

with the isotopically sensitive step ( $K_{int}$ ) can also now be evaluated readily.<sup>16</sup>

**Acknowledgment.** This work was supported by NSF PCM-8316118 (J.P.K.) and NIH GM-30885 (R.G.M.). We thank W. W. Cleland, Jeremy Knowles, and Jeffrey Hermes for helpful discussions regarding possible limitations of this approach.

(16) Where multiple preisotopic complexes occur in a reversible reaction and contribute more significantly to the steady-state composition in one direction, the calculated value for  $K_{int}$  will deviate from a value measured directly. For example, in the mechanism described by eq 1

$$K_{int}(\text{calcd}) = K_{int}/(1 + k_4/k_3)$$

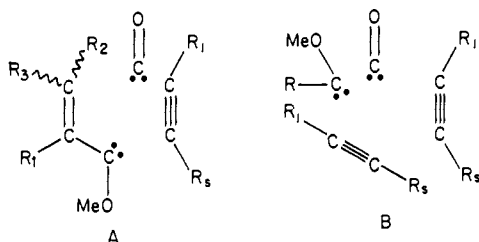
## Two-Alkyne Annulations of Transition-Metal Carbene Complexes via in Situ Generated Vinyl Carbene Complexes<sup>1</sup>

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Received October 19, 1984

Among the many transition-metal-mediated six-membered ring syntheses,<sup>2</sup> the benzannulation of vinyl carbene complexes of chromium with alkynes is quite novel and still relatively unexplored.<sup>3,4</sup> This annulation involves the overall incorporation of an acetylene, a carbon monoxide ligand, the carbene carbon, and its vinyl substituent as indicated schematically by A. Depending



on the substitution pattern of the vinyl group in complex 1 the ultimate annulation products can be either cyclohexadienones or phenols<sup>3c</sup> and have recently been employed as intermediates in natural product synthesis.<sup>3</sup>

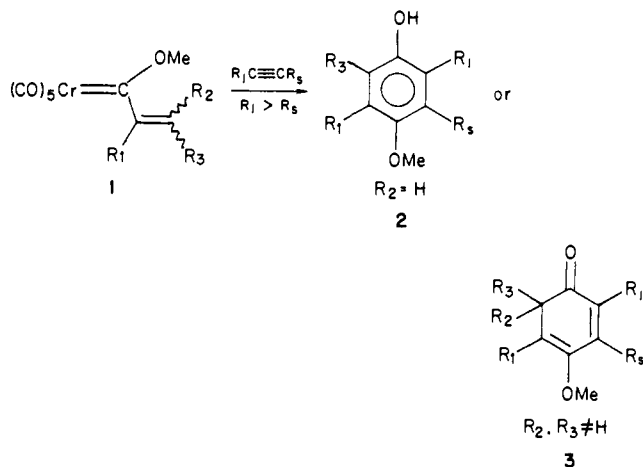
We wish to describe the first examples of a new type of six-membered annulation (indicated schematically by B) of transition-metal carbene complexes which involves the incorporation of 2 equiv of an acetylene, a carbon monoxide ligand, and the carbene carbon. This new annulation is based upon the premise

(1) This work was presented in preliminary form at the 186th National Meeting of the American Chemical Society, Washington, DC, Aug 28-Sept 2, 1983.

(2) Colquhoun, H. M.; Holton, J.; Thompson, D. J.; Twigg, M. V. "New Pathways for Organic Synthesis"; Plenum Press: New York, 1984; pp 105-120.

(3) (a) Wulff, W. D.; Yang, D. C. *J. Am. Chem. Soc.* **1984**, *106*, 7565-7567. (b) Wulff, W. D.; Chan, K. S.; Tang, P. C. *J. Org. Chem.* **1984**, *49*, 2293-2295. (c) Tang, P. C.; Wulff, W. D. *J. Am. Chem. Soc.* **1984**, *106*, 1132-1133. (d) Wulff, W. D.; Tang, P. C. *J. Am. Chem. Soc.* **1984**, *106*, 434-436. (e) Dötz, K. H.; Kuhn, W. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 732.

(4) For reviews, see: (a) Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreisss, F. R.; Schubert, U.; Weiss, K. "Transition Metal Carbene Complexes"; Verlag Chemie International: Deerfield Beach, FL, 1984. (b) Wulff, W. D.; Tang, P. C.; Chan, K. S.; McCallum, J. S.; Yang, D. C.; Gilbertson, S. R. *Tetrahedron* in press. (c) Dötz, K. H. *Pure Appl. Chem.* **1983**, *55*, 1689. (d) Casey, C. P. *React. Intermed.* **1981**, *2*. (e) Brown, F. J. *Prog. Inorg. Chem.* **1980**, *27*, 1.



that the in situ generated tetracarbonyl vinyl carbene complex 8 (Scheme I) will react with an acetylene in the same manner as the pentacarbonyl vinyl carbene complex 1 and give the cyclohexadienone 10. On the basis of the proposed<sup>4d,5</sup> mechanism for the annulation of the pentacarbonyl vinyl carbene complexes 1, the coordinatively unsaturated vinyl carbene complex 8 is envisioned to form from the methyl complex 4 via dissociation of a carbon monoxide ligand, followed by reaction with an alkyne to give the metallacyclobutene 7 and electrocyclic ring opening. On this same basis, the vinyl carbene complex 8 could be expected to react with an acetylene to give the annulated product 10 that is a result of the overall reaction of 4 with 2 equiv of the acetylene.<sup>6a</sup>

The reactions of the chromium methyl methoxy carbene complex 4<sup>7</sup> with 1-pentyne and propyne proceed as expected with the incorporation of two equivalents of the alkyne. The ultimate products are, however, the phenols 15,<sup>8</sup> the formation of which can be attributed to an in situ reduction of 10 via a chromium(0) species (vide infra).<sup>6b</sup> The reaction of complex 4 with phenylacetylene has previously been reported to give as the sole product a 12% yield of the naphthol 16 as its chromium tricarbonyl complex.<sup>10</sup> However, we have found that this reaction in fact gives primarily the two-alkyne annulated phenol 15c (28%) along with the naphthol 16 as the minor product in 8% yield. The formation of these two different types of annulated products may be attributed to the fact that two different isomeric forms of intermediate 11c (Scheme II) are possible.

The addition of the second equivalent of alkyne to the intermediate 8 is apparently disfavored for more sterically hindered acetylenes. It has been observed<sup>11</sup> that the reaction of complex 4 with diphenylacetylene produces the cyclobutenone 13 in 28% yield and we have been unable to find any two-alkyne annulated products from this reaction. The reaction of the corresponding

(5) Fischer, H.; Muhlemeister, J.; Markl, R.; Dötz, K. H. *Chem. Ber.* **1982**, *115*, 1355.

(6) (a) We recently observed the reaction of a vinyl carbene complex that gave a low yield of a two-alkyne annulated product along with the normal "monoalkyne" annulated product.<sup>3c</sup> (b) An alternative mechanism for formation of the phenols of 15 (or 22) involves insertion of a carbon monoxide into 8 to give a vinyl ketene complex<sup>4</sup> that subsequently reacts with the second equivalent of alkyne.

(7) For preparation of these complexes, see: Wulff, W.; Gilbertson, S. R. *J. Am. Chem. Soc.* **1985**, *107*, 503.

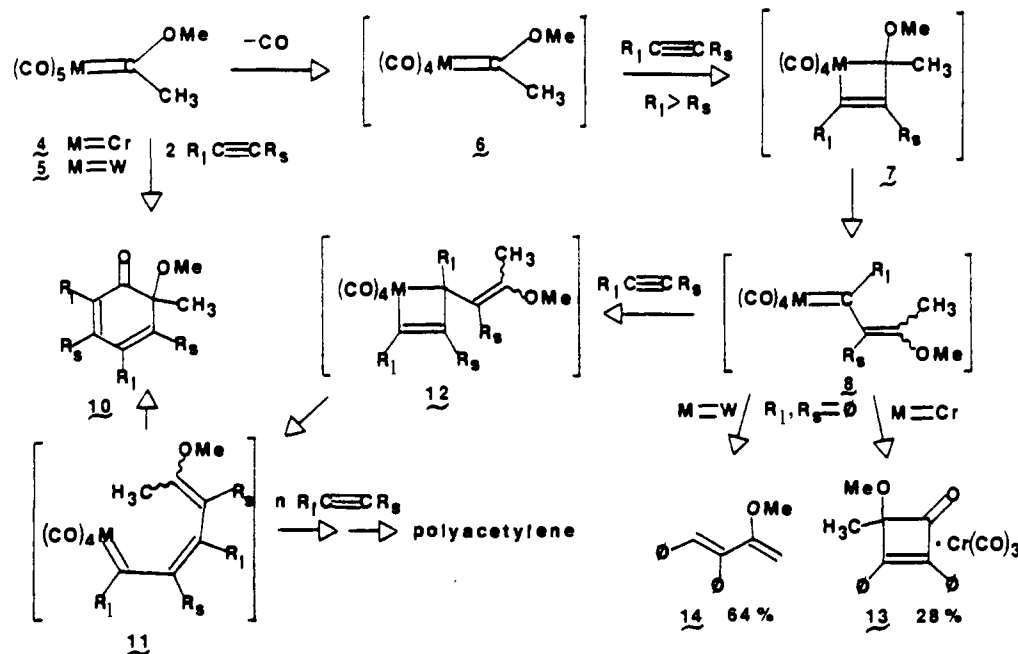
(8) Despite the low yield, the phenols 15a and 15b were the major products and small amounts of unidentified products were obtained. The substitution pattern of these phenols is that expected from the known regiochemistry of acetylene incorporation<sup>3b</sup> and is confirmed in the case of 15b by comparisons of its spectral data with that of an authentic sample (see supplementary material). The reactions of complex 4 with propyne and 1-pentyne were run at 0.07 M in carbene complex, whereas the reaction with phenylacetylene was carried out exactly as described in ref 10 (0.53 M).

(9) (a) Wulff, W. D.; Tang, P. C.; McCallum, J. S. *J. Am. Chem. Soc.* **1981**, *103*, 7677. (b) Dötz, K. H.; Muhlemeister, J.; Schubert, U.; Orama, O. *J. Organomet. Chem.* **1983**, *247*, 187.

(10) Dötz, K. H.; Dietz, R. E.; Neugebauer, D. *Nouv. J. Chim.* **1978**, *2*, 59.

(11) Dötz, K. H.; Dietz, R. *J. Organomet. Chem.* **1978**, *157*, C55.

Scheme I

Table I. Intramolecular Two-Alkyne Annulations<sup>a</sup>

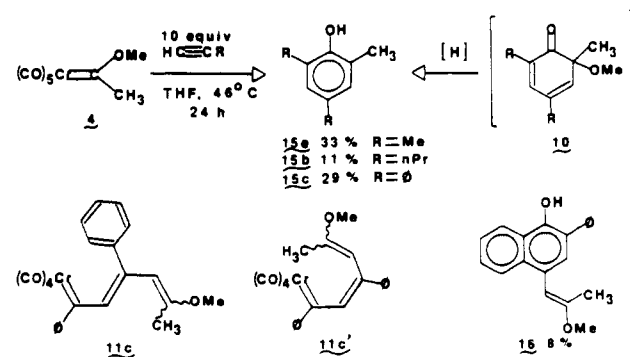
series	4	complex		diyne X	equiv of diyne	time, h	21, % yield	22, % yield
		M	R					
a	4	Cr	CH <sub>3</sub>	CH <sub>2</sub>	1.2	6.5		57
		Cr	CH <sub>3</sub>	CH <sub>2</sub>	1.2	2 (0.1 M)		20 <sup>b</sup>
		Cr	CH <sub>3</sub>	CH <sub>2</sub>	1.2	84 (0.1 M)		52 <sup>b,c</sup>
		Cr	CH <sub>3</sub>	CH <sub>2</sub>	1.2	6.5		26
b	4	Cr	CH <sub>3</sub>	O	1.1	9		31
c	4	Cr	CH <sub>3</sub>	C(CO <sub>2</sub> Et) <sub>2</sub>	1.0	15.5		57
d	4	Cr	CH <sub>3</sub>	CH <sub>2</sub> CH <sub>2</sub>	1.2	32		32 <sup>f</sup>
a	23	Mo	CH <sub>3</sub>	CH <sub>2</sub>	3.5	4	5	62 <sup>g</sup>
		Mo	CH <sub>3</sub>	CH <sub>2</sub>	4.0	1.2	10	29 <sup>d</sup>
a	5	W	CH <sub>3</sub>	CH <sub>2</sub>	5.0	59		56
		W	CH <sub>3</sub>	CH <sub>2</sub>	5.0	44	23	8 <sup>d</sup>
		W	CH <sub>3</sub>	CH <sub>2</sub>	2.5	4		56 <sup>h</sup>
		W	CH <sub>3</sub>	CH <sub>2</sub>	6.0	133		71 <sup>i</sup>
c	5	W	CH <sub>3</sub>	C(CO <sub>2</sub> Et) <sub>2</sub>	5.5	65		72 <sup>i</sup>
d	5	W	CH <sub>3</sub>	CH <sub>2</sub> CH <sub>2</sub>	4.0	50		32
e	24	W	<i>n</i> -Bu	CH <sub>2</sub>	7.0	65		71 <sup>i</sup>

<sup>a</sup> Unless otherwise specified all reactions were run at 0.0044 M in carbene complex in a deoxygenated THF solution (-196 to 25 °C, 3 cycles) under argon at 70 °C for 4 and 23 and 95 °C for 5. <sup>b</sup> 0.1 M in 4. <sup>c</sup> Slow addition of the diyne (84 h) to a 0.1 M solution of 4 in THF. <sup>d</sup> Acetonitrile solvent. <sup>e</sup> (Acetonitrile)pentacarbonylchromium also formed in these reactions. <sup>f</sup> 50 °C. <sup>g</sup> Sequential addition of the diyne in 4 portions. <sup>h</sup> Reaction at 20 °C induced by irradiation at 2537 Å through quartz in a Rayonett reactor. <sup>i</sup> Sequential addition of the diyne in 6 portions.

tungsten complex 5 with diphenylacetylene, on the other hand, gives the acyclic diene 14, which was postulated to occur via either a  $\beta$ -hydride elimination in 7 or a 1,5-sigmatropic shift of hydrogen from 8.<sup>12</sup> Under certain conditions tungsten complexes have been observed to induce polymerization of acetylenes<sup>13</sup> (via a mechanism suggested<sup>13</sup> to involve 8 and 11) which can be competitive with the formation of cyclized products particularly with terminal acetylenes where polymerization is the exclusive process.<sup>14</sup>

The two-alkyne annulation of group 6 carbene complexes can thus suffer from competition at various stages due to formation of side products (cyclobutenones and 1,3-dienes) and from polymerization. A high concentration of acetylene will favor addition of alkyne to intermediate 8 and disfavor the formation of side products 13 and 14; however, it will at the same time favor addition of alkyne to 11 and thus exacerbate the polymerization problem. A solution to these problems is provided by an intramolecular two-alkyne annulation as indicated in Scheme III. The local

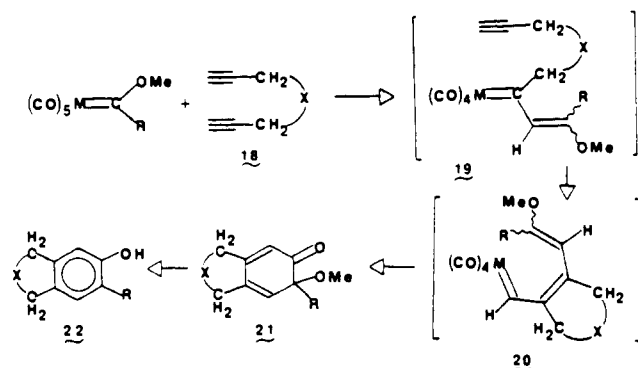
Scheme II



concentration of alkyne about intermediate 19 will be very high even if the concentration of the diyne 18 is kept low to minimize its intermolecular reaction with intermediate 20. A consequence of the intramolecular two-alkyne annulation is an inversion in the direction of addition of the second alkyne (19 to 20) providing an expected substitution pattern of the products different than

(12) Macomber, D. W. *Organometallics* 1984, 3, 1589.(13) Katz, T. J.; Lee, S. J. *J. Am. Chem. Soc.* 1980, 102, 422.(14) Foley, H. C.; Strubinger, L. M.; Targos, T. S.; Geoffroy, G. L. *J. Am. Chem. Soc.* 1983, 105, 3064.

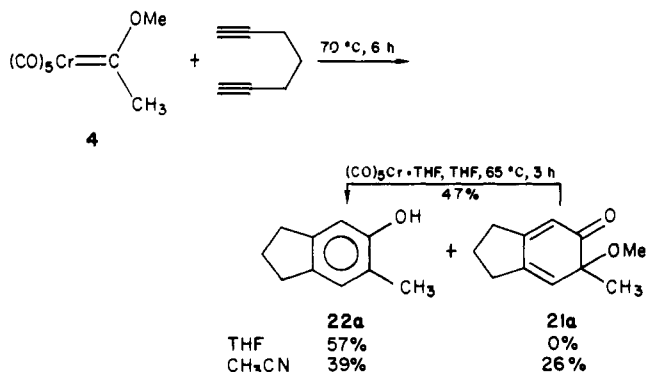
Scheme III



that from the intermolecular reactions.

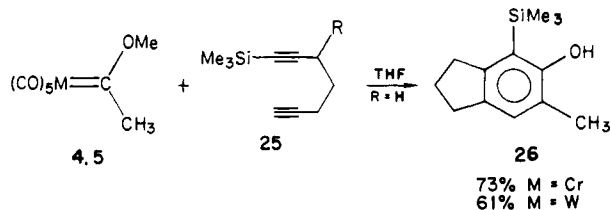
The success of the intramolecular version of the two-alkyne annulation is illustrated for several diynes in Table I. The chromium complex **4** reacts with 1,6-heptadiyne to give the indanol **22a** in 57% yield. As anticipated, these intramolecular reactions are sensitive to alkyne concentrations and a drop in yield of **22a** from 57% to 20% is observed when the concentration is raised from 0.0044 to 0.1 M. For practical considerations the use of lower concentrations can be obviated by employing a slow addition (84 h) of 1,6-heptadiyne to a 0.1 M solution of **4** providing a 52% yield of **22a**.

The cyclohexadienone **21a** can be isolated from the reaction of **4** with 1,6-heptadiyne in acetonitrile, which may be attributed



to the solvent's ability to more strongly coordinate to any chromium(0) species before reduction to the indanol can occur. The dienone **21a** can be reduced to the indanol **22a** with excess (tetrahydrofuran)pentacarbonylchromium(0)<sup>15</sup> lending credence to the suggestion that the phenol products are a result of an in situ reduction of the expected cyclohexadienones by chromium(0).

An important issue in the development of these reactions is the control of the regiochemistry of addition of unsymmetrical diynes. A possible solution is to employ a monosilylated diene such as **25**. The two-alkyne annulation of complex **4** with **25** occurs regioselectively with the incorporation of first the terminal and then the silylated alkyne to give a single isomer of indanol **26** in 73% yield. The same reaction of the tungsten complex **5**<sup>7</sup> gives a 61% yield **26**.<sup>16</sup>



(15) The reduction of a 0.0044 M solution of **21a** in acetonitrile with (acetonitrile)pentacarbonylchromium(0) is much slower resulting in a 1.9:1.0 mixture of **22a** and **21a** in 45% overall yield at 70 °C in 40 h.

(16) Chromium complex **4** reacted completely with 1.2 equiv of the diene **25**, whereas the reaction of the tungsten complex **5** required 10 equiv of **25**.

The yields of the reactions of the tungsten complexes with diynes **18a-d** (Table I) are generally slightly higher than for the chromium complexes despite the fact that substantial polymer formation occurs, thus requiring 5-7 equiv of diene to drive the reaction to completion. This, however, can be reduced to 2<sup>1</sup>/<sub>2</sub> equiv in the photoinduced reaction of the tungsten complex **5** with diene **18a**. It was quite surprising that the tungsten complexes also gave the indanols **22** since it has never been observed for tungsten complexes that a cyclized product can be obtained with terminal acetylenes<sup>14</sup> nor that cyclized products are formed with the incorporation of a carbon monoxide ligand.<sup>14,17</sup>

The continued investigation of the synthetic potential of the reactions of transition-metal carbene complexes<sup>18</sup> with diynes<sup>19</sup> is warranted particularly with regard to examining more functionalized acetylenes and optimization of the reaction for the formation of cyclohexadienones.

**Acknowledgment.** This work was supported by a grant from Dow Chemical Co. The NMR instruments used were funded in part by the NSF Chemical Instrumentation Program and by the NCI via the University of Chicago Research Center (CA 14599).

**Supplementary Material Available:** Spectral and physical data for **15a-c**, **16**, **21a**, **22a-e**, and **26** (3 pages). Ordering information is given on any current masthead page.

(17) Tungsten complex **5** (0.05 M in THF) was found to react with 1-pentyne (10 equiv) to give a 35% yield of **15b** in 18 h at 90 °C.

(18) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587.

(19) Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 539.

## A Tungsten-Bismuth Cluster Featuring Dibismuth as a Four-Electron Donor and a Bridging Bismuthinidene

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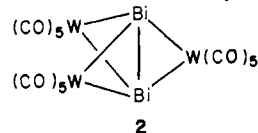
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The use of bulky ligands has permitted the isolation of compounds with P=P, P=As, and As=As bonds.<sup>1</sup> However, attempts to prepare analogous compounds with Sb=Sb or Bi=Bi bonds have been unsuccessful. We have therefore turned our attention to stabilizing such species by the attachment of transition-metal fragments. We describe the preparation and structure of a complex that involves (i) the first instance of Bi<sub>2</sub> functioning as a four-electron donor and (ii) the first example of a monomeric ligated bismuthinidene (RBi).

The bismuthine  $(\text{Me}_3\text{Si})_2\text{CHBiCl}_2$  (**1**) was prepared as a yellow oil (bp 108-110 °C at 10<sup>-4</sup> torr) in 51% yield in a similar fashion to the corresponding stibine.<sup>2</sup> Bismuthine **1** was treated with  $\text{Na}_2[\text{W}(\text{CO})_5]$  (5.0 mmol) in 30 mL of THF at 25 °C. After evaporation of the solvent, the crude product was separated by column chromatography (silica gel, 1:1 toluene/*n*-hexane) to afford a 5% yield of  $[\{\text{W}(\text{CO})_5\}_2(\mu_2-\eta^2-\text{Bi}_2)]$  (**2**) and a 12% yield of  $[\text{W}_2(\text{CO})_8(\mu_2-\eta^2-\text{Bi}_2)(\mu-\text{BiMeW}(\text{CO})_5)]$  (**3**). Compounds **2** and **3** were recrystallized from toluene/*n*-hexane and benzene, respectively.

As shown by Huttner et al.<sup>3</sup> the triangulated structure of **2**



(1) For reviews, see: Cowley, A. H. *Polyhedron* **1984**, *3*, 389. Cowley, A. H. *Acc. Chem. Res.* **1984**, *17*, 386.

(2) (a) Breunig, H. J.; Kanig, W.; Soltani-Neshan, A. *Polyhedron* **1983**, *2*, 291. (b) Cowley, A. H.; Lasch, J. G.; Norman, N. C.; Pakulski, M.; Whittlesey, B. R. *J. Chem. Soc., Chem. Commun.* **1983**, 881.