a**)

A deep greenish red solution of **3a** (0.2 g, 0.46 mmol) in $C_6H_5CH_3$ was refluxed for about 10 min or until it turned to pale yellow. The $C_6H_5CH_3$ was removed under vacuum and the colorless residue purified (TLC, silica, elutate n-C_6H_{14}–CH_3Cl_2 1:1) to give (**4a**) as a colorless oil.

Yield: 0.1 g (75% rel. **3a**). $C_{21}H_{16}N_2$ (296.37) molar mass by MS 296 g mol^{-1}. ^{1}H-NMR (200 MHz, $CDCl_3$): $\delta = 5.36$ (m, 2H, $H_{1,6}$), 6.32 (m, 2H, $H_{2,5}$), 6.64 (m, 2H, $H_{3,4}$), Ph (m, 10H, 7.15).—$^{13}C\{^1H\}$-NMR (100.62 MHz, C_7D_8): $\delta = 59.85$ ($C_{1,6}$), 123.4 ($C_{2,5}$), 127.4 ($C_{7,8}$), 139.5 ($C_{3,4}$), 125.8, 126.4, 126.9, 127.3 (Ph), 129.25 (C≡N).—$C_{21}H_{16}N_2$ (296.37): Anal. Calc.: C, 85.11; H, 5.44; N, 9.45. Found: C, 85.28; H, 5.51; N, 9.37%.

3.8. 7,8-Bis(trimethylsilyl)-9-N-cyano-9-azabicyclo[4.2.1]-nona-2,4,7-triene (**4b**)

A solution of complex **3b** (0.15 g, 0.35 mmol) in $C_6H_5CH_3$ (10 ml) was stirred with an aq. solution (3 ml) of cerium(IV) ammonium nitrate for 5 min at until it turned pale yellow. The $C_6H_5CH_3$ was removed in vacuo and the residue organic phase purified (TLC, silica, elutate C_6H_{14}–CH_2Cl_2) to give **4b** as a clear oil.

Yield: 0.080 g (80% rel. **3b**). $C_{15}H_{24}N_2Si_2$ (288.54) molar mass by MS 288 g mol^{-1}. ^{1}H-NMR (200 MHz, $CDCl_3$): $\delta = 0.26$ (s, 18H, $SiMe_3$), 4.96 (m, 2H $H_{1,6}$), 5.96 (m, 2H, $H_{2,5}$), 6.42 (m, 2H, $H_{3,4}$).—$^{13}C\{^1H\}$-NMR (100.62 MHz, C_7D_8): $\delta = 1.31$ ($SiMe_3$), 62.70 ($C_{1,6}$), 125.4 ($C_{2,5}$), 124.8 ($C_{7,8}$), 141.3 ($C_{3,4}$), 129.25 (C≡N).—$C_{15}H_{24}N_2Si_2$ (296.37): Anal. Calc.: C, 62.44; H, 8.38; N, 9.71. Found: C, 62.86; H, 8.48; N, 9.80%.

Acknowledgements

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