ORGANOMETALLICS

1,3-Dipolar cycloaddition to the C=N-Fe fragment. 6. Formation of 1,4,3a,6a-tetrahydropyrrolo[3,2-b]pyrrole through double addition of dimethyl acetylenedicarboxylate to (1,4-diisopropyl-1,4-diaza-1,3-butadiene)(tert-butylisocyanide)dicarbonyliron, utilizing both imine units of the 1,4-diaza-1,3-butadiene ligand

Paul P. M. De Lange, Hans Werner Fruhauf, Maarten Van Wijnkoop,
Kees Vrieze, Yuanfang Wang, Dick Heijdenrijk, and Casper H. Stam

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Communications

1,3-Dipolar Cycloaddition to the C=N—Fe Fragment. 6.[1] Formation of 1,4,3a,6a-Tetrahydropyrrolo[3,2-*b*]pyrrole through Double Addition of Dimethyl Acetylenedicarboxylate to (1,4-Diisopropyl-1,4-diaza-1,3-butadiene)(*tert*-butyl isocyanide)dicarbonyliron, Utilizing Both Imine Units of the 1,4-Diaza-1,3-butadiene Ligand

Paul P. M. de Lange, Hans-Werner Frühauf,* Maarten van Wijnkoop, and Kees Vrieze

Laboratorium voor Anorganische Chemie
J. H. van 't Hoff Instituut, Universiteit van Amsterdam
Nieuwe Achtergracht 166
1018 WV Amsterdam, The Netherlands

Yuanfang Wang, Dick Heijdenrijk, and Casper H. Stam

Laboratorium voor Kristallografie
J. H. van 't Hoff Instituut, Universiteit van Amsterdam
Nieuwe Achtergracht 166
1018 WV Amsterdam, The Netherlands

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Summary: The reaction of (1,4-diisopropyl-1,4-diaza-1,3-butadiene)(*tert*-butyl isocyanide)dicarbonyliron with an electron-deficient alkyne results in the formation of a tetrahydropyrrolo[3,2-*b*]pyrrole complex. The structure has been determined by X-ray crystallography. With Ce(IV) salts the heterocycle can be displaced from the complex.

Many examples are known of C–C coupling reactions of 1,4-diaza-1,3-butadienes (DAB) in the coordination sphere of transition metals,[2] while the occurrence of C–N coupling reactions of DAB complexes is much less common.[3]

We now present a reaction in which two successive C–C and C–N coupling reactions of the coordinated DAB with two molecules of dimethyl acetylenedicarboxylate (DMADC) take place, leading to the formation of 2,6-diisopropyl-3,4,7,8-tetracarbomethoxy-2,6-diazabicyclo[3.3.0]octa-3,7-diene (or a tetrahydropyrrolo[3,2-*b*]pyrrole in the Hantzsch–Widman nomenclature).

The reaction of Fe(CO)$_3$DAB with dipolarophilic alkynes has been shown to give coordinated 1,5-dihydropyrrol-2-ones.[1] In previous papers[4] we have reported the reaction sequence shown in Scheme I.

In the initial step, an electron-deficient alkyne reacts with Fe(CO)$_3$DAB (**1**) to give the intermediate [2.2.1] bicyclic compound **2**. This reaction has been described in terms of an oxidative 1,3-dipolar [3 + 2] cycloaddition in which the C=N—Fe fragment of Fe(CO)$_3$DAB represents an isolobal analogue of an azomethyne ylide, i.e. a classical 1,3-dipole.[5] The five-membered ring in the [2.2.1] bicyclic compound **2** is expanded by means of a CO insertion in the Fe—N σ bond. The coordinatively unsaturated complex **3** then accepts an additional two-electron-donating ligand to regain the 18-electron configuration. The thus formed [2.2.2] bicyclic compound **4** can isomerize via reductive elimination and recoordination to the 1.5-dihydropyrrol-2-one complex **5**.

To probe the influence of different ligands in the starting DAB complex and to expand the potential of this reaction, we substituted a CO ligand for an isocyanide ligand (*t*-Bu-NC) in Fe(CO)$_3$DAB. Isocyanide was chosen in anticipation of two possible effects. First, cycloaddition reactions are very sensitive to variations in the energetic disposition of the interacting frontier orbitals. Isocyanides are better σ-donating/less π-accepting than CO[6] and thus increase the amount of π-back-donation to the DAB ligand. This should lead to an enhanced 1,3-dipolar activity of the C=N—Fe fragment and allow the use of less activated alkynes (or olefins) as dipolarophiles. Second, isocyanides, just like CO, are known to undergo insertion reactions. It was therefore interesting to see whether a competition between the two could be observed in forming the [2.2.2]bicyclo intermediates **3** and **4**.

In the reaction of Fe(CO)$_2$(*t*-Bu-NC)(*i*-Pr-DAB) (**6**)[7] with DMADC no RNC insertion product is found; instead, complex **9**[8] with η^3-coordinated tetrahydropyrrolo[3,2-*b*]pyrrole is formed in high yield together with a very minor amount (less than 5%) of the CO-inserted [2.2.2]bicyclo complex **11**.[9]

The formation of the organometallic complex **9** is the result of two subsequent 1,3-dipolar [3 + 2] cycloadditions of two molecules of DMADC to both of the C=N—Fe units followed by two reductive eliminations (see Scheme II).

The unprecedented double addition of DMADC clearly demonstrates the strongly enhanced reactivity of **6** as

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[1] Part 5: Frühauf, H.-W.; Seils, F.; Stam, C. H. *Organometallics* **1989**, *8*, 2338.

[2] (a) Staal, L. H.; van Koten, G.; Vrieze, K.; van Santen, B.; Stam, C. H. *Inorg. Chem.* **1981**, *20*, 3598. (b) Keysper, J.; Polm, L. H.; van Koten, G.; Vrieze, K.; Stam, C. H.; Schagen, J. D. *Inorg. Chim. Acta* **1985**, *103*, 137. (c) Staal, L. H.; Polm, L. H.; Balk, R. W.; van Koten, G.; Vrieze, K.; Brouwers, A. M. F. *Inorg. Chem.* **1980**, *19*, 3343.

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[6] (a) Yamamoto, Y.; Yamazaki, H. *Coord. Chem. Rev.* **1972**, *8*, 225. (b) Treichel, P. M. *Adv. Organomet. Chem.* **1973**, *11*, 21. (c) Yamamoto, Y. *Coord. Chem. Rev.* **1980**, *32*, 193.

[7] Experimental details for the preparation and the properties of the starting compound **6** will be reported in a full paper.

[8] Preparation of **9**: A solution of 310 mg (0.93 mmol) of Fe(CO)$_2$(*t*-Bu-NC)(*N,N'*-*i*-Pr$_2$-DAB) (**6**)[7] in ca. 20 mL of tetrahydrofuran was cooled to −78 °C. Then 0.228 mL (1.86 mmol) of DMADC (Aldrich) was added, and the solution was stirred for 2 h. After removal of ca. 50% of the solvent, the product was precipitated by adding ca. 20 mL of pentane. The product was washed three times with ca. 20 mL of pentane and dried in vacuo (0.34 g, 87%). The crude product may be further purified (loss of product due to some decomposition occurs) by column chromatography (silica gel 60, Merck). A yellow solution of **9** was obtained by elution with diethyl ether and dried in vacuo (0.27 g, 80%). Pale yellow crystals were grown from a concentrated diethyl ether solution.

[9] With insufficient amounts of DMADC, the yield of **11** may reach ca. 10%. This demonstrates a partitioning of the reaction coordinate and the intermediacy of **7**.

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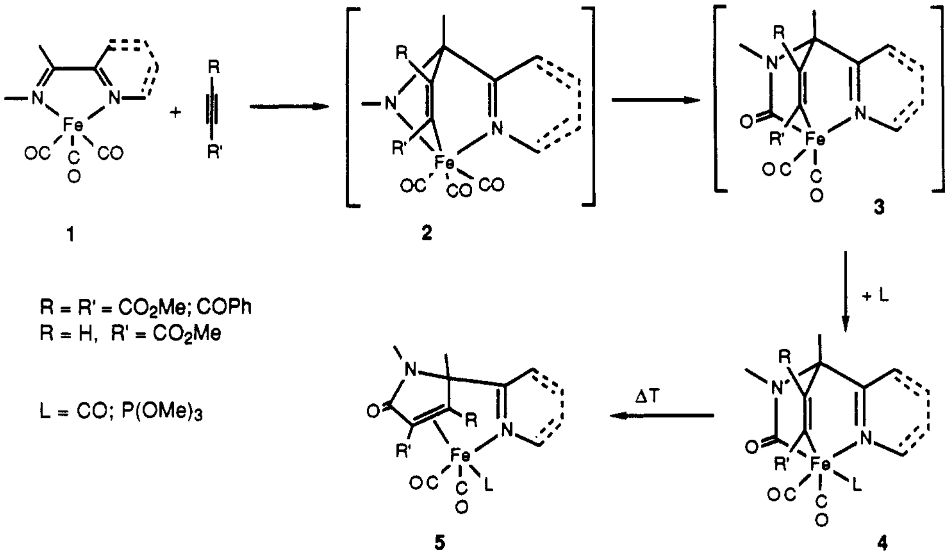
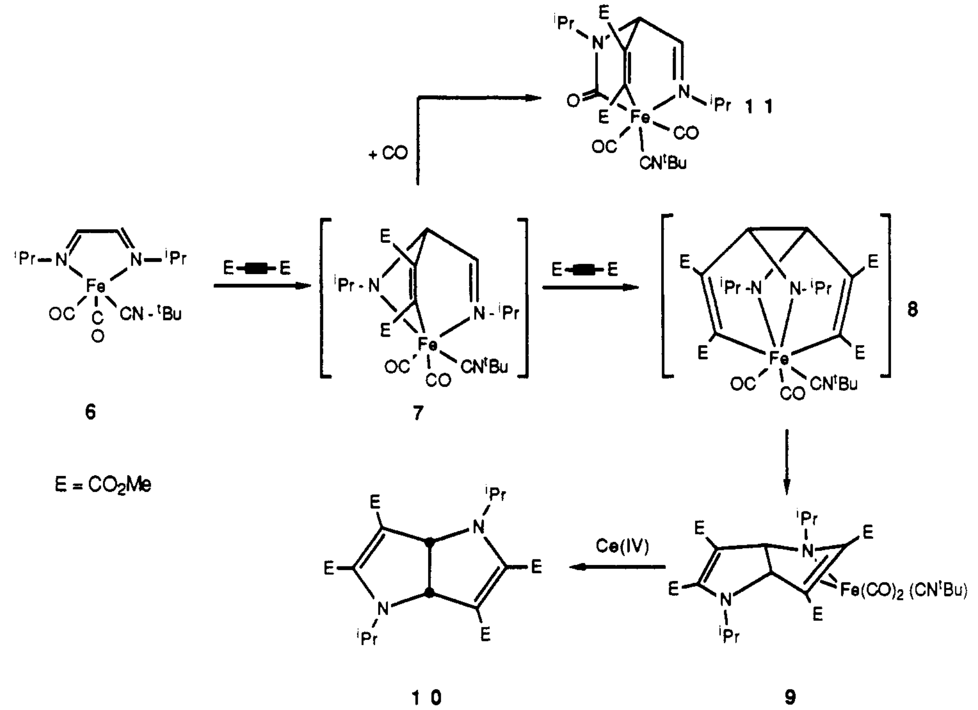
Scheme I



Scheme II



compared to that of the tricarbonyl complex **1**. Furthermore, until now, the intermediacy of structures **2** and **7** as the initial products has only been inferred from circumstantial evidence. The alternative of a concerted attack of the alkyne on the imine carbon and iron with simultaneous migration of nitrogen from iron to the carbonyl atom could not be rigorously excluded. Now it is obvious that cycloaddition and CO insertion are two separate, successive events. Due to the high 1,3-dipolar reactivity, the second addition, generating **8**, is roughly more than 20 times (concluding from the less than 5% yield of **11**) faster than intramolecular CO insertion to give **11**. It is not clear, however, if the tricyclic structure **8** with 7-coordinated iron(IV) represents an actually existing intermediate. In any case it should readily undergo reductive elimination to form **9**.

The ^{1}H NMR spectrum reflects the asymmetric bicyclic structure of compound **9**.[10] As a consequence of the alkyne addition, the hybridization of the two imine carbon atoms has changed from sp^2 to sp^3, so the two former imine protons of the DAB ligand are shifted ca. 3 ppm upfield. Because of the inequivalence of the two pyrrole rings the four methoxy groups of the former DMADC give rise to four singlets at 3.85, 3.76, 3.60, and 3.55 ppm. The chemically nonequivalent, diastereotopic isopropyl groups give rise to four doublets. The asymmetry of the two pyrrole rings is also visible in the ^{13}C NMR spectrum. The four

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(10) **9** is formed as pale yellow crystals. IR (THF, cm^{-1}): ν_{CN} = 2135; ν_{CO} = 1993, 1943. ^{1}H NMR (250 MHz, 293 K, CDCl$_3$, δ (J in Hz)): 4.90 (1 H$_3$ (or H$_6$), d, $J_{H,H}$ = 9.0); 4.43 (1 H$_6$ (or H$_3$), d, $J_{H,H}$ = 9.0); 3.85, 3.76, 3.60, 3.55 (12 H, COOC*H*$_3$, s; 2 H, C*H*(CH$_3$)$_2$, m); 1.43 (9 H, *t-Bu*-NC, s); 1.33 (3 H, CH (*CH*$_3$)$_2$, d, $J_{H.H}$ = 7.5); 1.30 (3 H, CH(*CH*$_3$)$_2$, d, $J_{H.H}$ = 7.5); 1.23 (3 H, CH(*CH*$_3$)$_2$, d, $J_{H.H}$ = 7.0); 1.04 (3 H, CH(*CH*$_3$)$_2$, d, $J_{H.H}$ = 7.0). ^{13}C NMR (C$_6$D$_6$, 293 K, 25.2 MHz, δ): 214.6 (C23, C24); 174.8, 171.7 (C8, C21); 174.3 (C25); 165.4, 164.2 (C13, C16); 159.5 (C4); 103.6 (C1); 95.0 (C5); 71.8, 67.8 (C6, C3); 57.3 (C26); 55.9, 52.2, 52.1, 51.0, 50.6, 50.3 (C9, C10, C14, C17, C18, C22); 51.6 (C2); 30.8 (C27, C28, C29); 23.1, 20.6, 20.0, 18.9 (C11, C12, C19, C20). Anal. Calcd for $C_{27}H_{37}N_3O_{10}Fe$: C, 52.35; H, 6.02; N, 6.78. Found: C, 52.09; H, 5.93; N, 6.62.

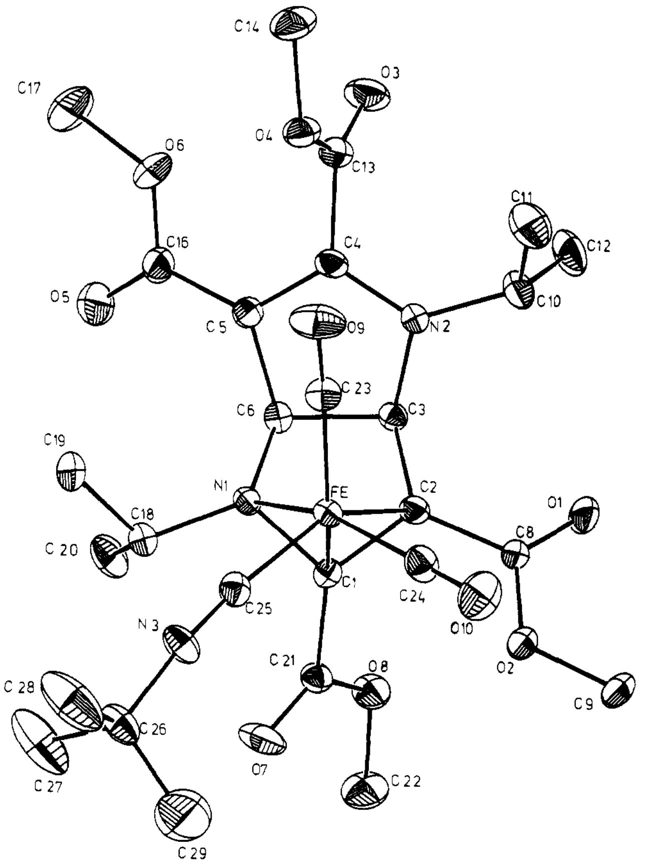

Figure 1. Molecular structure of **9**. Hydrogen atoms have been omitted for clarity. Selected bond distances (Å): C(1)–C(2) = 1.452 (6), C(1)–N(1) = 1.445 (6), C(2)–C(3) = 1.517 (6), C(3)–C(6) = 1.550 (6), C(3)–N(2) = 1.488 (6), C(4)–N(2) = 1.333 (6), C(4)–C(5) = 1.372 (6), C(5)–C(6) = 1.504 (7), C(6)–N(1) = 1.534 (6).

different methoxy carbon atoms resonate at four different frequencies; C(13) and C(26) of the uncoordinated pyrrole ring resonate at 164.2 and 165.4 ppm, and C(8) and C(21) of the coordinated pyrrole ring (see Figure 1) resonate at 174.8 and 171.7 ppm. A large difference in frequencies is visible for the olefinic carbon atoms C(1), C(2), C(4), and C(5). The uncoordinated atoms C(4) and C(5) resonate at 159.5 and 95.0 ppm, which is in close agreement with the values found in the free pyrrolopyrrole (see below), while the coordinated carbon atoms C(1) and C(2) resonate at 103.6 and 51.6 ppm. These coordination shifts Δδ of ca. 53 and 43 ppm to high field are in the normal range found for π-coordinated olefins.[11] The carbonyl carbon atoms appear as one signal at 214.6 ppm, which suggests a rapid scrambling of the two CO's.

The structure of **9** has been determined by X-ray crystallography[12] (see Figures 1 and 2).

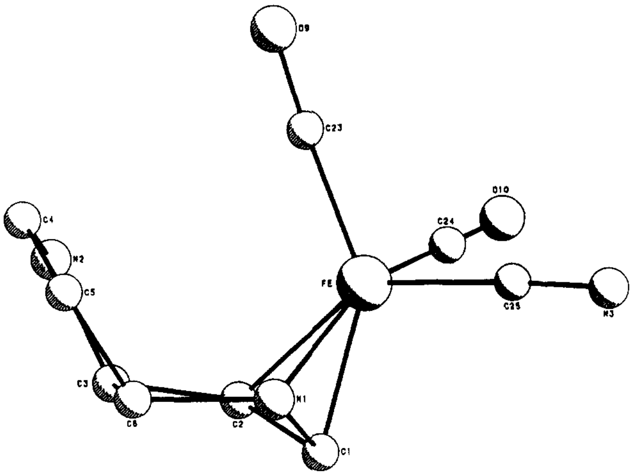

Figure 2. Side view of **9**. Only the ring atoms and the Fe(CO)$_2$(CN) fragment are shown for clarity. Angles between the planes (deg): C(2)–C(1)–N(1)/C(2)–C(3)–C(6)–N(1) = 126.2, C(2)–C(3)–C(6)–N(1)/C(3)–N(2)–C(4)–C(5)–C(6) = 146.6.

The organometallic complex adopts a folded structure in which the uncoordinated pyrrole ring makes an angle of 146.6° with the plane (±0.06 Å) defined by C(2), C(3), C(6), and N(1). This plane again makes an angle of 126.2° with the plane containing the coordinated atoms C(2), C(1), and N(1). This distortion from planarity in the coordinated pyrrole ring, caused by the η^3 coordination, is also found in organometallic complexes with η^3-coordinated bicyclic indenyl ligands. In those complexes the angle between the η^3-coordinated carbon atoms and the remaining carbon atoms of the η^3-indenyl ligand varies between 102 and 118°.[13] The planar (±0.05 Å) uncoordinated pyrrole ring has bond angles and bond distances comparable to those of a free tetrahydropyrrolopyrrole.[14] Noteworthy is the delocalization of the nitrogen lone pair and the double bond in the C(5)–C(4)–N(2) moiety. This delocalization is obvious from the sp^2 bond angles of 119.6° (average) around N(2) and from the relatively short bond distance of 1.333 (6) Å for C(4)–N(2). As a consequence of coordination to the metal the C(2)–C(1)–N(1) moiety is bent away; the average bond angles around C(2), C(1), and N(1) are decreased to, respectively, 107.4, 106.4, and 107.3°, angles normally found for sp^3-hybridized atoms. The bond distances of C(1)–N(1) and C(1)–C(2) are increased to 1.445 (6) and 1.452 (6) Å, respectively. These bond angles and bond distances also indicate delocalization of the nitrogen lone pair and the double bond in the metal-coordinated C(2)–C(1)–N(1) moiety.

The synthetically interesting[15] heterocycle **10**[16] can be

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[11] Mann, B. E. *Adv. Organomet. Chem.* **1974**, *12*, 135.

[12] Crystal data for **9**: space group *Cc*, a = 15.756 (2) Å, b = 17.790 (2) Å, c = 11.356 (5) Å, β = 91.13 (1)°, Z = 4, d_{calc} = 1.29 g cm^{-3}, μ(Mo Kα) = 5.24 cm^{-1}. The 5134 reflections were measured on a Nonius CAD-4 diffractometer; 2266 were above the 2.5$\sigma(I)$ level and were treated as observed. The non-hydrogen atoms were found by using the method of Patterson minimum function. The hydrogen atoms were found by theoretical calculations. After isotropic block-diagonal least-squares refinement an empirical absorption correction was applied. Continued anisotropic refinement for non-hydrogen atoms converged to R = 0.036 (R_w = 0.050). A weighting scheme with $w = 1/(5.48 + F_o + 0.0151F^2{}_o)$ was applied, and the anomalous dispersion of Fe was taken into account. The calculations were carried out with XRAY76. The scattering factors were taken from: Cromer, D. T.; Mann, J. B. *Acta Crystallogr.* **1968**, *A24*, 321. The dispersion corrections were taken from: *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

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[16] Liberation of **10**: 131.1 mg (0.21 mmol) of complex **2** was dissolved in ca. 15 mL of benzene. Then 402.1 mg (0.63 mmol) of $(NH_4)_4(SO_4)_4Ce\cdot 2H_2O$ (Merck) was added, and the solution was refluxed for 3 days. After removal of the solvent the oily product was obtained by column chromatography (silica gel 60, Merck) with diethyl ether as eluent and dried in vacuo (67.5 mg, 76%). ^{1}H NMR (100 MHz, 293 K, CDCl$_3$, δ (J in Hz)): 5.31 (2 H, H$_3$ and H$_6$, s); 3.63, 3.89 (12 H, COOCH_3, s; 2 H, CH(CH$_3$)$_2$, m); 1.21 (12 H, CH(CH_3)$_2$, d, $J_{H.H}$ = 6). ^{13}C NMR (C$_6$D$_6$, 293 K, 25.2 MHz; carbon numbering as in **9**; δ): 164.5, 164.0 (C8, C13, C16, C21); 155.7 (C1, C4); 96.5 (C2, C5); 69.8 (C3, C6); 51.7, 49.9, 49.2 (C9, C10, C14, C17, C18, C22); 19.9, 19.8 (C11, C12, C19, C20).

displaced from the metal by treating the organometallic complex with a Ce(IV) salt (see Scheme II). The potent reactivity of **10** is due to two eneamide units. The two pyrrole rings in compound **10** are now equivalent, which can be derived from the ^{1}H NMR spectrum. The ^{1}H NMR spectrum shows a singlet at 5.31 ppm due to the two former imine protons. The four methoxy groups give rise to two singlets at 3.63 and 3.89 ppm. Also, the ^{13}C NMR spectrum shows the high degree of symmetry of **10**. The four methoxy carbon atoms resonate at 164.5 and 164.0 ppm. The olefinic carbon atoms now give rise to only two signals at 155.7 and 96.5 ppm, from which it becomes clear that all four olefinic carbon atoms are sp^2-hybridized. These frequencies are comparable to those of the olefinic and the methoxy carbon atoms of the uncoordinated pyrrole ring of complex **9**. From this can be concluded that the metal does not influence the uncoordinated pyrrole ring. This reaction is another example for and an expansion of the synthetic potential of 1,3-dipolar additions in metal-promoted organic synthesis.

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Registry No. **6**, 126217-90-1; **9**, 126255-43-4; **10**, 126217-89-8; **11**, 126294-47-1; DMADC, 762-42-5.

Supplementary Material Available: A summary of crystal data and details of X-ray data collection and tables of atomic fractional coordinates, thermal parameters, and selected interatomic distances and angles (12 pages); a list of observed and calculated structure factors (12 pages). Ordering information is given on any current masthead page.

Kinetics of the Cyclization of 5-Hexyn-1-yllithiums

William F. Bailey* and Timo V. Ovaska

Department of Chemistry, University of Connecticut
Storrs, Connecticut 06269-3060

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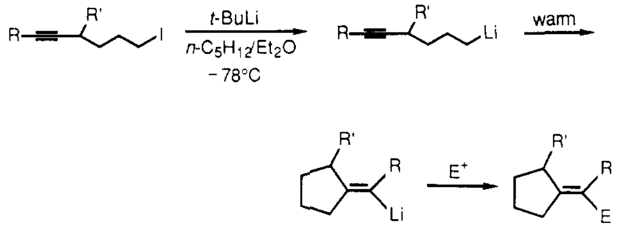
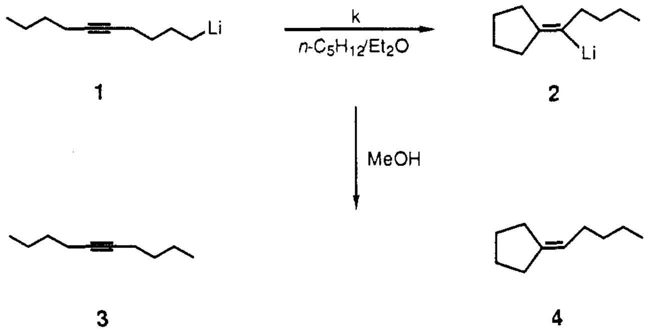
Summary: The kinetics of the 5-exo-dig cyclization of 5-decyn-1-yllithium (**1**) to (1-cyclopentylidenepent-1-yl)lithium (**2**) are characterized by $\Delta H^{\ddagger} = 23.0 \pm 0.9$ kcal/mol and $\Delta S^{\ddagger} = +4.8 \pm 3.3$ eu ($E_a = 23.6 \pm 0.9$ kcal/mol; $\ln A = 32.9 \pm 3.5$). The phenyl-substituted analogue (6-phenyl-5-hexyn-1-yl)lithium (**5**) cyclizes much more rapidly than the alkyl-substituted systems: $k = (1.97 \pm 0.08) \times 10^{-3}$ at −50.6 °C ($t_{1/2}$ = 6 min).

We recently reported that 5-alkyn-1-yllithiums undergo clean 5-exo-dig cyclization via syn addition of CH_2Li to the carbon–carbon triple bond upon warming to room temperature.[1] As shown below, this anionic cyclization provides a convenient regiospecific and stereoselective route to functionalized cyclopentylidene-containing products:[1-3]



While limited kinetic data for the sluggish cyclization of 5-hexynyl Grignard reagents have been reported in pioneering studies by Richey's group,[4] activation parameters for the rather facile cyclization of 5-hexyn-1-yllithiums are unavailable. Prompted by the potential synthetic utility of the isomerization of acetylenic alkyllithiums, we have investigated the kinetics of the cyclization of 5-decyn-1-yllithium (**1**) to (1-cyclopentylidenepent-1-yl)lithium (**2**). The results of these experiments are summarized in Table I.

The requisite organolithium was prepared by our general protocol for low-temperature lithium–iodine interchange.[1,5,6] Thus, treatment of a 0.05 M solution of 1-iodo-5-decyne[7] in *n*-pentane–diethyl ether (3:2 by volume) with 2.1 equiv of *tert*-butyllithium (*t*-BuLi) at −78 °C under argon affords **1** in essentially quantitative yield.[8] The isomerization of **1** to **2** was monitored at four temperatures[9] between 0 and +28.8 °C by rapid removal of aliquots and quench of the organolithiums with dry, deoxygenated methanol to give 5-decyne (**3**) and pentylidenecyclopentane[7] (**4**). The relative proportions of hydrocarbons **3** and **4** were determined by GC (25 m × 0.2 mm HP-1 capillary column; 80 °C for 8 min, then 20 °C/min to 250 °C) with use of *n*-decane as an internal standard.



The isomerization of **1** to **2** is a cleanly first-order process when care is taken to exclude moisture and oxygen from the system. There was no evidence of products derived from prototropic rearrangement of **1**, and no trace of allene was observed in any of the reaction mixtures. Cyclizations were followed through 3–8 half-lives by monitoring both the disappearance of **1** (assayed as **3**) and the appearance

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(2) Bailey, W. F.; Ovaska, T. V. *Tetrahedron Lett.* **1990**, *31*, 627.

(3) For the sake of pictorial clarity, organolithiums are represented as monomeric. The degree of aggregation of the acetylenic alkyllithiums **1**, **2**, **5**, and **6** under the reaction conditions is unknown.

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(5) (a) Bailey, W. F.; Patricia, J. J.; Nurmi, T. T.; Wang, W. *Tetrahedron Lett.* **1986**, *27*, 1861. (b) Bailey, W. F.; Patricia, J. J.; Nurmi, T. T. *Tetrahedron Lett.* **1986**, *27*, 1865.

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(8) Lithium–iodine interchange between *t*-BuLi and a primary alkyl iodide invariably results in the formation of a small but non-negligible amount of hydrocarbon formally derived from the reduction of the halide. As noted elsewhere,[6] formation of the hydrocarbon is an unavoidable consequence of the rapid reaction of RLi with the cogenerated *t*-BuI to give RH, 2-methylpropene, and LiI.

(9) The temperature of samples used in the kinetic experiments was maintained at ±0.2 °C with a Braun Model 1495 refrigerated constant-temperature bath.

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