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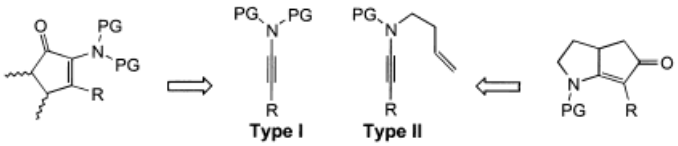
N-Functionalized 1-Alkynylamides: New Building Blocks for Transition Metal Mediated Inter- and Intramolecular [2+2+1] Cycloadditions**

Bernhard Witulski* and Thomas Stengel

Functionalized alkynes are versatile building blocks for transition metal mediated cycloadditions and cyclizations.[1] An exception in this respect are 1-alkynylamines (ynamines).[2] These electron-rich acetylene derivatives have certainly gained some significance with respect to transformations with electrophiles and to Diels – Alder reactions with inverse electron demand;[2, 3] nevertheless they were mostly ignored as building blocks in synthesis.[4] The latter can be attributed to a lack of functionality at the nitrogen atom, because previously known syntheses gave access to "simple" N,N-alkyl or aryl-substituted 1-alkynylamines only.[2a]

Herein we report on the synthesis of N-functionalized and electronically tunable 1-alkynylamines/1-alkynylamides of type **I** and **II** (Scheme 1), as well as their application in regio- and stereoselective inter- and intramolecular [2+2+1] cycloadditions. The protective groups (PGs) of these compounds perform two functions: On the one hand they might act as temporary masking groups of the primary or secondary amine moiety, on the other hand by varying their electron-withdrawing capacities—transformation of the amine into a carbamide, toluenesulfonamide, or trifluorsulfonamide—a tuning of electron density and reactivity of the neighboring triple bond should be possible.



PG: $PhCH_2$, $TolSO_2$, PhCO, CF_3CO, CF_3SO_2, . . . EWG . . .
R: H, $SiMe_3$, . . .

Scheme 1. 1-Alkynylamine and 1-alkynylamide building blocks of type **I** and **II**. EWG = electron-withdrawing group.

The key step for the synthesis of this new class of compounds is the ethynylation of the amides **1a – j** with the readily available trimethylsilylethynyliodonium triflate **2**.[5] Additions of nitrogen nucleophiles to alkynyliodonium salts, in which 2,3-dihydropyrroles are formed *via* alkylidene carbene intermediates and intramolecular 1,5-C – H insertions, were recently reported by Feldman et al.[6] With respect to the cases studied herein, and in accordance with a very high aptitude of silyl groups for 1,2-migrations towards carbenoid centers such as in **3**,[7] preferential formation of 1-alkynylamines and 1-alkynylamides (Scheme 2) is expected. Indeed the alkynes **4a – j** were obtained as single products after deprotonation of **1a – j** with *n*-butyllithium in toluene followed by addition of **2** at 20 °C (Table 1).[8] Dihydropyrroles **5** were not observed. This method is compatible with other functional groups (alkenyl-, alkynyl-, and alkoxycarbonyl residues). However, in some cases α-branched amides (**1h – j**) gave lower yields, reflecting an increase of steric hindrance in the nucleophilic addition of **1** to **2**. Desilylation with tetrabutylammonium fluoride (TBAF) in wet THF yielded the 1-alkynylamides **6a – j** in 78 – 98 % (Table 1). The acetylene derivatives **6** are often crystalline, air stable, and widely insensitive to hydrolysis. Unlike their *N,N*-dialkyl-substituted analogues, the 1-alkynylamides **4** and **6** withstand aqueous work-up procedures as well as chromatographic purification on silica gel. This stability and the ^{13}C NMR spectroscopic data,[9] which are atypical in comparison to those for regular ynamines, are results of electron-withdrawing features of the protective group (PG) affecting the alkyne moiety.

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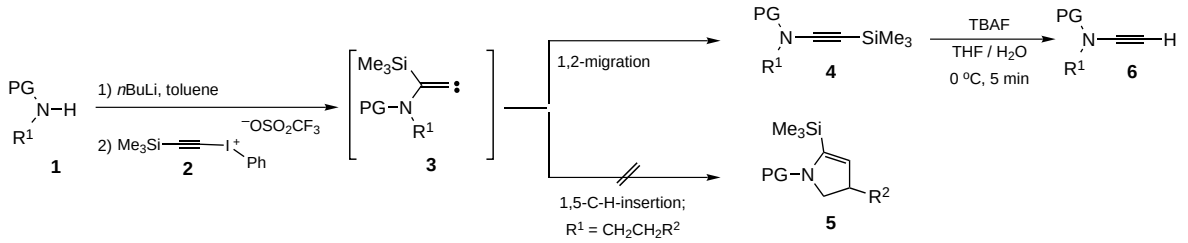


Scheme 2. Synthesis of functionalized 1-alkynylamides **6** (see Table 1).

Table 1. Ethynylation of **1** with **2** to give **4**, and its desilylation to give **6** (Figure 2).

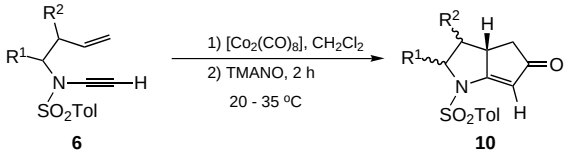
Entry	**1**	PG	R^1	**4**	Yield [%]	**6**	Yield [%]
1	**a**	$TolSO_2$	*n*Bu	**a**	86	**a**	95
2	**b**	$TolSO_2$	$PhCH_2$	**b**	75	**b**	95
3	**c**	CF_3SO_2	$PhCH_2$	**c**	65	**c**	55[a]
4	**d**	CF_3CO	$PhCH_2$	**d**	77	**d**	–[b]
5	**e**	PhCO	$PhCH_2$	**e**	81	**e**	98
6	**f**	$TolSO_2$	$CH_2{=}CH(CH_2)_2$	**f**	89	**f**	93
7	**g**	$TolSO_2$	$CH_2{=}CH(CHPh)CH_2$	**g**	70	**g**	78
8	**h**	$TolSO_2$	$CH_2{=}CHCH_2CH(Ph)$	**h**	28	**h**	89
9	**i**	$TolSO_2$	$CH_2{=}CHCH_2CH(n\text{Bu})$	**i**	50	**i**	91
10	**j**	$TolSO_2$	$(CH_2{=}CHCH_2)_2CH$	**j**	43	**j**	83

[a] Yields based on **1c**. [b] Not determined.

To explore the efficiency of these new building blocks in transition metal mediated transformations we tested their applicability in inter- and intramolecular Pauson–Khand reactions;[10] these [2+2+1] cycloadditions, which simultaneously form three bonds and up to two stereocenters in one step, are broadly recognized as reliable methods for generating five-membered rings.

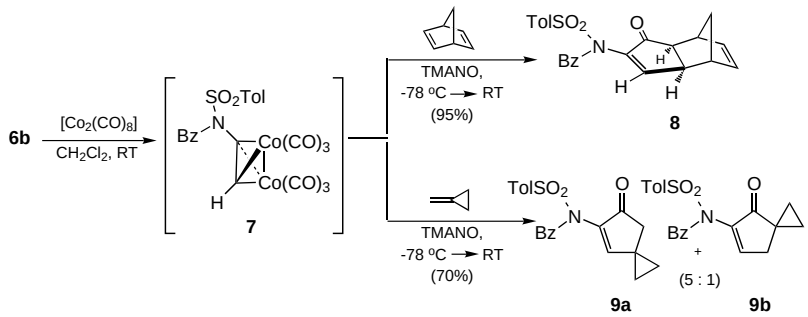
The $[Co_2(CO)_6]$-alkynylamide complex **7** forms almost quantitatively by addition of **6b** to a solution of $[Co_2(CO)_8]$ (1.1 equiv) in CH_2Cl_2. Complex **7** can be isolated; however, it was transformed immediately to [2+2+1] cycloaddition products by adding an olefin (norbornadiene, or methylenecyclopropane, −78 °C to RT, Scheme 3) and trimethylamine *N*-oxide (TMANO) as promoter.[11] Alternatively intermolecular cycloadditions could be initiated by heating to 80–90 °C, while omitting a promoter. Pauson–Khand reactions with **6b** gave yields of 95% for norbornadiene (only *exo* adduct **8** formed) and 70% for methylenecyclopropane (ratio of regioisomers **9a**:**9b** = 5:1). The cycloadditions were exceptionally regioselective with respect to 1-alkynylamide **6b,** and only α,β-unsaturated α-amidocyclopentenones were formed. Regio- and stereoselectivity with respect to the olefinic cycloaddition partner are comparable to those of other Pauson–Khand reactions.[9b, 12]

The steric and electronic effects that govern the regioselectivity of the *inter*molecular reaction are unfavorable for the use of a building block of type **II** in *intra*molecular [2+2+1] cycloadditions. Nevertheless in presence of the reaction promoter TMANO, *intra*molecular [2+2+1] cycloadditions yielded the products **10** in 40–60% after chromatographic purification[13] on aluminum oxide (Scheme 4, Table 2). Surprisingly, the intramolecular cycloadditions are exceedingly diastereoselective for β-branched (**6g**), as well as for α-branched 1-alkynylamides (**6h–j**)—in all cases only one diastereoisomer was observed. The elucidation of the structure of **10b** is based on NMR spectroscopic data and an X-ray structure analysis,[14] those of the bicyclic products **10c–e** on H,H- and C,H-COSY experiments[15] by analysis of distinct NOE relationships between the pseudoaxial protons of the pyrrole moiety (Table 2).



Scheme 4. $[Co_2(CO)_8]$-mediated intramolecular [2+2+1] cycloadditions of **6f–j** (see Table 2).

We consider the application of the type **I** and **II** building blocks in inter- and intramolecular Pauson–Khand reactions, cycloadditions frequently difficult to achieve with polarized acetylenes,[16] as evidence for a successful electronic modulation of the 1-alkynylamides introduced here. The preferred *exo*-orientation of the phenyl substituent of **10b** corresponds to that in carbocyclic analogues.[17] However, the observed diastereoselectivity is remarkable and should be attributed to governing effects of the toluenesulfonyl group. Similar arguments are advanced for the exclusive formation of **10c–e**. Pseudoaxial interactions between the α-substituent and the cobalt carbonyl fragment at the postulated reaction intermediate **B** seem to control the diastereoselectivity (Scheme 5).



Scheme 3. $[Co_2(CO)_8]$-mediated intermolecular [2+2+1] cycloadditions of **6b** with norbornadiene and methylenecyclopropane.

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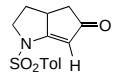
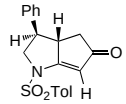
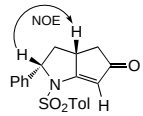
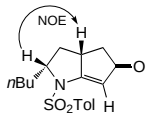
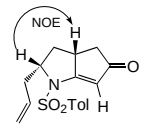
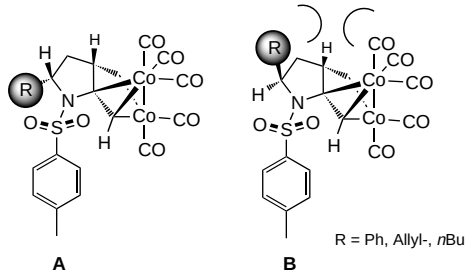
Table 2. Intramolecular [2+2+1] cycloadditions.

Entry	6	R^1	R^2		10	Yield [%][a]
1	**f**	H	H		**a**	40[b]
2	**g**	H	Ph		**b**	60
3	**h**	Ph	H		**c**	45
4	**i**	*n*Bu	H		**d**	54
5	**j**		H		**e**	50

[a] Yields obtained after column chromatography with Alox III/N. [b] Reaction at −78 to 25 °C.



A **B**

Scheme 5. Postulated reaction intermediates **A** and **B**.

The synthesis of functionalized and electronically modulated 1-alkynylamides and their application in intramolecular $[Co_2(CO)_8]$-mediated [2+2+1] cycloadditions outlines fundamental novel strategies for the stereoselective synthesis of nitrogen-containing heterocycles. The concept should be further applicable to other transition metal mediated cyclizations and cycloadditions.

Experimental Section

4g: *n*BuLi (5.19 mmol, 3.25 mL of a 1.6 M solution in hexane) was added to a solution of **1g** (1.3 g, 4.3 mmol) in absolute toluene (60 mL) under argon at 0 °C. After the mixture was allowed to warm to room temperature, iodonium salt **2** (1.13 g, 2.5 mmol) was added in small portions. The reaction mixture was stirred for 12 h and then filtered through a plug of silica gel. Purification by column chromatography (silica gel, petroleum ether:diethyl ether = 9:1 (v/v)) gave analytically pure **4g** (1.19 g, 3.0 mmol, 70 %). ^{1}H NMR (200 MHz, $CDCl_3$/TMS): $\delta = 0.15$ (s, 9H), 2.42 (s, 3H), 3.42–3.80 (m, 3H), 5.06–5.14 (m, 2H), 5.88–6.05 (m, 1H), 7.14–7.33 (m, $J = 8.1$ Hz, 7H), 7.67 (d, $J = 8.1$ Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 144.41$ (s), 140.1 (s), 134.46 (s), 137.53 (d), 129.44 (d), 128.60 (d), 127.94 (d), 127.74 (d), 126.98 (d); 117.11 (t), 94.86 (s), 73.93 (s), 55.22 (t), 48.06 (d), 21.58 (q), 0.14 (q); elemental analysis for $C_{22}H_{27}NO_2SiS$ (397.6): calcd.: C 66.46, H 6.84, N 3.52; found: C 66.85, H 6.60, N 3.44.

10b: **6g** (92 mg, 0.28 mmol) was added to a suspension of $[Co_2(CO)_8]$ (116 mg, 0.34 mmol) in CH_2Cl_2 at 20–36 °C. The formation of the cobalt carbonyl–**6g** complex was monitored by thin-layer chromatography (R_f: 0.48, SiO_2, petroleum ether:ethyl acetate = 8:2 (v/v)). After complete formation a solution of trimethylamine *N*-oxide (115 mg, 1.53 mmol) in CH_2Cl_2 (8 mL) was added by syringe pump over 2 h. The reaction mixture was then filtered through a plug of Alox III/N and eluted with CH_2Cl_2/ethyl acetate. Purification by column chromatography (Alox III/N, petroleum ether: diethyl ether = 1:1 (v/v)) gave analytically pure **10b** (60 mg, 0.17 mmol, 60 %).

10b: colorless plates, m. p.: 176–177 °C; ^{1}H NMR (400 MHz, $CDCl_3$/TMS): $\delta = 2.21$ (dd, $J = 16.7$ Hz, $J = 4.9$ Hz, 1H), 2.47 (s, 3H), 2.58 (dd, $J = 16.7$ Hz, $J = 6.7$ Hz, 1H), 3.00–3.08 (m, $J = 7.5$ Hz, 1H), 3.28–3.34 (m, $J = 2.1$ Hz, $J = 14.0$ Hz, $J = 4.9$ Hz, $J = 6.7$ Hz, 1H), 3.85 (dd, $J = 10.6$ Hz, $J = 10.6$ Hz, 1H), 4.30 (dd, $J = 10.6$ Hz, $J = 7.5$ Hz, 1H), 5.86 (d, $J = 2.07$ Hz, 1H), 7.15–7.39 (m, 7H), 7.81 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 205.58$ (s), 175.26 (s), 145.63 (s), 136.43 (s), 134.22 (s), 130.31 (d), 129.11 (d), 128.02 (d), 127.26 (d), 126.89 (d), 106.15 (d), 59.1 (t), 49.15 (d), 47.91 (d), 40.31 (t), 21.71 (q); elemental analysis for $C_{20}H_{19}NO_3S$ (353.4): calcd.: C 67.97, H 5.42, N 3.97; found: C 67.52, H 5.39, N 3.93.

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[9] Selected ^{13}C-NMR chemical shifts ($CDCl_3$) of the acetylene carbon atoms of the 1-alkynylamides: **4b**: $\delta = 95$ (s), 74 (s); **4c**: $\delta = 91$ (s), 76 (s); **4d**: $\delta = 92$ (s), 78 (s); **4e**: $\delta = 98$ (s), 76 (s); in comparison: trimethylsilyl-*N,N*-dialkyl-1-alkynylamines: $\delta = 111$ (s), 61 (s); **6b**: $\delta = 76$ (s), 60 (d); **6e**: $\delta = 79$ (s), 62 (d); in comparison *N*-methyl-*N*-phenyl-1-alkynylamine: $\delta = 84$ (s), 56 (d).

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[13] In all cases complete conversion of the starting material was observed. However the products were labile towards silica gel and tended to hydrolyze.

[14] Details of the X-ray analysis (U. Bergsträsser, B. Witulski, Universität Kaiserslautern, **1997)** will be published elsewhere.

[15] We would like to express our thanks to Prof. Dr. L. Ernst (Technische Universität Braunschweig) for NOE and 2D-NMR measurements.

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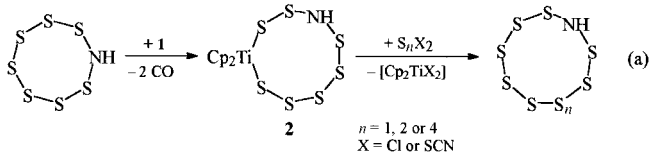
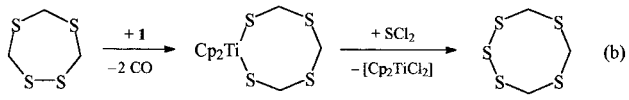
S_4NR (R = Methyl, *n*-Octyl) as Novel Chelating Ligands in Titanocene Complexes and First Synthesis of Small Sulfurimide Heterocycles S_nNR ($n = 5, 6$)**

Ralf Steudel,* Oliver Schumann, Jürgen Buschmann, and Peter Luger

Recently it has been shown that titanocene dicarbonyl $[Cp_2Ti(CO)_2]$ **1** reacts with the S–S bonds of certain homo- and heterocycles with insertion of the titanocene unit and liberation of the two CO ligands.[1] In this way a number of novel chelate complexes has been prepared that are useful reagents for the synthesis of new chain- and ringlike derivatives by ligand transfer reactions. Examples are the complexes **2** and **3**, which allowed the preparation of the cyclic sulfurimides S_8NH, S_9NH, $S_{11}NH$,[2] and of the natural product pentathiocane 1,3,5-$(CH_2)_3S_5$,[1b] respectively [Eq. (a), (b), $Cp = \eta^5$-C_5H_5].

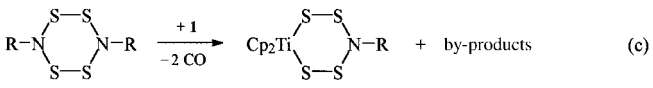


2 (a)



3 (b)

While cycloheptasulfurimide S_7NH and its organic derivatives S_7NR have been known for a long time,[3] the six- and seven-membered rings S_5NR and S_6NR have never been observed although the corresponding homocycles S_6 and S_7[4] as well as their carbon-substituted analogues CH_2S_5 and CH_2S_6[5] are well known as pure materials. Herein we show how cyclic penta- and hexasulfurimides may be prepared in very good yield by ligand transfer from the novel chelate complexes **4** and **5,** respectively. Complex **1** reacts in *n*-hexane at 20 °C with *N*-alkyl-substituted derivatives of the cyclic diimide $HN(\mu$-$S_2)_2NH$[6] to give titanocene derivatives which, however, do not contain the expected seven-membered but a six-membered metallacycle [Eq. (c), *n*Oct = *n*-octyl].



(c)

4 (R = Me)
5 (R = *n*Oct)
6 (R = *n*Oct; Cp = C_5H_4Me)

Contrary to the behavior of S_7NH and S_7NMe[2] there is no insertion into the S–S bond of the diimide, but one NR group is extruded (the fate of this group has not been investigated). Working with two different groups R (Me, *n*Oct) and two different cyclopentadienyl ligands (C_5H_5, C_5H_4Me) only *one* complex was obtained in each case (yields 25–34%). This contained the ligand SSN(R)SS, which has not been observed before.[7] Compound **4** forms black orthorhombic crystals with a melting point of 134 °C, while **5** and **6** are dark brown oils; all three compounds are stable in air for several days and soluble in *n*-hexane, dichloromethane, and carbondisulfide. Decomposition of the brown solutions occurs after several days at 20 °C.

Complex **4** was characterized by single-crystal X-ray structural analysis,[8] which revealed a metallacycle with a chair conformation (Figure 1) similar to the one in $[Cp_2TiS_5]$[9] and in the analogous complex $[Cp_2Ti(\mu$-$S_2)_2AsMe]$.[10] The molecules of **4** occupy general positions but approximately exhibit C_s symmetry. The geometrical parameters show the expected values, for example, d(S–S) = 206.0 pm, d(S–N) =

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