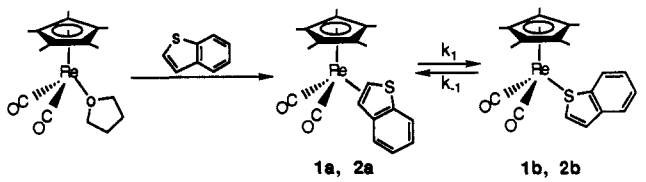
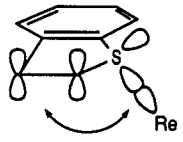
Scheme I



and 1874 cm^{-1}) of the S-bound thiophene complex $Cp^*(CO)_2Re(T)$[16] strongly suggest that **1b** contains an S-coordinated BT. Since all structures[3,17] of S-coordinated thiophene complexes contain pyramidal sulfur (approximately sp^3 hydridized), the sulfur in **1b** presumably has the same geometry.

Spectroscopic data[18] for the Cp analogue of **1**, $Cp(CO)_2Re(BT)$ (**2**), indicate that **2** also exists in solution as an equilibrium mixture of η^2 (**2a**) and S (**2b**) isomers, however, in a 1:3 ratio in $CDCl_3$ solvent at room temperature. Thus, the S-bound isomer is the major form of **2**, but the η^2-bound isomer predominates in **1**. The additional electron density provided by the Cp* ligand in **1** presumably reduces the Lewis acid character of the Re, which weakens the bond with the electron-donating sulfur in the S-bonded isomer (**1b**); at the same time, the higher electron density on Re increases π-back-bonding to the 2,3-η^2-olefinic bond of the BT ligand, which favors the η^2-bound isomer (**1a**).

The η^2-bound isomers (**1a** and **2a**) can be separated by hand from the S-bound isomers (**1b** and **2b**) on the basis of the morphology of the crystals. After the η^2-bound isomers were dissolved in CH_2Cl_2, rates of isomerization to the S-bound isomers at room temperture were determined by following the changes in intensity of the reactant and product CO bands until they reached equilibrium. The isomerization of **1a** ($k_1 = 9.0 \times 10^{-4}$, $k_{-1} = 15 \times 10^{-4}$ s^{-1}; $t_{1/2} = 13$ min for k_1) was approximately 8 times slower than that ($k_1 = 7.0 \times 10^{-3}$, $k_{-1} = 2.3 \times 10^{-3}$ s^{-1}; $t_{1/2} = 1.7$ min for k_1) of **2a**. These isomerizations must occur intramolecularly, since BT does not dissociate from either the η^2- or S-bound isomer during the time of the isomerization. This was shown by observing that no $Cp^*(CO)_2Re(2\text{-MeBT})$ formed when a $CDCl_3$ solution of $Cp^*(CO)_2Re(BT)$ (**1**) and 2-MeBT (2-methylbenzo[*b*]-thiophene) was stirred at room temperature for 26 h. Also there was no formation of $Cp^*(CO)_2Re(PPh_3)$ when **1** and PPh_3 were stirred in CD_2Cl_2 at room temperature for 24 h; at longer times (2 weeks) $Cp^*(CO)_2Re(PPh_3)$ was observed. The intramolecular interconversion of the η^2- and S-bound isomers presumably involves migration of the Re between sulfur and carbon orbitals on the same side of the BT ring.



These studies suggest that BT may coordinate to metal sites on HDS catalysts via either the sulfur or the C2-C3 olefin, and these S- and η^2-bound isomers may interconvert. Hydrogenation of BT could reasonably occur by insertion of the η^2 form into a metal hydride to give an alkyl intermediate, which would, with another hydride, reductively eliminate to give 2,3-dihydrobenzo[*b*]thiophene (DHBT). In fact, the homogeneous hydrogenation of BT to DHBT is catalyzed by complexes of Ru,[19,20] Os,[20] Rh,[20,21] and Ir[20] under mild conditions (85-175 °C). A similar process may also occur over heterogeneous HDS catalysts since much evidence[22-25] indicates that hydrogenation of BT to DHBT is the first step in an important pathway for the HDS of BT. Thus, the observed η^2-BT ligand in **1a** and **2a** provides for the first time a reasonable intermediate for understanding BT hydrogenation on HDS catalysts.

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(18) **2**: EIMS (15 eV) *m/e* 442 (M^+ based on ^{187}Re), 386 ($M^+ - 2CO$), 308 ($M^+ - BT$), 280 ($M^+ - (BT + CO)$), 252 ($M^+ - (BT + 2CO)$), 134 (BT). Anal. Calcd for $C_{15}H_{11}ReO_2S$: C, 40.81; H, 2.51. Found: C, 40.63; H, 2.30. **2a**: IR (hexanes) ν(CO) 1977 (w), 1909 (w) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.3-7.1 (3 m, 4 H, BT), 5.31 (d, 1 H, BT), 5.11 (d, 1 H, BT), 4.95 (s, 5 H, Cp); ^{13}C NMR ($CDCl_3$) δ 202.5 and 201.9 (CO), 126.2, 124.4, 124.0, 122.5, 45.5 and 44.1 (BT), 88.6 (C of Cp). **2b**: IR (hexanes) ν(CO) 1947 (s), 1885 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.9-7.4 (3 m, 4 H, BT), 7.20 (d, 1 H, BT), 7.14 (d, 1 H, BT), 4.81 (s, 5 H, Cp); ^{13}C NMR ($CDCl_3$) δ 201.6 (CO), 151.8, 140.7, 138.5, 127.2, 125.0 and 123.9 (BT), 83.0 (C of Cp).
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One-Step Construction of the Stemodane Framework via the Cobalt-Catalyzed Cyclization of Monocyclic Enynes: A Formal Total Synthesis of Stemodin

Juris Germanas, Corinne Aubert, and K. Peter C. Vollhardt*

Department of Chemistry, University of California at Berkeley, and the Chemical Sciences Division Lawrence Berkeley Laboratory, Berkeley, California 94720

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Aphidicolin (**1**)[1] and stemodin (**2**)[2] are members of a class of diterpenes that are attractive targets for total synthesis due to their unique spirocyclic constitution, numerous stereocenters, and biological activity.[3] The many synthetic approaches to the framework[4,5] have generally relied on classical strategies.[6] An

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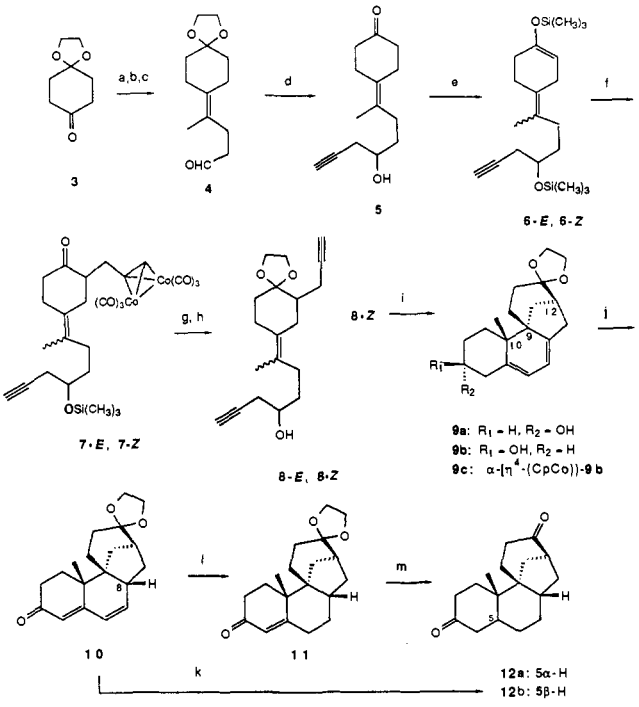
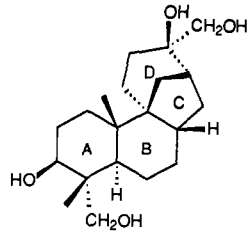
Scheme I[a]



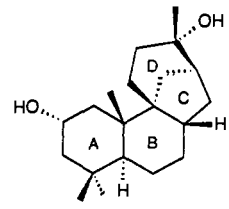
[a] (a) $CH_3(C{=}CH_2)MgBr$ (1.3 equiv), THF; 89%; (b) $CH_3CH_2OC{-}H{=}CH_2$, $Hg(O_2CCF_3)_2$, triethylamine; 70%; (c) 110 °C; 95%; (d) (i) 2-propynylmagnesium bromide (2.0 equiv); (ii) HCl, acetone; 80%; (e) $(CH_3)_3SiOSO_2CF_3$ (2.1 equiv), triethylamine; (f) (μ_2-η^2-1-methoxy-2-propyne)dicobalt hexacarbonyl (1.0 equiv), $(CH_3CH_2)_2AlCl$ (2.0 equiv); (g) $Fe(NO_3)_3{\cdot}9H_2O$ (2.0 equiv), methanol; 60% from **5**; (h) 1,2-ethanediol, 4-methylbenzenesulfonic acid, $(CH_3CH_2O)_3CH$; 85%; (i) $CpCo(CO)_2$ (1.0 equiv); 35% of **9a**, 20% of **9b**, 4% of **9c**; (j) (i) Dess-Martin reagent (1.5 equiv), pyridine, CH_2Cl_2; (ii) DBU, methanol; 58% (k) (i) H_2, 10% Pd/C; (ii) HCl, $(CH_3)_2CO$; 90%; (l) Li (3.0 equiv), NH_3, ethanol; 95%; (m) (i) Li (10.0 equiv), NH_3; (ii) HCl, $(CH_3)_2CO$; 70%.

entirely novel and rapid (one step) construction of these skeleta would produce complexes of the type **9c** from monocyclic precursors such as **8** by treatment with $CpCo(CO)_2$ (Scheme I).[7a] This cyclization would be the first involving an exocyclic alkene and unprecedented in its steric and strain-related restrictions.[8] On the other hand, should it succeed, the same attributes present in the diene ligand suggested its potential labilization to the point of turning the reaction catalytic.[7b] We now report that enediyne **8**-Z indeed cyclizes in a reaction that is catalytic in $CpCo(CO)_2$ to produce **9** en route to a formal synthesis of stemodin (**2**);[5h] enediyne **8**-E, on the other hand, fails to provide the corresponding isomeric tetracycle, foiling an attempt to reach **1**.

Condensation of the ethylene glycol monoacetal of cyclohexane-1,4-dione with propenyl-2-magnesium bromide, followed by etherification of the resultant alcohol and thermal rearrangement, resulted in aldehyde **4**.[9] Two steps provided ketone **5**, which was transformed in one pot to hydroxy-protected enol ethers **6**-E and **6**-Z (1:1 ratio). Alkylation of **6**-E and **6**-Z with 3-methoxy-1-propyne according to Schreiber's protocol[10] afforded the complexes **7**-E and **7**-Z. Oxidative demetalation and acetalization gave enediynes **8**-E and **8**-Z, respectively, in nine steps from **3**.



1



2

Gratifyingly, exposure of **8**-Z to 1 equiv of $CpCo(CO)_2$ furnished air-sensitive dienes **9a** and **9b** (2:1) along with a small amount of a single cobalt complex **9c**. Three stereocenters in **9**, at C9, C10, and C12, two of them quaternary, are produced with complete specificity in this transformation. The reaction could be repeated successfully with catalytic $CpCo(CO)_2$ (30 mol %) without a change in yield or ratio of the products. In contrast to the successful conversion of **8**-Z, we were unable to obtain any of the corresponding polycycles from **8**-E. For the purposes of a stereoselective synthesis and to confirm stereochemistry, enediyne **8**-Z was also synthesized stereospecifically.[11]

The synthetic elaboration of tetracyclic dienes **9a** and **9b** reveals hitherto unknown reactivity patterns of this system. Thus, the mixture was oxidized with the Dess-Martin reagent[12] and isomerized with base to provide fully conjugated dienone **10**, in contrast to the outcome of a similar isomerization in a steroid.[13] The configuration of C8 in the product of this stereospecific reaction was confirmed by X-ray crystallography (see supplementary material). While catalytic hydrogenation of **10** (10% Pd/C) occurred exclusively from the α-face to produce ketone **12b**, a result attributable to the bulkiness of the C ring, two successive dissolving metal reductions furnished **12a** and **12b** (1:1 ratio). Interestingly, an analogous reduction of an aphidicolin intermediate occurred stereoselectively.[4d] Dione **12a** displayed spectral properties identical with those recorded by Piers and co-workers in a total synthesis of stemodin,[5h] thus completing a formal synthesis of the latter. The overall yield to **12a** from commercially available starting material (1.3%) is comparable to those of similar tetracyclic intermediates in other total syntheses (3.1%, Piers et al.;[5h] 3.5%, Corey et al.;[5b] 3.6%, Bettolo et al.[5f]).

The stereoselective assembly of **9** constitutes a novel application of the cobalt-catalyzed [2 + 2 + 2] cycloaddition reaction furnishing a strained and highly sterically encumbered spirocyclic diene incorporating the stemodane framework that can be further elaborated into the natural product. The synthetic utility of dienones such as **10** invites application of the cobalt cyclization to gain access to other complex diterpene systems, such as stemarin[14] and strobane.[15]

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synthesis and to Dr. F. J. Hollander, Chexray facility, University of California at Berkeley, for carrying out the X-ray structural determination of **10**.

Supplementary Material Available: ^{1}H NMR, ^{13}C NMR, IR, HRMS, and combustion analysis data for **4–12** and intermediates and ORTEP rendition, X-ray parameters, and tables of atomic coordinates, thermal parameters, bond angles, and bond distances of **10** (13 pages). Ordering information is given on any current masthead page.

Coupling of a Vinyl Ligand and a Vinylidene Ligand at an Iridium Center: Generation of an Unusual Iridium(III) Butadienyl Complex Stabilized by a δ-Agostic C–H–Ir Interaction

Henry E. Selnau and Joseph S. Merola*

Department of Chemistry
Virginia Polytechnic Institute and State University
Blacksburg, Virginia 24061-0212

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The formation of carbon–carbon bonds at transition-metal centers via migratory insertion reactions of metal alkylidene species has received a great deal of attention in the recent past. Much of the driving force for this work came from the desire to determine the validity of the various proposals for the chain-growth step in the Fischer–Tropsch reaction,[1] with a new proposal suggesting the intermediacy of surface vinyl species appearing quite recently.[1a] In addition, the desire to develop new methods for carbon–carbon bond formation of use in organic synthesis has spurred many such investigations.[2] From these studies, several examples of alkyl migration to a metal alkylidene group have been reported for a variety of metal systems.[3] In this communication, we report on what we believe to be the first example of the migratory insertion of a vinylidene group into a metal–vinyl bond and the implications that such a reaction may have for alkyne oligomerization catalysis.

In 1989, we showed that *mer*-$(C_6H_5)Ir(H)(Cl)(PMe_3)_3$ (**1**) reacted with 2-butyne (following chloride removal) to form a methallyliridium compound. A necessary step in the 2-butyne reaction is a β-hydride elimination step which allows the σ-butenyl group to rearrange to a π-methyl allyl fragment. When the alkyne has no hydrogens on carbon α to the triple bond, the reaction is forced to follow quite a different course. Reaction between **1** and an excess of *tert*-butylacetylene following chloride removal by $Tl[PF_6]$ leads to the production of a new complex, **2**, whose spectroscopy and elemental analysis indicate that *2 equiv* of *tert*-butylacetylene has been incorporated (eq 1).[5] Our original

$$\underset{\mathbf{1}}{(C_6H_5)Ir(H)(Cl)(PMe_3)_3} + \text{excess } {}^t\text{BuC}{\equiv}\text{CH} \xrightarrow[-TlCl]{Tl[PF_6]} \underset{\mathbf{2}}{[(C_6H_5)(Me_3P)_3Ir({}^t\text{BuC}{\equiv}\text{CH})_2][PF_6]} \quad (1)$$

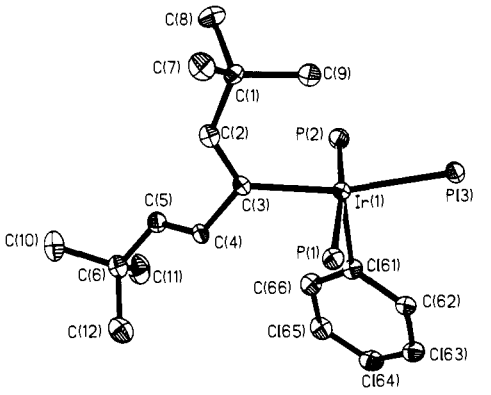
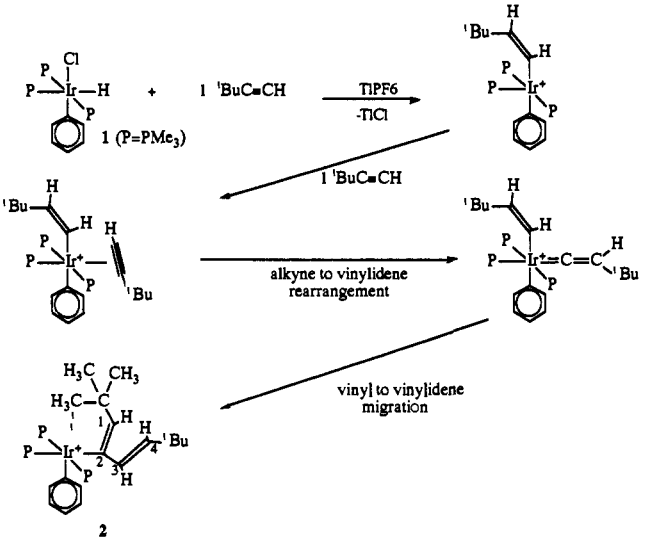


Figure 1. ORTEP plot of **2** (phosphine methyl groups removed for clarity). Some important bond distances (Å): Ir(1)–P(1), 2.363 (3); Ir(1)–P(2), 2.366 (3); Ir(1)–P(3), 2.398 (3); Ir(1)–C(61), 2.053 (9); Ir(1)–C(3), 2.109 (10); C(1)–C(2), 1.523 (13); C(2)–C(3), 1.352 (13); C(3)–C(4), 1.485 (12); C(4)–C(5), 1.314 (13); C(5)–C(6), 1.503 (13).

Scheme I



supposition was that, following the initial insertion to yield a vinyl compound, a second insertion occurred to form a σ,π-butadienyl complex. Double insertions of this type had been reported previously by both Bruce[6a,b] and Nixon.[6c] Resonances due to the vinylic protons in **2** clearly indicate that there are two protons that couple to each other with constants consistent with a trans disposition. The third vinylic proton is not coupled to the other two, but is strongly coupled to a phosphine. The ^{13}C NMR data indicate that the carbon directly bonded to the iridium is a quaternary carbon. These data are not in keeping with any form of a σ,π-butadienyl group.

A single-crystal X-ray structure determination of **2** was carried out, and the resulting ORTEP plot of the cation is shown in Figure 1.[7] Overall, the structure consists of a distorted octahedral iridium

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(3) In addition to refs 2a–c, see also: (a) Thorn, D. L.; Tulip, T. H. *Organometallics* **1982**, *1*, 1580. (b) Thorn, D. L. *Organometallics* **1985**, *4*, 192. (c) Thorn, D. L.; Tulip, T. H. *J. Am. Chem. Soc.* **1981**, *103*, 5984.

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(5) Data for **2**: ^{1}H NMR (200 MHz, CD_2Cl_2) δ 0.53 (br s, 9 H, $C(CH_3)_3$), 1.06 (s, 9 H, $C(CH_3)_3$), 1.49 (t, J_{P-H} = 3.5 Hz, 18 H, mutually trans PMe_3), 1.68 (d, J_{P-H} = 7.6 Hz, cis PMe_3), 5.57 (d, J_{H-H} = 15.5 Hz, 1 H), 5.88 (br d, J_{H-H} = 15.5 Hz, 1 H), 6.20 (br d, J_{P-H} = 14.6 Hz, 1 H, 6.75–7.15 ppm (m, 5 H, phenyl). ^{13}C NMR (50 MHz, CD_2Cl_2): δ 15.55 (t, J_{P-C} = 18 Hz, mutually trans PMe_3), 18.8 (d, J_{P-C} = 27 Hz, PMe_3), 26.6 (br s, $C(CH_3)_3$), 29.1 (s, $C(CH_3)_3$), 33.0 (s, $C(CH_3)_3$), 36.5 (br s, $C(CH_3)_3$), 111.2 (q, J_{P-C} = 4.5 Hz, Ir–C of phenyl), 123.8, 126.7 (vinylic C), 141.8 (d of t, $J_{P(trans)-C}$ = 93 Hz, $J_{P(cis)-C}$ = 12 Hz, Ir–C of vinyl), 136.3, 138.3, 145.2 (phenyl C). ^{31}P NMR (81 MHz, CD_2Cl_2) δ −34.0 (d, J_{P-P} = 18 Hz, mutually trans PMe_3), −46.0 (t, J_{P-P} = 18 Hz, cis PMe_3). Anal. C, H.

(6) (a) Blackmore, T.; Bruce, M. I.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1974**, 106. (b) Bruce, M. I.; Gardner, R. C. F.; Howard, J. A. K.; Stone, F. G. A.; Welling, M.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1977**, 621. (c) Eshtiagh-Hosseini, H.; Nixon, J. F.; Poland, J. S. *J. Organomet. Chem.* **1979**, *164*, 107.

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