

## A One-step Synthesis of Alkenyl-, Dienyl- and Trienyl-idene Complexes of Chromium and Tungsten Carbonyl

Hubert Le Bozec, Christophe Cosset and Pierre H. Dixneuf

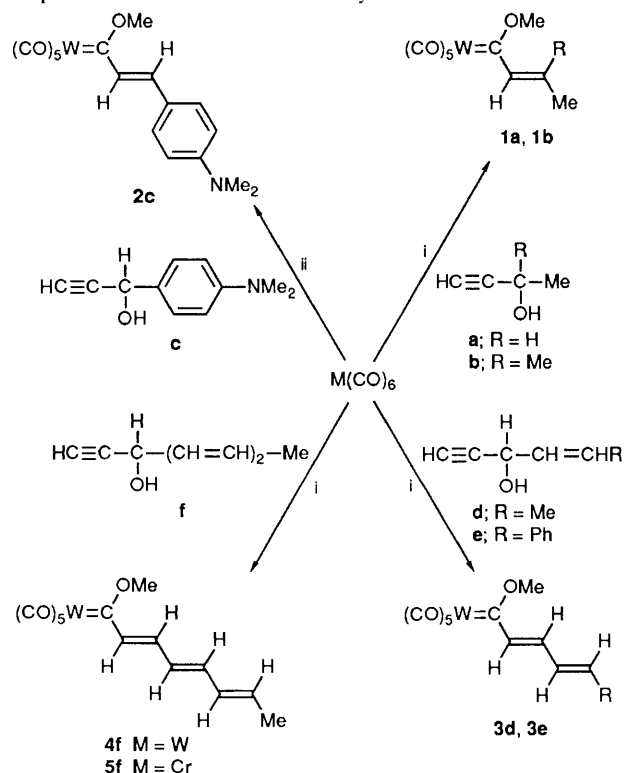
Laboratoire de Chimie de Coordination Organique, URA CNRS 415, Campus de Beaulieu, Université de Rennes, 35042 Rennes Cédex, France

Alkenyl-, dienyl- and trienylidene-chromium and tungsten complexes  $(\text{CO})_5\text{M}=\text{C}(\text{OMe})\{\text{CH}=\text{CH}(\text{CH}=\text{CH})_n\text{-R}\}$  [ $n = 0, 1, 2$ ] are produced in one step by photolysis of  $\text{M}(\text{CO})_6$  [ $\text{M} = \text{Cr}, \text{W}$ ] in the presence of 2-propyn-1-ol derivatives  $\text{H}-\text{C}\equiv\text{C}(\text{H})(\text{OH})\{(\text{CH}=\text{CH})_n\text{-R}\}$  and methanol.

$\alpha,\beta$ -Unsaturated carbene complexes of group 6 transition metal carbonyls have found numerous applications in organic synthesis. Their reactions with alkynes lead to cyclohexadienones, phenol derivatives<sup>1</sup> and bicyclic lactones<sup>2</sup>. Alkenyl carbene complexes offer at the same time cyclopropanations<sup>3</sup> or inter<sup>4</sup>- and intra-molecular<sup>5</sup> Diels-Alder reactions. Unsaturated carbene tungsten derivatives have been used in organometallic synthesis to prepare bimetallic compounds<sup>6</sup> and metal-carbene-containing polymers.<sup>7</sup> The potential of the alkenylcarbene derivatives is often limited by the difficulty in building the unsaturated group. Alkenyl carbene chromium and tungsten complexes are usually prepared by multistep procedures involving either the condensation of an aldehyde,<sup>8</sup> ketone<sup>9</sup> or enol ether<sup>10</sup> with a deprotonated carbene species  $[(\text{CO})_5\text{M}=\text{C}(\text{OMe})\text{CH}_2]^-$ , or the Fischer method by addition of an alkenyllithium to  $\text{M}(\text{CO})_6$  followed by alkylation.<sup>4f,6c,11</sup> We recently discovered a new route to alkenyl carbene ruthenium cations based on the initial displacement of chloride of arene ruthenium(II) complexes  $\text{RuCl}_2(\text{PR}_3)(\eta^6\text{-arene})$  by 2-propyn-1-ol derivatives.<sup>12</sup> We now report that alkenyl-carbene tungsten and chromium carbonyl complexes can easily be generated from  $\text{M}(\text{CO})_6$  [ $\text{M} = \text{W}, \text{Cr}$ ] and 2-propyn-1-ol derivatives in one step on photolysis.

Photolysis of a  $\text{MeOH-Et}_2\text{O} 1:1$  solution of  $\text{W}(\text{CO})_6$  with 1-methyl-propyn-1-ol **a** or with 1,1-dimethylpropyn-1-ol **b**, using a mercury-vapour lamp, resulted, after 6 h, in the formation of the methoxy-propenyl carbene<sup>6a</sup> and methoxy-isobutenyl carbene<sup>6a</sup> tungsten complexes **1a** and **b**<sup>†</sup> isolated in 30 and 24% yield, respectively, after separation from the

unreacted  $\text{W}(\text{CO})_6$  (Scheme 1). By irradiation of  $\text{W}(\text{CO})_6$  with the 2-propyn-1-ol derivative **c** in  $\text{MeOH-THF}$  ( $\text{THF} = \text{tetrahydrofuran}$ ), the pink *para*-dimethylaminostyryl carbene complex **2c**<sup>†</sup> was obtained in 56% yield.

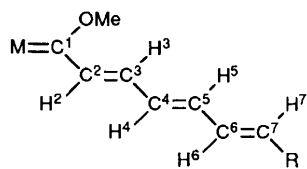
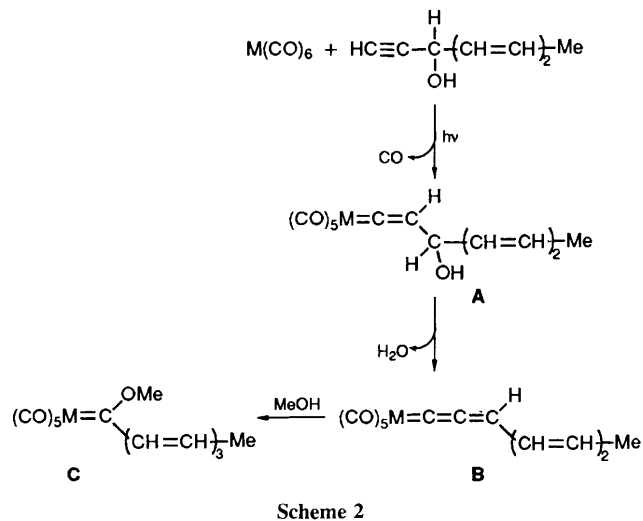


<sup>†</sup> All compounds gave satisfactory analyses. <sup>1</sup>H NMR data for **4f** (300.13 MHz, 297 K, CD<sub>2</sub>Cl<sub>2</sub>) δ 7.26 (d, H<sup>2</sup>, <sup>3</sup>J<sub>H<sup>2</sup>H<sup>3</sup></sub> 14.6 Hz), 6.95 (dd, H<sup>3</sup>, <sup>3</sup>J<sub>H<sup>3</sup>H<sup>2</sup></sub> 14.6, <sup>3</sup>J<sub>H<sup>3</sup>H<sup>4</sup></sub> 11.4 Hz), 6.78 (dd, H<sup>5</sup>, <sup>3</sup>J<sub>H<sup>5</sup>H<sup>4</sup></sub> 14.8, <sup>3</sup>J<sub>H<sup>5</sup>H<sup>6</sup></sub> 10.6 Hz), 6.23 (ddq, H<sup>6</sup>, <sup>3</sup>J<sub>H<sup>6</sup>H<sup>7</sup></sub> 15.0, <sup>3</sup>J<sub>H<sup>6</sup>H<sup>5</sup></sub> 10.5 Hz, <sup>4</sup>J<sub>H<sup>6</sup>H<sup>(Me)</sup></sub> 1.4 Hz), 6.16 (dd, H<sup>4</sup>, <sup>3</sup>J<sub>H<sup>4</sup>H<sup>5</sup></sub> 14.8, <sup>3</sup>J<sub>H<sup>4</sup>H<sup>3</sup></sub> 11.4 Hz), 6.08 (dq, H<sup>7</sup>, <sup>3</sup>J<sub>H<sup>7</sup>H<sup>6</sup></sub> 15.0, <sup>3</sup>J<sub>H<sup>7</sup>H<sup>(Me)</sup></sub> 6.7 Hz), 4.53 (s, OMe) 1.78 (d, Me, <sup>3</sup>J<sub>H<sup>H</sup>7</sub> 6.7 Hz).

**Scheme 1** Reagents and conditions: (room temp.) i,  $\text{HC}\equiv\text{C}-\text{C}(\text{R})(\text{R}')(\text{OH})$  [**a, b, d, e, f**],  $\text{MeOH-Et}_2\text{O}$ , *hν*, 6 h; ii,  $\text{HC}\equiv\text{C}-\text{C}(\text{H})(p\text{-Me}_2\text{NC}_6\text{H}_4)(\text{OH})$  [**c**],  $\text{MeOH-THF}$ , *hν*, 6 h

**Table 1** Selected  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts ( $\delta$ ) of the alkenylidene ligands in compounds **1–5**<sup>a</sup>

Compound	C-1	C-2 (2-H)	C-3 (3-H)	C-4 (4-H)	C-5 (5-H)	C-6 (6-H)	C-7 (7-H)
<b>1a</b>	309.8	149.3 (7.25)	137.1 (6.58)	— —	— —	— —	— —
<b>1b</b>	311.7	146.4 (7.26)	145.2 —	— —	— —	— —	— —
<b>2c</b>	299.4	140.8 (7.70)	138.4 (7.40)	— —	— —	— —	— —
<b>3d</b>	307.2	145.2 (7.21)	137.1 (6.88)	131.2 (6.15)	145.6 (6.41)	— —	— —
<b>3e</b>	305.4	147.0 (7.42)	135.2 (7.05)	129.7 (6.83)	145.0 (7.12)	— —	— —
<b>4f</b>	305.0	146.8 (7.26)	137.2 (6.95)	129.1 (6.16)	146.4 (6.78)	132.4 (6.23)	137.9 (6.08)
<b>5f</b>	330.6	147.9 (7.42)	138.4 (6.99)	129.6 (6.35)	142.6 (6.99)	132.9 (6.35)	142.1 (6.14)

<sup>a</sup> Recorded in  $\text{CD}_2\text{Cl}_2$  at 297 K.

The activation by tungsten hexacarbonyl of unsaturated 2-propyn-1-ols such as alkenylpropyn-1-ols **d** and **e** has also been investigated. Pentadienylidene complexes **3d** and **e**† were obtained in better yield, 55 and 70%, respectively. The irradiation for 6 h of 1-methylbutadienyl-2-propyn-1-ol **f** with either  $\text{W}(\text{CO})_6$  or  $\text{Cr}(\text{CO})_6$  in  $\text{MeOH}-\text{Et}_2\text{O}$  allowed the formation of the new octatrienylidene metal complexes **4f**† and **5f**† isolated in 53 and 46% yield (Scheme 1).

The structure of the alkenylidene complexes was determined by  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^1\text{H}-^{13}\text{C}$  correlated NMR spectroscopy (Table 1). All these reactions gave exclusively the *E*-isomers as shown by the strong vicinal coupling constants of the vinylic protons [ $^3J_{\text{HH}} > 14 \text{ Hz}$ ] as in **4f**.†

These reactions may involve, after coordination of the  $\text{C}\equiv\text{C}$  bond, the formation of an unsaturated vinylidene intermediate **A** and then of an alkenylallenylidene **B**, which can add methanol to give a methoxyalkenylcarbene **C**, as shown in Scheme 2 (for the formation of **4f** and **5f**). Indeed,

several allenylidene chromium or tungsten compounds are known; they have been prepared either by alcohol elimination of the ethoxyalkenylcarbene complexes  $(\text{OC})_5\text{M}=\text{C}[\text{OEt}][\text{CH}=\text{C}(\text{Ph})(\text{NEt}_2)]$ ,<sup>13</sup> via a process that is actually the reverse of the **C**→**B** reaction and is promoted by Lewis acids, or by a multistep reaction between dianions  $\text{LiC}\equiv\text{C}-\text{CR}_2\text{OLi}$  ( $\text{R} = \text{aryl}$ ) with  $\text{M}(\text{CO})_6$ .<sup>14</sup>

The novel, one-step route to alkenylcarbene complexes of group 6 metals described here provides easy access to potentially interesting polyenylidene-metal complexes and should offer new development for organic synthesis.

Received, 21st March 1991; Com. 1/013451

## References

- For recent reviews, see: K. H. Dötz, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 587; W. D. Wulff, P. C. Tang, K. S. Chang, J. S. McCallum, D. C. Yang and S. R. Gilbertson, *Tetrahedron*, 1985, **41**, 5813.
- T. A. Brandvold, W. D. Wulff and A. L. Rheingold, *J. Am. Chem. Soc.*, 1990, **112**, 1645.
- C. K. Murray, D. C. Yang and W. D. Wulff, *J. Am. Chem. Soc.*, 1990, **112**, 5660; D. F. Harvey and M. F. Brown, *J. Am. Chem. Soc.*, 1990, **112**, 7806.
- (a) W. D. Wulff, W. E. Bauta, R. W. Kaesler, P. J. Lankford, R. A. Miller, C. K. Murray and D. C. Yang, *J. Am. Chem. Soc.*, 1990, **112**, 3642; (b) K. H. Dötz, W. Kuhn, G. Müller, B. Huber and H. G. Alt, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 812; (c) N. H. Tran Huy and F. Mathey, *Organometallics*, 1988, **7**, 2233.
- K. H. Dötz, R. Noack, K. Harms and G. Müller, *Tetrahedron*, 1990, **46**, 1235.
- (a) A. Parlier, M. Rudler, H. Rudler and J. C. Daran, *J. Organomet. Chem.*, 1987, **323**, 353; (b) D. W. Macomber, M. H. Hung and A. G. Verma, *Organometallics*, 1988, **7**, 2072.
- D. W. Macomber, M. H. Hung, M. Liang, A. G. Vermaand and P. Madhukar, *Macromolecules*, 1988, **21**, 1187.
- C. P. Casey and W. R. Brunsvold, *Inorg. Chem.*, 1977, **16**, 391; R. Aumann and H. Heinen, *Chem. Ber.*, 1987, **120**, 537.
- W. D. Wulff and S. R. Gilbertson, *J. Am. Chem. Soc.*, 1985, **107**, 503.
- M. Rudler-Chauvin and H. Rudler, *J. Organomet. Chem.*, 1981, **212**, 203.
- J. W. Wilson and E. O. Fischer, *J. Organomet. Chem.*, 1973, **57**, C63.
- H. Le Bozec, D. Pilette and P. H. Dixneuf, *New J. Chem.*, 1990, **14**, 793.
- E. O. Fischer, H. J. Kalder, A. Frank, H. Köhler and G. Huttner, *Angew. Chem., Int. Ed. Engl.*, 1976, **15**, 623.
- H. Berke, P. Härter, G. Huttner and L. Zsolnai, *Z. Naturforsch., Teil B*, 1981, **36**, 929.