

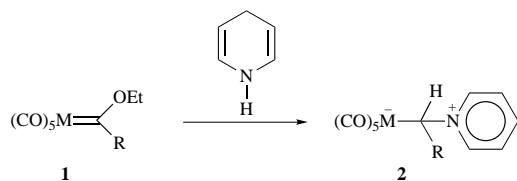
# Alkynyl-pyridinium ylid complexes of tungsten(0) and chromium(0): synthesis and cascade insertion reactions

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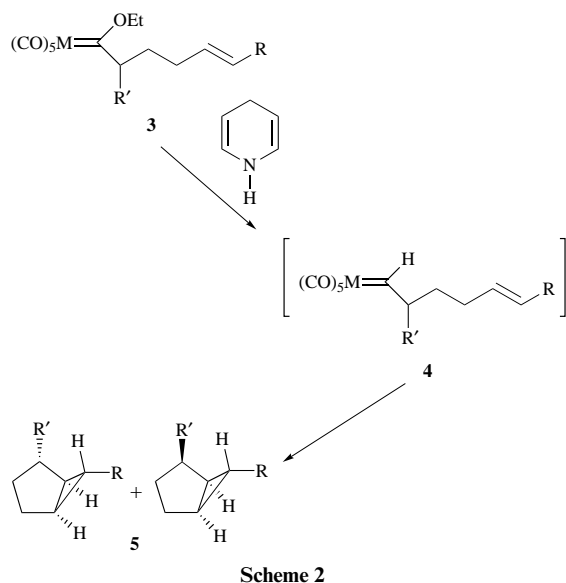
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1,2-dihydropyridine reacts with (1-ethoxy-5-phenylpent-4-ynylidene)pentacarbonyltungsten(0) complex **7** to give the alkynyl pyridinium ylid complex **9** which upon thermolysis leads to an intermediate ketene as the result of the insertions of the triple bond and of CO and which can be trapped by methanol to give the esters **11** and **12** and by dihydrofuran to give the adducts **13** and **14**.

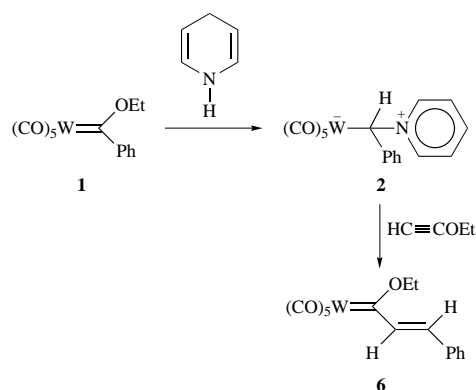
The interaction of dihydropyridines with alkoxy-carbene complexes of chromium and tungsten parallels their behaviour towards carbonyl compounds and confirms the striking analogy which exists between Fischer-type alkoxy-carbene complexes and carbonyl compounds.<sup>1</sup> Indeed, a complex reaction is observed, one step being the formal transfer of a hydride from dihydropyridine to the carbene carbon of **1** leading finally, after elimination of alcohol and fixation of pyridine on the carbene carbon, to pyridinium ylids of tungsten(0) and chromium(0) **2** (Scheme 1).



We first demonstrated that these ylid complexes can be used as cyclopropanation reagents, especially for nucleophile olefins. Of special interest was the behaviour of alkenyl alkoxy-carbene complexes **3** which led, in a one pot reaction, to polycyclic products, such as **5**, as the result of the formation of unstable alkynyl alkylidene complexes of W<sup>0</sup> **4** and their intramolecular reaction with the carbon-carbon double bond (Scheme 2).<sup>1</sup>

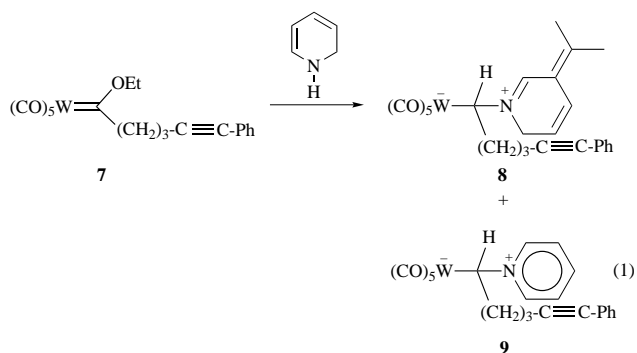


We also showed that the triple bond of an activated alkyne, an yno-ether, reacted with the pyridinium ylid complex **2** (R = Ph), to give, albeit in low yield, a new carbene complex **6** as the result of the insertion of the triple bond into the alkyldene complex (Scheme 3).



The purpose of this paper is to extend this approach to the intramolecular version for the synthesis of polycyclic systems starting from alkynyl alkoxy-carbene complexes of chromium and tungsten.

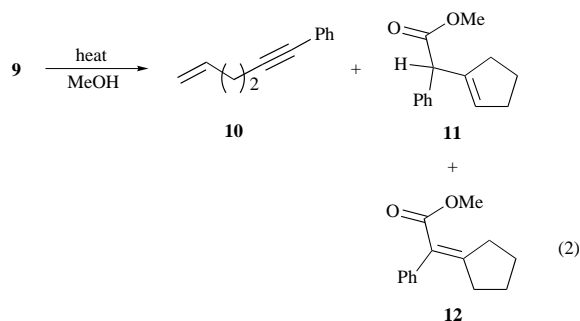
Thus, the reaction of complex **7** with 1,2-dihydropyridine led to a mixture of two complexes which could be separated by silica gel chromatography (Eqn. 1). The less polar product iso-



lated as an orange solid (20% yield) was assigned structure **8** on the grounds of its spectroscopic data which confirmed the presence of a 2,5-dihydropyridine moiety.<sup>2</sup> The elemental analysis and the NMR spectroscopic data † of the slightly more polar complex (red crystals, 45% yield) agreed with structure **9**, a pyridinium ylid complex with a typical shift for carbon C-1 at  $\delta$  63.4 ppm and for the proton linked to it at  $\delta$  4.73 ppm. The related chromium complex behaved similarly.

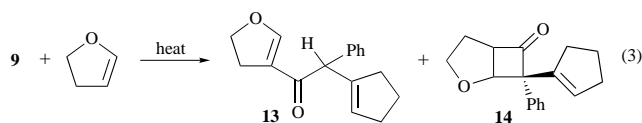
† Complex **9**:  $\delta_{\text{H}}$  8.51 (d, 2H,  $J$  7.0), 7.81 (t, 1H,  $J$  7.0), 7.55 (m, 1H), 7.30 (m, 5H), 4.73 (dd, 1H,  $J$  10.3 and 5.4), 2.72 (m, 2H), 2.43 (t, 2H,  $J$  6.0), 1.49 (m, 2H);  $\delta_{\text{C}}$  204.6, 201.9, 140.0, 136.9, 131.6, 128.4, 127.8, 126.9, 123.8, 89.7, 81.3, 63.4, 43.2, 28.4 and 16.9 (Found:  $M^+$ , 545.  $C_{22}H_{17}NO_5W$  requires  $M$ , 545).

Heating of complex **9** in refluxing benzene for one hour in the presence of a slight excess of methanol led to three organic compounds which could be separated by silica gel chromatography (Eqn. 2). Structure **10** was assigned to the less polar



compound (14%) on the grounds of its physical data: the presence of the triple bond of the starting compound as well as a terminal double bond together with two methylene groups was clearly established by NMR spectroscopy. The second product, isolated as a colorless oil (31%) was assigned structure **11**, an unsaturated non-conjugated methyl ester. Both the IR spectrum ( $\nu_{\text{CO}}$ , 1741  $\text{cm}^{-1}$ ) and the NMR spectroscopic data ( $\delta_{\text{CO}}$ , 172.75 ppm) with a multiplet for an olefinic proton at  $\delta$  5.51, a singlet at  $\delta$  4.39 ppm for an isolated benzylic proton, and three methylene groups, agreed with such a structure.<sup>‡</sup> Finally, the more polar product (28%) was assigned structure **12**, a conjugated ester ( $\nu_{\text{CO}}$ , 1720  $\text{cm}^{-1}$ ,  $\delta_{\text{CO}}$ , 167.8 ppm). Both the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra confirmed the presence of four methylene groups.<sup>§</sup>

When the thermolysis of complex **9** was carried out in the presence of an excess of dihydrofuran, two polycyclic ketones could be isolated in **20** and 8% yield respectively after one hour of reaction (Eqn. 3). The less polar product was assigned struc-



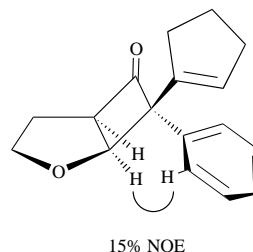
ture **13**. Its infra-red spectrum agreed with the presence of a cyclobutanone ( $\nu_{\text{CO}}$ , 1778  $\text{cm}^{-1}$ ); its  $^{13}\text{C}$  NMR spectrum confirmed this hypothesis ( $\delta_{\text{CO}}$ , 212.34 ppm) and was also in agreement with the presence of five methylene groups. The  $^1\text{H}$  NMR spectrum showed a multiplet for an olefinic proton at  $\delta$  5.90 ppm and a doublet for the proton geminal to the oxygen atom at  $\delta$  5.25 ppm.

Confirmation of the structure and of the stereochemistry of this tricyclic compound could be established by extensive COSY and NOE NMR experiments. Of special interest for the stereochemistry was the irradiation of the OCH hydrogen at the ring junction which gave a NOE enhancement of the *ortho* hydrogens of the phenyl group thus confirming the *cis* relationship between this group and the hydrogen atoms at the ring junction.

The more polar product was isolated as a white solid, mp 54–56 °C. The  $^1\text{H}$  NMR spectrum confirmed the presence of the

<sup>‡</sup> Compound **11**:  $\nu_{\text{max}}(\text{neat})/\text{cm}^{-1}$  1741;  $\delta_{\text{H}}$  7.33–7.25 (m, 5H), 5.51 (m, 1H), 4.39 (br s, 1H), 3.70 (s, 3H), 2.38–2.21 (m, 4H), 1.86 (m, 2H);  $\delta_{\text{C}}$  172.75, 141.28, 137.37, 128.61, 128.49, 128.06, 127.30, 53.78, 52.09, 34.20, 32.47 and 23.38 (Calc. for  $\text{C}_{14}\text{H}_{16}\text{O}_2$ : C, 77.70; H, 7.40. Found: C, 76.37; H, 7.47).

<sup>§</sup> Compound **12**:  $\nu_{\text{max}}(\text{neat})/\text{cm}^{-1}$  1720;  $\delta_{\text{H}}$  7.67–7.07 (m, 5H), 3.58 (s, 3H), 2.83 (t, 2H, *J* 7.4), 2.11 (t, 2H, *J* 7.1), 1.70 (m, 2H), 1.55 (m, 2H);  $\delta_{\text{C}}$  167.8, 164.28, 139.04, 129.26, 128.26, 128.12, 126.81, 51.43, 35.37, 34.18, 26.80 and 25.83 (Calc. for  $\text{C}_{14}\text{H}_{18}\text{O}_2$ : C, 77.70; H, 7.40. Found: C, 76.67; H, 7.50).



same benzylcyclopentenyl fragment as in compound **11** with signals at  $\delta$  5.42 ppm for the olefinic proton, and at 4.76 ppm for the benzylic proton. Both the IR and the  $^{13}\text{C}$  NMR spectra were in agreement with the presence of a carbonyl group, precisely a  $\beta$ -alkoxy- $\alpha,\beta$ -unsaturated carbonyl group ( $\nu_{\text{CO}}$ , 1630  $\text{cm}^{-1}$ ,  $\nu_{\text{C-C}}$ , 1600  $\text{cm}^{-1}$ ;  $\delta_{\text{CO}}$ , 192.67 ppm). Finally, the observation of a highly deshielded signal for one proton ( $\delta$  between 7.37 and 7.26 ppm) confirmed the assigned structure **14**.

It is interesting to notice that the related chromium complex gave only the cyclobutanone derivative in 15% yield.

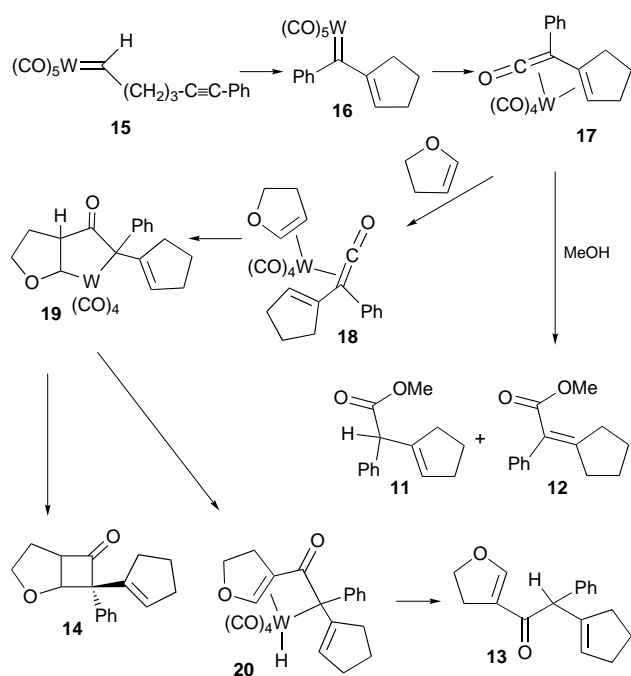
From a mechanistic point of view, the formation of the two series of products can be explained in the following way (Scheme 4): it seems clear that the first step of the reaction is the insertion of the triple bond into the alkylidene function of **15**, as in the model reaction of Scheme 3, leading to a new cyclopentenylcarbene complex **16**. Insertion of CO can then give a ketene complex **17**. Depending on the reaction conditions, this ketene might suffer either alcoholysis to give upon 1,2 addition, the ester **11**, and upon 1,4 addition, the conjugated ester **12**. Conversely, in the presence of dihydrofuran, cycloaddition *via* complexes **17** and **18** would lead, with high stereoselectivity, to the observed cyclobutanone **14**. Alternatively, a  $\beta$ -elimination involving the same complex **18** followed by a hydride migration from the metal to the carbon bearing the phenyl group, might give the ketone **13** *via* the complexes **19** and **20**.

Two points warrant comment: although the photochemical and thermal insertions of CO into Fischer-type carbene complexes of chromium leading to cyclobutanones are well documented,<sup>3–5</sup> such reactions are scarce in the case of tungsten carbene complexes and could, in most cases, only be observed under high CO pressure.<sup>6</sup> Second, a striking difference of behaviour is nevertheless observed between tungsten and chromium, the latter leading only to the cycloaddition product whereas the former gave mainly a product resulting formally from the insertion of the metal into a vinylic carbon–hydrogen bond of the olefin.

## Experimental

A solution of complex **9** (0.43 g, 0.8 mmol) in dry benzene (10  $\text{cm}^3$ ) was heated at 50–60 °C in the presence of dihydrofuran (0.36  $\text{cm}^3$ , 4.8 mmol, 6 equiv.) until, according to TLC, no more starting complex was present (1 h). After evaporation of the solvent, the residue was chromatographed on silica gel to afford first the enyne **10** (20 mg, 16%) as an oil, then with 4% diethyl ether in hexanes, compound **14** (40 mg, 20%) as an oil;  $\nu_{\text{max}}(\text{neat})/\text{cm}^{-1}$  1778;  $\delta_{\text{H}}$  7.41–7.26 (m, 5H, Ar), 5.90 (m, 1H, =CH), 5.25 (d, 1H, *J* 5.9, OCH), 4.13 (ddd, 1H, *J* 8.6, 8.1 and 2.0, OCHH), 3.96–3.86 (m, 2H, OCHH), 2.50–2.40 (m, 1H, CH), 2.34–2.26 (m, 3H,  $\text{CH}_2$ , CH), 2.05 (m, 1H, CH), 1.98 (m, 1H, CH), 1.90–1.75 (m, 2H,  $\text{CH}_2$ );  $\delta_{\text{C}}$  212.34, 139.97, 137.58, 128.89, 127.29, 126.86, 79.63, 76.00, 70.24, 61.77, 32.51, 32.03, 28.49 and 22.99 (Found:  $M^+$ , 254.  $\text{C}_{17}\text{H}_{18}\text{O}_2$  requires  $M$ , 254); and finally, with 6% diethyl ether in hexanes, compound **13** (16 mg, 8%) as a white solid, mp 54–56 °C;  $\nu_{\text{max}}(\text{CHCl}_3)/\text{cm}^{-1}$  1630 and 1600;  $\delta_{\text{H}}$  7.37–7.26 (m, 6H, Ar, OCH=), 5.42 (m, 1H, =CH),

<sup>¶</sup> *J* Values are given in Hz.



Scheme 4

5.42 (m, 1H, =CH), 4.76 (br s, 1H, CHPh), 4.55 (m, 2H, OCH<sub>2</sub>), 2.85 (m, 2H, CH<sub>2</sub>), 2.36–2.28 (m, 4H, 2 CH<sub>2</sub>), 1.88 (m, 2H, CH<sub>2</sub>);  $\delta_c$  192.67, 157.08, 141.65, 137.34, 127.70, 127.43, 127.21, 125.94, 118.88, 72.41, 56.26, 33.53, 31.36, 26.57 and 22.36

(Calc. for C<sub>17</sub>H<sub>18</sub>O<sub>2</sub>: C, 80.31; H, 7.15. Found: C, 80.21; H, 7.46%).

### Acknowledgements

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