

Preliminary communication

Synthesis of mixed bis(alkenylcarbene) ditungsten complexes by sequential activation of dialkynols

Vincent Péron, Emmanuel Porhiel, Vincent Ferrand, Hubert Le Bozec \*

Laboratoire de Chimie de Coordination Organique, associé au CNRS, Université de Rennes 1, Campus de Beaulieu, 35042 Rennes Cedex, France

Received 22 October 1996; revised 13 January 1997; accepted 16 January 1997

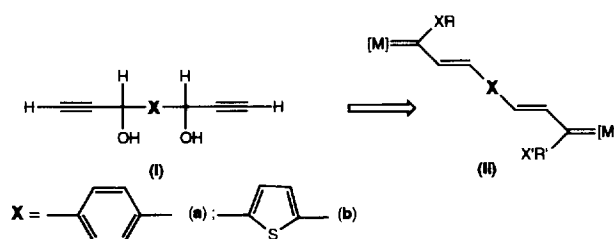
Abstract

The synthesis of new bis(alkenylcarbene) ditungsten complexes **2a–b**, **5a** and **6a** has been achieved from  $W(CO)_5(THF)$ , via activation of the dialkynol derivatives **a** and **b**. The reaction of **5a** with piperazine affords a dissymmetric bis(aminocarbene) complex **7a**. © 1997 Elsevier Science S.A.

Keywords: Tungsten; Methoxyalkenylcarbene; Aminoalkenylcarbene; Bis(carbene);  $\pi$ -Conjugated bridges

Dimetal complexes with  $\pi$ -conjugated bridges are attractive synthetic goals due to their potentially useful chemical and physical properties. Recent examples of such bimetallic species include symmetrical bis Fischer carbene complexes containing phenyl [1,2], biphenyl [3], binaphthyl [1,2], alkenyl [4] and ammonium penta-dienide [5] bridges. By contrast, conjugated binuclear complexes with two different carbene fragments are rare [2,6]. We have previously reported a very efficient method for the preparation of ruthenium, chromium and tungsten alkoxyalkenylcarbene complexes which involves terminal and silylated propargylic alcohols as starting materials [7–9]. A similar sequential activation of dialkynols of type I should afford the related mixed bis(carbene) derivatives II. In this communication we report the first result of this study and show that this methodology opens the route to new bimetallic complexes with two types of  $\pi$ -conjugated bridges, and

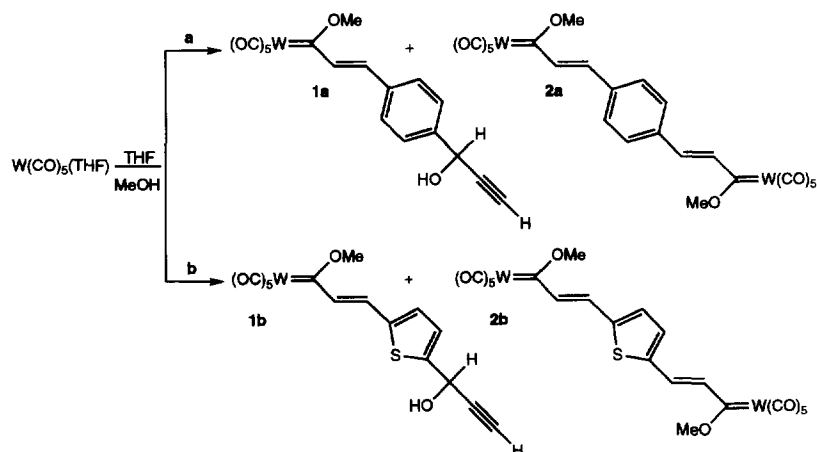
allows the introduction of two different metal–carbene fragments.



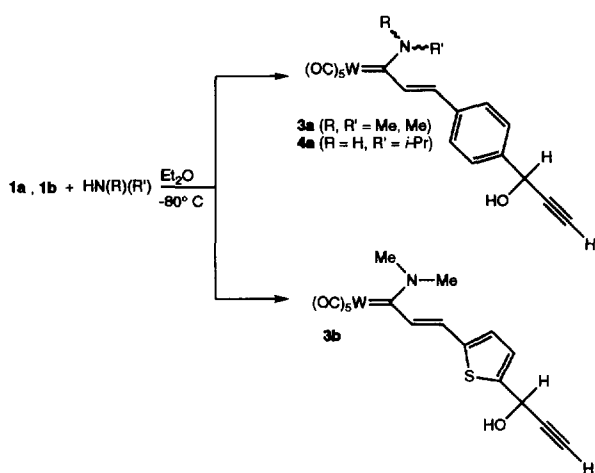
1,4-Di(1-hydroxyprop-2-yn-1-yl)benzene **a** and 2,5-di(1-hydroxyprop-2-yn-1-yl)thiophene **b** were readily prepared by addition of  $Li\equiv CH$  to the corresponding dialdehydes. The reaction of **a** and **b** (1.5 equiv.) with  $W(CO)_5(THF)$  in THF–methanol at room temperature afforded, after chromatographic workup, the monometallic methoxyalkenylcarbene complexes **1a** and **1b** in 41% and 38% yields respectively (Scheme 1).

Besides **1a** and **1b**, the corresponding bis(methoxy-carbene)ditungsten complexes **2a** and **2b** were also

\* Corresponding author.



Scheme 1.



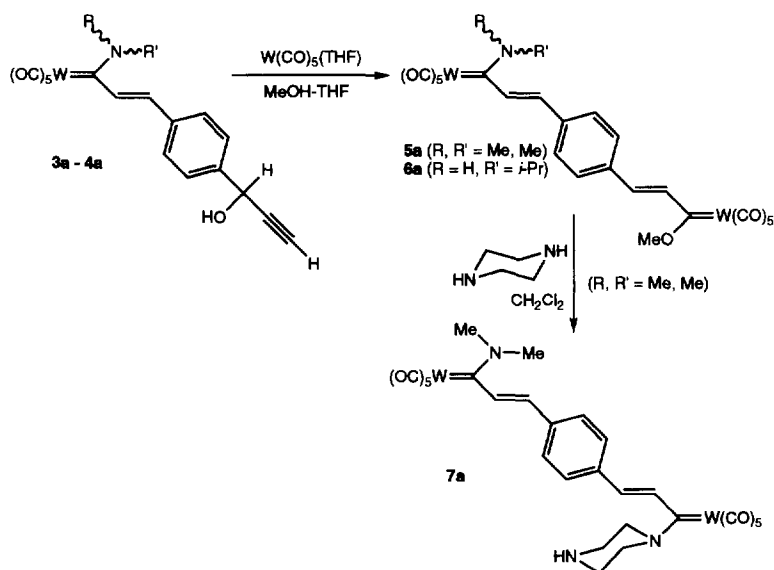
Scheme 2.

isolated in modest yield (15%). The dimethyl aminocarbene complexes **3a** and **3b** were easily obtained in high yield by low temperature treatment of **1a** and **1b** with

dimethylamine. Addition of *i*-propylamine to **1a** led to the isolation of **4a** in 88% yield as a mixture of *E* and *Z* isomers (*E* >> *Z*) (Scheme 2).

Complexes **3a** and **4a** were found to slowly react (r.t., 3 days) with one equivalent of  $W(CO)_5(THF)$  in the presence of methanol to give the new mixed  $\mu$ -bis(carbene)ditungsten complexes **5a** and **6a** in 54% and 75% yields respectively (Scheme 3). These complexes were characterised by  $^1H$  and  $^{13}C$  NMR spectroscopy. The  $^1H$  NMR spectra showed four expected doublets for the  $CH=$  protons with strong vicinal coupling constants ( $J_{HH} = 15\text{--}16$  Hz), which are characteristic of *E* geometry for the alkenyl groups. In the  $^{13}C$  NMR spectra, the most noticeable resonances were two low field signals at ca. 305 and 245 ppm in the range usually observed for alkoxy carbene and aminocarbene complexes respectively.

Like the monometallic methoxycarbene complexes, **6a** underwent a rapid aminolysis reaction with piperazine ( $CH_2Cl_2$ , r.t.) to afford the  $\mu$ -bis(aminocarbene)



Scheme 3.

complex **7a** in 63% yield (Scheme 3). We are currently exploring the possibility of producing tetrakis(carbene) tetrametal complexes from **7a** and extending the chemistry to prepare other  $\pi$ -conjugated bridged complexes.

All new compounds were fully characterised by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra, IR, HRMS and/or elemental analysis. Selected spectroscopic data for **1a**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.88 (d, 1H,  $J = 15.5$  Hz), 7.62 (d, 2H,  $J = 8.5$  Hz), 7.58 (d, 2H,  $J = 8.5$  Hz), 7.19 (d, 1H,  $J = 15.5$  Hz), 5.46 (s, 1H), 4.64 (s, 3H), 2.69 (d, 1H,  $J = 2.2$  Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  307.4, 203.8, 197.5, 143.8, 142.8, 134.8, 132.2, 129.5, 127.4, 83.0, 75.2, 69.0. **1b**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.63 (d, 1H,  $J = 15.0$  Hz), 7.29 (dd, 1H,  $J = 15.0$  and 0.6 Hz), 7.28 (d, 1H,  $J = 3.8$  Hz), 7.14 (dd, 1H,  $J = 3.8$  and 0.6 Hz), 5.61 (d, 1H,  $J = 2.1$  Hz), 5.29 (s, 1H), 4.59 (s, 3H), 2.73 (d, 1H,  $J = 2.3$  Hz). **2b**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.70 (d, 2H,  $^3J = 15.1$  Hz), 7.34 (s, 2H), 7.24 (d, 2H,  $^3J = 15.1$  Hz), 4.60 (s, 6H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  304.6, 197.9, 191.9, 145.0, 143.9, 135.5, 125.7, 69.5. **3a**:  $^1\text{H}$  NMR ( $\text{CD}_3\text{COCD}_3$ )  $\delta$  7.56 (m, 4H), 7.30 (d, 1H,  $J = 16.7$  Hz), 6.16 (d, 1H,  $J = 16.7$  Hz), 5.48 (d, 1H,  $J = 2.0$  Hz), 5.10 (s, 1H), 3.93 (s, 3H), 3.57 (s, 3H), 3.08 (d, 1H,  $J = 2.0$  Hz);  $^{13}\text{C}$  NMR ( $\text{CD}_3\text{COCD}_3$ )  $\delta$  248.6, 204.6, 199.5, 142.6, 140.4, 136.7, 127.9, 127.5, 124.4, 85.6, 75.1, 63.9, 54.3, 45.0. **3b**:  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ )  $\delta$  7.04 (dd, 1H,  $J = 3.5$  and 0.6 Hz), 6.89 (d, 1H,  $J = 3.5$  Hz), 6.88 (d, 1H,  $J = 16.4$  Hz), 6.14 (dd, 1H,  $J = 16.4$  and 0.6 Hz), 5.61 (s, 1H), 5.30 (s, 1H), 3.78 (s, 3H), 3.37 (s, 3H), 2.73 (d, 1H,  $J = 2.0$  Hz);  $^{13}\text{C}$  NMR ( $\text{CD}_3\text{COCD}_3$ )  $\delta$  246.6, 204.4, 199.4, 146.8, 142.0, 139.1, 127.8, 126.4, 119.7, 84.6, 75.0, 60.2, 54.4, 45.1. **5a**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.81 (d, 1H,  $J = 15.4$  Hz), 7.54 (d, 2H,  $J = 8.3$  Hz), 7.36 (d, 2H,  $J = 8.3$  Hz), 7.12 (d, 1H,  $J = 15.4$  Hz), 7.05 (d, 1H,  $J = 16.7$  Hz), 5.86 (d, 1H,  $J = 16.7$  Hz), 4.87 (s, 3H),

3.77 (s, 3H), 3.36 (s, 3H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  306.5, 252.1, 203.9, 203.4, 198.3, 197.6, 143.3, 139.6, 138.6, 134.3, 133.3, 129.9, 127.3, 122.0, 69.1, 53.5, 44.5. **7a**:  $^1\text{H}$  NMR ( $\text{CD}_3\text{COCD}_3$ )  $\delta$  7.54 (s, 4H), 7.32 (d, 2H,  $J = 16.7$  Hz), 6.17 (d, 1H,  $J = 16.7$  Hz), 6.09 (d, 1H,  $J = 16.7$  Hz), 4.37 (m, 2H), 4.11 (m, 2H), 3.94 (s, 3H), 3.59 (s, 3H), 3.20 (m, 2H), 3.01 (m, 2H);  $^{13}\text{C}$  NMR ( $\text{CD}_3\text{COCD}_3$ )  $\delta$  248.3, 245.0, 204.7, 204.5, 199.5, 199.3, 140.3, 139.4, 136.9, 136.8, 127.9, 124.3, 122.9, 65.2, 56.7, 54.3, 48.5, 48.2, 45.0.

### Acknowledgements

The authors acknowledge financial support from the HCM program (contract CHRXCT 940501) and the INTAS program (contract 94-0541).

### References

- [1] E.O. Fischer, W. Röhl, N. Hoa Tran Huy, K. Ackermann, *Chem. Ber.* 115 (1982) 2951.
- [2] M. Havranek, M. Husak, D. Dvorak, *Organometallics* 14 (1995) 5024.
- [3] N. Hoa Tran Huy, P. Lefloch, F. Robert, Y. Jeannin, *J. Organomet. Chem.* 327 (1987) 211.
- [4] A. Rabier, N. Lugan, R. Mathieu, G.L. Geoffroy, *Organometallics* 13 (1994) 4676; A. Geisbauer, S. Mihan, W. Beck, *J. Organomet. Chem.* 501 (1995) 61.
- [5] R. Aumann, B. Jasper, R. Fröhlich, S. Kotila, *J. Organomet. Chem.* 502 (1995) 137.
- [6] H. Fischer, F. Leroux, G. Roth, R. Stumpf, *Organometallics* 15 (1996) 3723.
- [7] D. Pilette, K. Ouzzine, H. Le Bozec, P. Dixneuf, C.E.F. Rickard, W.R. Roper, *Organometallics* 11 (1992) 809.
- [8] C. Cosset, I. Del Rio, H. Le Bozec, *Organometallics* 14 (1995) 1938.
- [9] C. Cosset, I. Del Rio, V. Péron, B. Windmüller, H. Le Bozec, *Synlett.* (1996) 436.