directly bonded to a transition metal (M–P(E)YZ) can migrate to a Cp ring, whereas a trivalent tricoordinated phosphorus on a transition metal (M–PYZ) cannot migrate, though both of the M–P(E)YZ and M–PYZ bonds are formally covalent in nature. Further studies of the phosphorus migration process are in progress.

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Registry No. **1a**, 34738-99-3; **1b**, 120058-91-5; **1d**, 120058-94-8; **2a**, 120058-89-1; **2b**, 120058-92-6; **3a**, 120058-90-4; **3b**, 120058-93-7.

Group V Metallacyclopropenes in Synthesis. An Efficient Route to Polyfunctional Ring Systems via the Cocyclization of Diynes with Substituted Monoacetylenes[1]

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Summary: A variety of monosubstituted alkynes have been shown to undergo facile trimerization to the corresponding arenes in the presence of the $CpNbCl_4/Mg$ catalyst system. A novel benzocycle annulation procedure (e.g., **1** → **3**) is described that relies on the use of the above low-valent organoniobium species.

Zirconocene–alkyne complexes have recently emerged as an important new class of synthetic intermediates.[3-5] Despite the intense interest which has been shown in the alkyne complexes of group IV metals, relatively few synthetic applications of group V–alkyne complexes have been recorded.[6,7] In this communication we wish to report the first examples of benzocycle annulation (e.g., 1 → 3) via the cocyclization of diynes and monoacetylenes on low-valent group V metal centers. Curtis and Real have recently described the direct synthesis of several thermally stable cyclopentadienylniobium(III)–alkyne complexes from *diarylacetylenes.*[7a] The possibility that related group V metallacyclopropenes might serve as versatile synthetic intermediates prompted us to investigate the preparation and reactivity of these species.

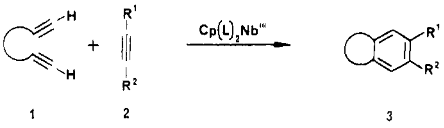
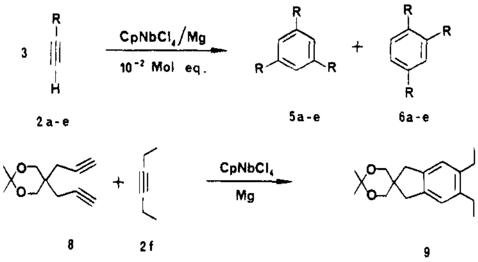
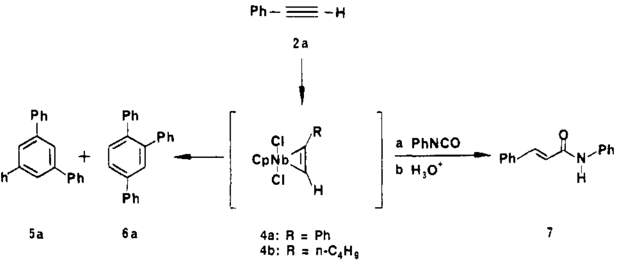


Table I. Catalytic Trimerization of Alkynes by $CpNbCl_4/Mg$



RC≡CH	yield 5 + 6, %	ratio 5/6
2a: R = Ph	90	7
2b: R = n-C_4H_9	91	1.22
2c: R = $(CH_2)_3OSi$-t-$BuMe_2$	95	1.17
2d: R = $(CH_2)_2OCO$-i-Bu	83	1.16
2e: R = $SiMe_3$	0	...

The reactive metallacyclopropenes utilized in this study were generated by the reduction of $CpNbCl_4$[8] with Mg^0 (100 mesh) under argon in the presence of the appropriate alkyne in THF at 0 °C. Complexation of phenylethyne (**2a**) in the above manner gave a solution of the corresponding metallacycle **4a** that underwent slow decomposition at 25 °C with concomitant formation of a mixture of the isomeric triphenylbenzenes **5a** and **6a** (**5a**/**6a** = 7) that could be isolated in 83% yield. Evidence for the intermediacy of **4a** was provided by its interception with PhNCO and subsequent hydrolysis to furnish N-phenylcinnamide (**7**) in 55% yield.[9,10] The analogous $CpNbCl_2$-1-hexyne complex **4b** was found to be consid-



[†] Montana State University Undergraduate Dissertation Fellow, 1987–1989.

[‡] Montana State University Summer Undergraduate Fellow, 1988.

[1] Part 1 in a series on the synthetic applications of group V metallacyclopropenes.

[2] Fellow of the Alfred P. Sloan Foundation, 1989–1991.

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[7] (a) Curtis, M. D.; Real, J. *Organometallics* **1985**, *4*, 940. (b) Curtis, M. D.; Real, J. *J. Am. Chem. Soc.* **1986**, *108*, 4668.

[8] Cardoso, A. M.; Clark, R. J. H.; Moorhouse, S. *J. Chem. Soc. Dalton Trans.* **1980**, *7*, 1156.

[9] The scope and limitations of trapping reactions involving the functionalization of group V metallacyclopropenes with carbon-based electrophiles is under current investigation.

[10] A representative experimental procedure is as follows: An oven-dried 12-cm Pyrex test tube equipped with a rubber septum, magnetic stirring bar, and argon inlet was charged with 100 mesh magnesium powder (24 mg, 1 mg-atom) and cyclopentadienylniobium tetrachloride (300 mg, 1 mmol). The tube was purged with argon and cooled to 0 °C whereupon phenylethyne (102 mg, 1 mmol) and dry THF (4 mL) were added by syringe. The reaction mixture was then stirred at 0 °C for 1 h at which time all of the magnesium had dissolved and a homogeneous dark red solution of the metallocyclopropene **4a** had been formed. A solution of phenyl isocyanate (119 mg, 1 mmol) in dry THF (1 mL) was then added, and the resultant solution was stirred at 50 °C for 12 h. The reaction mixture was cooled to 25 °C, and saturated aqueous NH_4Cl (1 mL) was added. After being stirred for 30 min, the mixture was diluted with ether (15 mL) and the organic layer was separated and then dried with brine (10 mL). The mixture was filtered through Florisil, and the solvents were removed in vacuo. The residue was then subjected to chromatography (20% ethyl acetate–hexane for elution) to afford 123 mg (55%) of N-phenylcinnamide (**7**) as a white solid: mp 154–157 °C (authentic 156–158 °C); ^1H NMR (300 MHz, $CDCl_3$) δ 8.16 (br s, 1 H, NH), 7.73 (d, 1 H, J = 15.6 Hz PhCH=CHCONHPh), 7.60 (d, 2 H, J = 7.8 Hz, ArH), 7.36–7.24 (m, 5 H, ArH), 7.10 (d, 1 H, J = 7.4 Hz, ArH), 6.65 (d, 1 H, J = 15.6 Hz, PhCH=CHCONHPh); IR ($CHCl_3$) 3684, 3620, 3429, 3319, 3027, 2977, 2895, 1679, 1632, 1597, 1578, 1439, 1380, 1336, 1285 cm^{-1}. Efforts to isolate the metallocyclopropene **4a** by removal of the THF at 20 °C resulted in the rapid decomplexation–cyclotrimerization of the phenylethyne to give the triphenylbenzenes **5a** and **6a** (**5a**/**6a** = 7).

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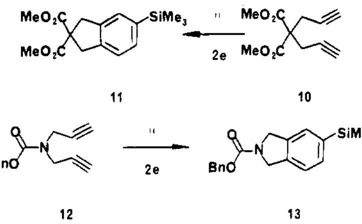
erably more labile in the thermal sense than the phenylethyne derivative and underwent rapid decomplexation to the isomeric tributylbenzenes **5b** and **6b** (**5b**/**6b** = 1.22) at room temperature.[11] That the low-valent niobium center could also function as a catalyst[12a] for alkyne trimerization was demonstrated by the following experiment. Reduction of CpNbCl$_4$ with Mg^0 (1 equiv) in the presence of 1-hexyne (100 equiv) in THF at 25 °C gave the arenes **5b** and **6b** (**5b**/**6b** = 1.22) in 91% isolated yield. A series of terminal alkynes was subsequently subjected to the catalytic low-valent niobium system described above. The results of this study are compiled in Table I.

Cotton has reported that *internal* alkynes are efficiently polymerized in the presence of catalytic quantities of [(NbCl$_3$)$_2$·(tetrahydrothiophene)$_3$].[12b] It is therefore of considerable interest that *representative internal alkynes (e.g., 3-hexyne, 1-phenyl-1-propyne,*[13] *etc.) were found to undergo neither polymerization nor cyclotrimerization in the presence of the CpNbCl$_4$/Mg^0 catalyst system.* These results strongly suggested that annulation reactions involving the cocyclization of diynes with relatively unhindered internal acetylenes or hindered terminal acetylenes (e.g., Table I, entry **2e**) would be achievable employing the CpNbCl$_4$/Mg^0 system. Accordingly, addition of the diyne **8** over 6 h to a prereduced solution of CpNbCl$_4$ (0.35 equiv[14]) and 3-hexyne (10 equiv) under argon in THF maintained at 50 °C and subsequent stirring for 12 h provided the indan **9** in 80% chromatographed yield. In a similar fashion, the diester **10** and the urethane **12** were cocyclized with (trimethylsilyl)acetylene (**2e**) to furnish the indan **11** and the isoindolene **13** in isolated yields of 74% and 52%, respectively.[15]



The significance of the foregoing results derives from the ability of monoacetylenes less hindered than bis(trimethylsilyl)acetylene to participate selectively in binary annulations involving diynes. By way of contrast, the successful utilization of cobalt-based catalysts (e.g., CpCo(CO)$_2$) is largely restricted to the use of (Me$_3$SiC)$_2$ as a cocyclization addend.[16,17] The above examples also illustrate the functional group compatibility of this new method for benzocycle annulation.[18]

Additional applications of niobium(III)- and tantalum(III)-alkyne complexes to synthesis will be the topic of future reports from this laboratory.

Acknowledgment. Support for this research by a grant from the National Institutes of Health is gratefully acknowledged.

Supplementary Material Available: Spectral data for the compounds **5a-d**, **6a-d**, **9**, **11**, and **13** (2 pages). Ordering information is given on any current masthead page.

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[11] Evidence has recently been provided for the intermediacy of tantalacyclopentadienes in the cyclotrimerization of alkynes by tantalum(III) complexes: (a) Strickler, J. R.; Wexler, P. A.; Wigley, D. E. *Organometallics* **1988**, *7*, 2067. (b) Bruck, M. A.; Copenhauer, A. S.; Wigley, D. E. *J. Am. Chem. Soc.* **1987**, *109*, 6525.

[12] Early precedence for the trimerization of *terminal alkynes* on low-valent group V centers [e.g., (NbCl$_3$)$_2$(THT)$_3$ and (TaCl$_3$)$_2$(THT)$_3$] has been provided by Cotton: (a) Cotton, F. A.; Hall, W. T. *J. Am. Chem. Soc.* **1979**, *101*, 5094. (b) Cotton, F. A.; Hall, W. T.; Cann, K. J.; Karol, F. J. *Macromolecules* **1981**, *14*, 233.

[13] Evidence for the generation of the CpNbCl$_2$-(1-phenyl-1-propyne) complex in a stoichiometric run was provided by its hydrolyses with 1 M HCl to furnish (*Z*)-1-phenyl-1-ethene in ~50% yield (GC).

[14] The use of greater than catalytic concentrations of CpNbCl$_4$/Mg^0 is recommended for runs that involve the slow addition of diynes as a result of competitive decomposition of the active Nb species at elevated temperatures. Temperatures of ca. 50 °C are required for internal alkynes or (trimethylsilyl)acetylene to efficiently participate in cocyclizations with representative diynes.

[15] All new compounds have been fully characterized by 300-MHz ^{1}H NMR and IR spectroscopy and possess satisfactory elemental (C, H) analyses or exact mass.

[16] Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 539. The present methodology is therefore complementary to well-established annulation procedures based on cobalt.

[17] Jonas, K.; Deffense, E.; Habermann, D. *Angew. Chem. Suppl.* **1983**, 1005-1016.

[18] A comprehensive account concerning the utilization of (Ph$_3$P)$_3$RhCl for effecting related diyne-monoacetylene cocyclizations has appeared recently. Grigg, R.; Scott, R.; Stevenson, P. *J. Chem. Soc., Perkin Trans. 1* **1988**, 1357.

Arene Complexes of p-Block Elements: [(η^6-C$_6$H$_6$)$_2$SnCl(AlCl$_4$)]$_2$. The First Bis(arene) Coordination Compound of a Group 14 Element

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Summary: From the reaction of the molten salt Sn(AlCl$_4$)$_2$ with benzene the dimeric species [(η^6-C$_6$H$_6$)$_2$SnCl(AlCl$_4$)]$_2$·C$_6$H$_6$ (**1**) has been obtained. Compound **1**, which was characterized by X-ray diffraction analysis, represents the first example for double arene complexation of a group 14 post-transition element. Each Sn center is η^6-bonded to two molecules of benzene. The two benzene planes are inclined with respect to each other and form angles of 101.9° (Sn1) and 99.7° (Sn2), respectively. The two (η^6-C$_6$H$_6$)$_2$Sn units of the dimer are linked by two direct chlorine bridges and two 1,3-bidentate AlCl$_4$ groups. The crystal benzene molecule has no metal contacts. The coordination of the tin(II) centers is thus pseudooctahedral, and the entire dimer approaches noncrystallographic C_{2h} symmetry.

It is now well established that most of the low-valent p-block metals are capable of forming coordination compounds with aromatic hydrocarbons. These complexes display a large variety of stoichiometries and structural features, regarding (1) the hapticity of the aromatic rings bound to the metal center, (2) the individual arene:metal ratio in an "open sandwich", "sandwich", "inverse sandwich", or "cage" type arrangement, and (3) the aggregation of these units to yield dimers, tetramers, polymeric chains, or three-dimensional networks. Moreover, the crystalline compounds very often contain different amounts of noncoordinating (interstitial) aromatic hydrocarbons.

Typical examples with neutral arene donors have been described for the complete triads Ga/In/Tl[1] and As/

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