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Asymmetric Benzopentaannulation from Tungsten ((−)-Menthyloxy)(aryl)carbene Complexes, Alkynyllithiums, and Methyl Triflate

José Barluenga,*,† Andrés A. Trabanco,† Josefa Flórez,†
Santiago García-Granda,‡ and María-Amparo LLorca‡

Instituto Universitario de Química Organometálica
"Enrique Moles", Unidad Asociada al CSIC, and
Departamento de Química Física y Analítica,
Universidad de Oviedo, Julián Clavería 8
33071 Oviedo, Spain

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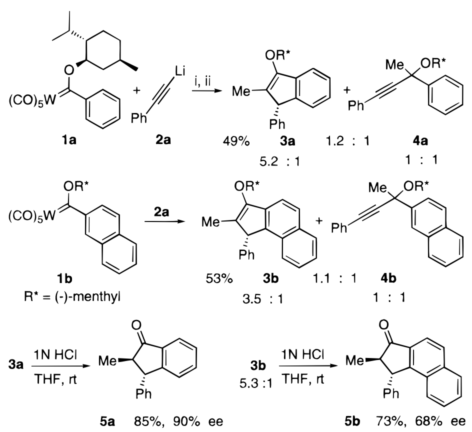
We recently reported the regio- and stereoselective conjugate nucleophilic addition of *sec*-butyl-, *tert*-butyl-, or phenyllithium to the aromatic nucleus of (menthyloxy)(aryl)carbene complexes of chromium. Further reaction with methyl triflate of the initially formed 1,4- or 1,6-adducts resulted in the development of a new asymmetric dearomatization reaction.[1] To evaluate the scope of this reaction depending on the nature of the organolithium compound, we decided to study the behavior of alkynyllithiums, which indeed underwent a completely different type of reaction, 1,2-addition followed by 1,3-propargylic shift, leading to the synthesis of enantiomerically enriched *trans*-2,3-disubstituted-1-indanones through a novel metal-assisted diastereoselective benzopentaannulation.[2] The addition of alkynyllithiums to the carbene carbon of complexes bearing a small alkoxy group (methoxyphenyl- or alkylcarbene complexes of tungsten) has been previously described.[3] The reactions of the propargyl metallic species thus generated with electrophiles have been proposed to occur with 1,2-migration of the metal group to generate a vinylmetal species which was detected by NMR studies of the protonation reaction with methanol, but whose exact structure is still unknown.[4]

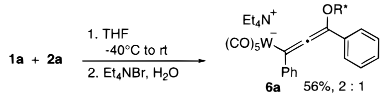
The reactions of tungsten ((−)-menthyloxy)(aryl)carbene complexes **1a,b** with phenylethynyllithium (**2a**) were carried out in THF between −40 °C and room temperature (rt). Subsequent addition of methyl triflate in Et_2O having previously removed THF under reduced pressure resulted in the formation with moderate chemical yields of a nearly equimolecular mixture of a five-membered ring benzannulated product **3** and a propargylic ether **4**, each one as a mixture of diastereoisomers (Scheme 1). Whereas the propargylic ethers **4a,b** were isolated as an 1:1 diastereoisomeric mixture, the indenyl ethers **3a,b** (only the major isomer is shown) were formed with acceptable diastereoselection (5.2:1 for **3a** and slightly lower 3.5:1 for **3b**).[5] The structural isomers **3** and **4** were separated by column chromatography on silica gel which in addition allowed, in each case, purification of the major C_5 annulated isomer **3a** or **3b** as well as the slower moving isomer of acetylenic products **4a,b**. Acid hydrolysis of enol ethers **3a** as a single diastereoisomer and **3b** as a 5.3:1 mixture of diastereoisomers furnished selectively the corresponding *trans*-2,3-disubstituted-benzocyclopentanones **5a,b** as enantiomerically enriched compounds (90−68% ee, determined by HPLC analysis on a chiral support in comparison with the corresponding racemic mixtures). The *trans* relative configuration of ketones **5** was ascertained from NOE studies, and the assignment of the absolute configuration to compounds **3** and **5** was made on the grounds of an X-ray analysis as shown below.

Scheme 1[a]

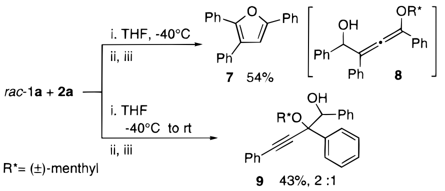


[a] (i) THF, −40 °C to rt; (ii) MeOTf, Et_2O, 0 °C.

Scheme 2



Scheme 3[a]



[a] (ii) PhCHO, $BF_3{\cdot}OEt_2$, −78 °C to rt; (iii) 1 N HCl.

To gain mechanistic insight, we focused on either the isolation or characterization of reaction intermediates. Thus, as shown in Scheme 2, the reaction of carbene complex **1a** with **2a** followed by cation exchange with an aqueous solution of tetraethylammonium bromide[6] gave **6a** as a stable yellow solid, which was further purified by recrystallization from CH_2Cl_2 at −20 °C. An X-ray structural analysis of **6a** showed it to be a novel anionic metal allenyl complex,[7] indicating that the intermediate formed at rt in the first reaction step has an allenic structure. On the other hand, the final product isolated when the reaction of *rac*-**1a** with **2a** was treated with benzaldehyde was different depending on the temperature of the first reaction step (Scheme 3). While furan **7**, which presumably is the evolution product during acidic work up of homoallenic alcohol **8**, was isolated when PhCHO was added to a reaction mixture kept at −40 °C, homopropargylic alcohol **9** was formed by adding PhCHO to a reaction mixture which had previously reached rt. In addition, the reaction of

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† Instituto Universitario de Química Organometálica "Enrique Moles".

‡ Departamento de Química Física y Analítica. X-ray analyses.

(1) Barluenga, J.; Trabanco, A. A.; Flórez, J.; García-Granda, S.; Martín, E. *J. Am. Chem. Soc.* **1996**, *118*, 13099.

(2) For a recent review on transition-metal-assisted cycloaddition reactions, see: Frühauf, H.-W. *Chem. Rev.* **1997**, *97*, 523.

(3) (a) Iwasawa, N.; Maeyama, K.; Saitou, M. *J. Am. Chem. Soc.* **1997**, *119*, 1486. (b) Iwasawa, N.; Maeyama, K. *J. Org. Chem.* **1997**, *62*, 1918.

(4) (a) Iwasawa, N.; Ochiai, T.; Maeyama, K. *Organometallics* **1997**, *16*, 5137. (b) Iwasawa, N.; Ochiai, T.; Maeyama, K. *J. Org. Chem.* **1998**, *63*, 3164.

(5) The diastereoselectivity of the benzopentaannulation reaction was significantly higher (8:1) when the (−)-8-phenylmenthyloxy derivative analogous to **1a** was used, but unfortunately, the major product of this reaction was an 1,2-dialkoxy-1,3-enyne. These results will be reported separately.

(6) Casey, C. P.; Polichnowski, S. W.; Tuinstra, H. E.; Albin, L. D.; Calabrese, J. C. *Inorg. Chem.* **1978**, *17*, 3045.

(7) To our knowledge, the only group 6 metal allenyl species which have been reported, are the following. Betaine compounds: (a) Berke, H.; Härter, P.; Huttner, G.; Zsolnai, L. *Z. Naturforsch. B* **1981**, *36*, 929. (b) Fischer, H.; Reindl, D.; Troll, C.; Leroux, F. *J. Organomet. Chem.* **1995**, *490*, 221. Neutral compounds: (c) Keng, R.-S.; Lin, Y.-C. *Organometallics* **1990**, *9*, 289. (d) Chen, M.-C.; Keng, R.-S.; Lin, Y.-C.; Wang, Y.; Cheng, M.-C.; Lee, G.-H. *J. Chem. Soc., Chem. Commun.* **1990**, 1138.

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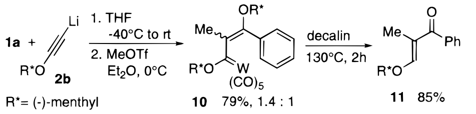
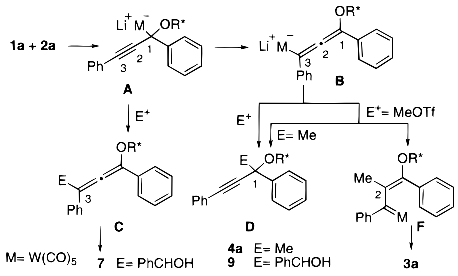
Scheme 4

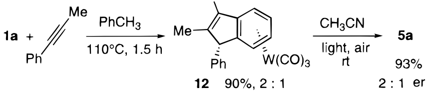


Scheme 5



carbene complex **1a** with the in situ generated enantiomerically pure lithium 2-alkoxyacetylide **2b**[8] afforded exclusively (alkoxy)-(2-phenylvinyl)carbene complex **10** as an 1.4:1 mixture of diastereoisomers (Scheme 4). Further thermolysis of this complex resulted in the diastereoselective formation of the open-chain 2-alkoxyvinyl ketone **11**. A reaction pathway accounting for all of these results is outlined in Scheme 5 with compounds **1a** and **2a**. Lithium acetylide **2a** reacts with (menthyloxy)(aryl)carbene complex **1a** to give selectively the 1,2-adduct **A**. This anionic propargyltungsten species is stable at low temperature (−40 °C), but on warming to rt, it undergoes a 1,3-propargylic rearrangement[9] to afford anionic allenyltungsten intermediate **B**. Direct evidence of this thermal 1,3-migration of the $(CO)_5W$ moiety was obtained by monitoring the conversion of a THF-d_8 solution of **A** to **B** by NMR spectroscopy. Between −40 and −10 °C the ^1H and ^{13}C NMR spectra showed exclusively the resonances attributed to **A**. Upon warming to 0 °C, new NMR signals grow in, and at 0 °C, only the resonances corresponding to **B** show up.[10] The driving force for this rapid isomerization may arise from the presumably greater stability of the alkenylmetal beside the alkylmetal and the relief of crowding at the quaternary propargyl terminus.[11] These organometallic derivatives **A** and **B** combine regioselectively with carbonyl electrophiles with concomitant rearrangement of the hydrocarbon fragment (S_E2' addition):[12] the acetylenic derivative **A** to an allenic structure **C** (attack at C3),[13] and the allenyl intermediate **B** to an acetylenic product **D** (attack at C1). However, in the reaction of allenyl complex **B** with MeOTf, in addition to propargyl ether **4a** (**D**, E = Me, attack at C1), the attack of the electrophile takes place at the central allenic carbon atom (C2), furnishing initially the nonheteroatom-stabilized 2-phenylvinylcarbene complex **F**, an undetected intermediate which is analogous to that accepted in the Dötz benzannulation reaction and which would undergo subsequent direct cyclization, according to one of the previously proposed mechanisms,[14] to yield indene-derived product **3a**.[15] The formation of intermediate **F** is supported by the isolation of heteroatom-stabilized 2-phenylvinylcarbene complex **10** (Scheme 4), although on heating, it did not yield the corresponding indene product despite the apparently structural similarity with a previously reported complex.[16] This different behavior could be a consequence of a more favorable thermal decomposition of **10** to enol ether **11** with elimination of the metal fragment and a menthyl group, the latter presumably as an alkene. If the methylation of **B** at C2 is not a diastereoselective reaction, as seems to indicate the result of Scheme 4, and given that only the *E* configuration shown for **F** in Scheme 5 has the appropriate geometry for cyclization, it could be possible that the presumably formed *Z* isomer of **F** would be undergoing decomposition to unidentified products which could account for the moderate yields of reactions in Scheme 1.

Scheme 6



Given that racemic methyl indenyl ethers analogous to compounds **3** have been formed either upon photolysis or in thermal reactions of tungsten (methoxy)(aryl)carbene complexes with internal alkynes,[15] we decided to test this thermal cycloaddition with chiral carbene complex **1a**.[17] Refluxing a toluene solution of complex **1a** and 1-phenylpropyne for 1.5 h led to the corresponding benzopentaannulated product as the tungsten tricarbonyl complex **12** with excellent chemical yield but low diastereoselectivity (only the major isomer is shown), presumably due to the much higher reaction temperature (110 *vs* 0 °C). Removal of the metal fragment by exposing an acetonitrile solution of **12** to air and light occurred with concurrent hydrolysis of the enol ether, affording the same ketone previously obtained **5a** as a 2:1 mixture of enantiomers. Yellow crystals of **12** were obtained by hexane/CH_2Cl_2 recrystallization of a 13:1 diastereoisomeric mixture, and a single-crystal X-ray structure determination allowed assignment of the absolute configuration depicted for compounds **3**, **5**, and **12** (Schemes 1 and 6).

In summary, we report a three-component benzopentaannulation of ((−)-menthyloxy)(aryl)carbene complexes via a novel anionic allenyltungsten intermediate. Ongoing efforts focus on increasing chemical yield and/or diastereoselectivity.

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Supporting Information Available: Experimental procedures, analytical and spectral data for compounds **3**−**7** and **9**−**12**, and X-ray crystallographic data of **6a** and **12** (32 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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[8] Kann, N.; Bernardes, V.; Greene, A. E. *Org. Synth.* **1996**, *74*, 13.

[9] An 1,3-propargylic migration of the $(CO)_5M$ (M = Cr, W) moiety has been invoked to explain a final reaction product but has not been directly observed: (a) Aumann, R.; Fröhlich, R.; Zippel, F. *Organometallics* **1997**, *16*, 2571. For 1,3-allylic migration of the $(CO)_5M$ unit, see: (b) Sleiman, H. F.; McElwee-White, L. *J. Am. Chem. Soc.* **1988**, *110*, 8700. (c) Hegedus, L. S.; Lundmark, B. R. *J. Am. Chem. Soc.* **1989**, *111*, 9194. (d) Fischer, H.; Schlageter, A.; Bidell, W.; Früh, A. *Organometallics* **1991**, *10*, 389.

[10] A similar variable-temperature NMR study carried out with [(methoxy)(phenyl)methylene]pentacarbonyltungsten and **2a** revealed that in this case the 1,3-shift of the $(CO)_5W$ moiety was a slower process which required slightly higher temperature (10 °C) to be complete. In addition, treatment of the allenylmetal species thus generated with MeOTf in Et_2O afforded exclusively the corresponding propargyl ether (attack at C1, 71%).

[11] Allenyl isomers are typically more stable than propargyl isomers: (a) Pu, J.; Peng, T.-S.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1992**, *11*, 3232. (b) Ogoshi, S.; Fukunishi, Y.; Tsutsumi, K.; Kurosawa, H. *J. Chem. Soc., Chem. Commun.* **1995**, 2485. (c) Cunico, R. F. *J. Org. Chem.* **1997**, *62*, 8955. (d) O'Connor, J. M.; Chen, M.-C.; Fong, B. S.; Wenzel, A.; Gantzel, P. *J. Am. Chem. Soc.* **1998**, *120*, 1100. See also refs 7c,d.

[12] (a) Yamamoto, H. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: New York, 1991; Vol. 2, p 81. (b) Chen, C.-C.; Fan, J.-S.; Lee, G.-H.; Peng, S.-M.; Wang, S.-L.; Liu, R.-S. *J. Am. Chem. Soc.* **1995**, *117*, 2933.

[13] Presumably, the reaction of the propargyl complex **A** with the aldehyde could occur through an initial 1,2-migration of the $(CO)_5W$ fragment: see ref 4 and references therein.

[14] Chan, K. S.; Peterson, G. A.; Brandvold, T. A.; Faron, K. L.; Challener, C. A.; Hyldahl, C.; Wulff, W. D. *J. Organomet. Chem.* **1987**, *334*, 9.

[15] For a review, see: (a) Schore, N. E. *Chem. Rev.* **1988**, *88*, 1081. (b) Foley, H. C.; Strubinger, L. M.; Targos, T. S.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1983**, *105*, 3064. (c) Yamashita, A.; Toy, A.; Watt, W.; Muchmore, C. R. *Tetrahedron Lett.* **1988**, *29*, 3403. (d) Dötz, K. H.; Larbig, H. *Bull. Soc. Chim. Fr.* **1992**, *129*, 579. (e) Barluenga, J.; Aznar, F.; Barluenga, S. *J. Chem. Soc., Chem. Commun.* **1995**, 1973.

[16] (a) Dötz, K. H.; Pruskil, I. *Chem. Ber.* **1978**, *111*, 2059. See also: (b) Dötz. K. H.; Neugebauer, D. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 851. (c) Aumann, R.; Jasper, B.; Fröhlich, R. *Organometallics* **1995**, *14*, 231.

[17] Dötz benzannulation reaction of the corresponding chromium carbene complex with a terminal alkyne has been described: Dötz, K. H.; Stinner, C.; Nieger, M. *J. Chem. Soc., Chem. Commun.* **1995**, 2535.