Unexpected and Easy Annulation of Fischer-type Phenylethenyl Carbene Complexes

José Barluenga,* Fernando Aznar and Sofía Barluenga

Instituto Universitario de Química Organometálica 'Enrique Moles', Unidad Asociada al CSIC, Julian Clavería 8, Universidad de Oviedo, 33071-Oviedo, Spain

The reaction between 2-aminobuta-1,3-dienes and Fischer-type phenylacetylenic carbene complexes leads under very mild conditions to highly functionalized dihydrofluorene derivatives in almost quantitative yields *via* annulation of a phenylethenyl carbene intermediate.

The broad, interesting and sometimes unpredictable reactivity shown by Fischer carbene complexes justifies the enormous amount of work that has been done since their discovery in 1964. The many advances in this field in recent years have stimulated the interest of synthetic organic chemists in this type of organometallic substrate.[1]

Probably one of the most useful applications of these complexes is the benzoannulation of α,β-unsaturated complexes with alkynes, the so-called Dötz reaction.[2] This process affords predominantly 4-methoxy-1-naphthol compounds along with variable amounts of indane derivatives as side products.[3]

However, the chemistry of dienylcarbene complexes, easily available by [4 + 2] cycloaddition reactions between phenylethynyl carbene complexes and 1,3-carbodienes, has been by far less well developed.[4] So far, these complexes have been applied in photochemical benzoannulation processes giving rise to six-membered rings with insertion of CO.[5] To the best of our knowledge, only two particular cases involving aminoalkoxydienylcarbene complexes have been reported to undergo ring closure to give cyclopentene derivatives without CO insertion.[6]

We are interested in the reactivity of 2-aminobuta-1,3-dienes towards α,β-unsaturated Fischer-type carbene complexes. In previous papers we have reported the formation of either seven-membered rings or Diels–Alder adducts depending on the metal used.[7]

We describe here our preliminary results on the cascade reaction of tungsten phenylethynyl carbene complexes with 2-aminobutadienes giving rise to dihydrofluorene derivatives.

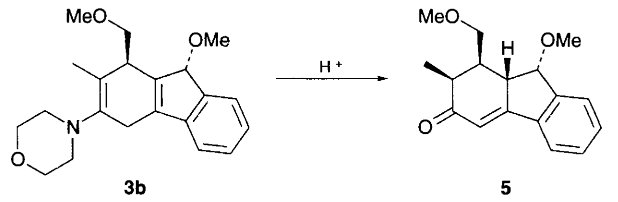
Thus, when the phenylacetylenic carbene **2** (Scheme 1) was treated in the dark with 1 equiv. of a 2-aminobuta-1,3-diene **1a**, **b** in THF under nitrogen (−20 °C for 12 h) and then allowed to reach room temperature, filtration through Celite and evaporation gave a yellow viscous oil, the ^1H and ^{13}C NMR spectra of which showed the tricyclic species **3** to be the major component (Table 1, entries **a**, **b**).

The annulation proceeds with very high diastereoselectivity; only the diastereoisomer **3b** was detected in the spectrum of the crude products (entry **b**). The *trans*-stereochemical arrangement of the substituents (CH_2OMe and OMe) (Scheme 2) was established on the basis of the ^1H NMR and NOE measurements carried out on compound **5**, obtained by acid hydrolysis of **3b** (Scheme 2).

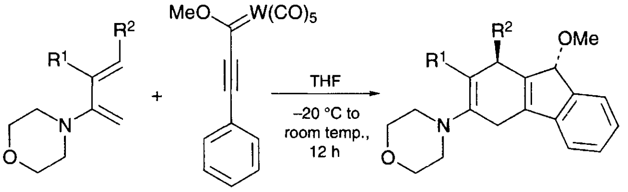
The formation of compound **3** can be explained by an initial [4 + 2] cycloaddition to produce the α,β-unsaturated intermediate **A**, followed by an electrocyclization process to afford the metallacycle **B** which gives the dihydrofluorene **3** by subsequent demetallation and [1, 5] H-shift. As a confirmation of the proposed pathway, intermediate **A** was identified by

Table 1 Compounds **3**

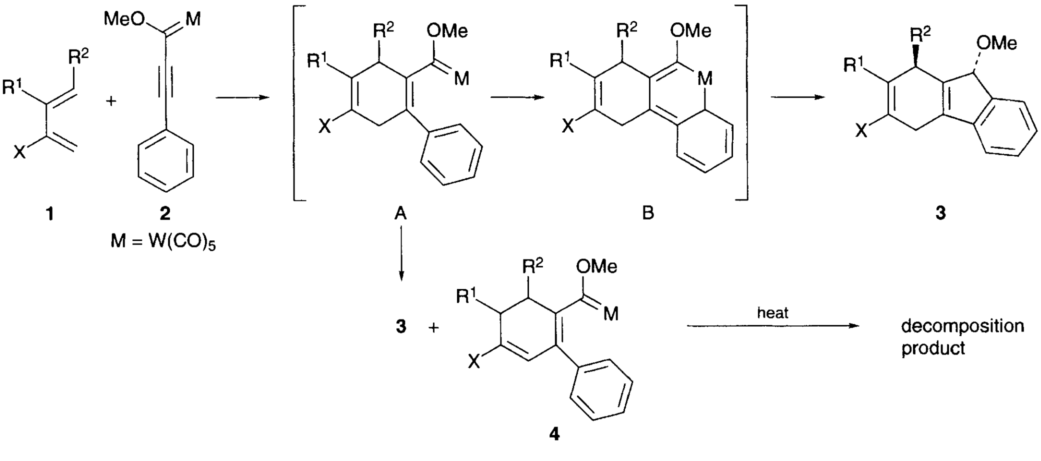
Entry	X	R^1	R^2	Yield (%)	Solvent
a	Morpholino	Me	H	>95	THF
b	Morpholino	Me	CH_2OMe	>95	THF
c	Me	Me	H	10	Neat
d	OMe	H	Ph	50	MeCN



Scheme 2



Scheme 3



Scheme 1

NMR at −20 °C when the reaction was carried out in $CDCl_3$ under the same conditions.

On the other hand, when the reaction mixture treated at −20 °C with SiO_2 for 10 h and then warmed to room temperature, partial isomerisation occured affording a mixture of **3** and dienylcarbene **4**. Moreover, when a solution of **4** in acetonitrile was heated to reflux, formation of the tricyclic compound **3** was not observed but instead a mixture of decomposition products was obtained.

In order to study the scope and the influence of the X group attached to C-2 of the diene the same reaction was carried out using dienes **1c** (X = Me) and **1d** (X = OMe) (Table 1, entries **c** and **d**). In the case of the 2-methoxydiene **1d**, the reaction was performed at room temperature (72 h) to afford **3d** in 50% yield. When 2,3-dimethylbuta-1,3-diene **1c** was used, the reaction took place at 50 °C (4 h) and only 10% of the corresponding tricyclic system was isolated. These observations clearly indicate that the nature of the isolated C–C double bond of **A** surprisingly plays an important role in determining the course of the reaction.

This research was supported by Dirección General de Investigación Científica y Técnica (DGICYT) PB 92-1005. A FICYT fellowship to S. B. is gratefully acknowledged.

Received, 19th June 1995; Com. 5/03930D

References

1 K. H. Dötz, *New J. Chem.*, 1990, **14**, 433; K. H. Dötz, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 587; L. S. Hegedus, *Pure Appl. Chem.*, 1990, **62**, 691.

2 K. H. Dötz, *Angew. Chem., Int. Ed. Engl.*, 1975, **14**, 433; J. S. McCallum, F. A. Kunng, S. R. Gilbertson and W. D. Wulff, *Organometallics*, 1988, **7**, 2346 and references cited therein. We have recently reported the isolation and characterization of two new intermediates in the Dötz reaction: J. Barluenga, F. Aznar, A. Martín, S. García-Granda and E. Pérez-Carreño, *J. Am. Chem. Soc.*, 1994, **116**, 11191.

3 M. E. Bos, W. D. Wulff, R. A. Miller, S. Chamberlin and T. A. Brandvold, *J. Am. Chem. Soc.*, 1991, **113**, 9293.

4 K. H. Dötz and W. Kuhn, *J. Organomet. Chem.*, 1985, **286**, C23–C26; W. D. Wulff, in *Advances in Metal Organic Chemistry*, ed. L. S. Liebeskine, JAI Press Inc., Greenwich, CT, 1989; vol. 1; W. D. Wulff and D. C. Yang, *J. Am. Chem. Soc.*, 1984, **106**, 7565; B. A. Anderson, W. D. Wulff, T. S. Powers, S. Tribbitt and A. Rheingold, *J. Am. Chem. Soc.*, 1992, **114**, 10784.

5 C. A. Merlic and D. Xu, *J. Am. Chem. Soc.*, 1991, **113**, 7418; C. A. Merlic, D. Xu and B. G. Gladstone, *J. Org. Chem.*, 1993, **58**, 538.

6 R. Aumann, H. Heinen, P. Hinterding, N. Sträter and B. Krebs, *Chem. Ber.*, 1991, **124**, 1229; R. Aumann, H. Heinen, M. Dartmann and B. Krebs, *Chem. Ber.*, 1991, **124**, 2343; K. H. Kötz and I. Pruskil, *Chem. Ber.*, 1978, **111**, 2059.

7 J. Barluenga, F. Aznar, C. Valdés, A. Martín, S. García-Granda and E. Martín, *J. Am. Chem. Soc.*, 1993, **115**, 4403; J. Barluenga, F. Aznar, A. Martín, S. Barluenga, S. García-Granda and A. A. Paneque-Quevedo, *J. Chem. Soc., Chem. Commun.*, 1994, 843.