

Direct Formation of Fischer-type Carbene Complexes from $W(CO)_6$ and Alkynes

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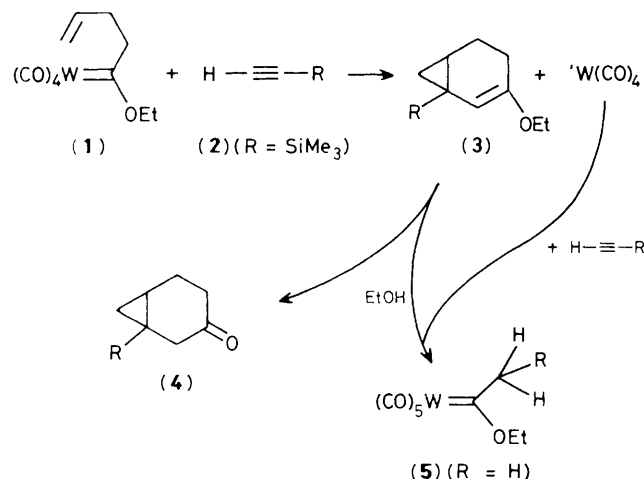
Co-ordinatively unsaturated tungstacarbonyl species, formed either chemically or photochemically, react with alkynes $H-C\equiv C-R$ to give, after solvolysis of presumed vinylidene complexes by $R'OH$, in the presence of SiO_2 , the Fischer-type carbene complexes $(CO)_5W=C(OR')(CH_2R)$.

Carbene complexes of transition metals are known to induce both olefin metathesis and alkyne polymerization.¹⁻⁴ Whereas in the case of the olefin metathesis reaction the origin of the first carbene complex, which promotes the reaction, is well established, little is known about the mechanism of formation of such species in the polymerization of alkynes. This is for example the case for the polymerization of alkynes induced by $(CO)_4W(cod)$ (cod = cyclo-octa-1,5-diene).⁵ The aim of this communication is to show, for the first time, that the interaction of co-ordinatively unsaturated tungsten carbonyl species with alkynes leads to the formation of carbene complexes.

In a previous paper,⁶ we described the interaction of complex (1) with alkynes, a reaction which leads to bicyclo[4.1.0]heptane derivatives (Scheme 1), with release of $W(CO)_4$. Interestingly, we also observed that the so-formed $W(CO)_4$ moiety further reacts with the alkyne to give new Fischer-type carbene complexes. Thus, the interaction of (1) with (2) ($R = SiMe_3$), which leads mainly to the enol ether (3) gives, after silica gel chromatography of the reaction mixture, besides the expected hydrolysis product (4), the carbene complex (5) in a 12% yield with respect to (1). With but-3-ynol, (1) leads to, besides (4) ($R = [CH_2]_2OH$), the cyclic carbene complex (7)[†] in a 34% yield with respect to (1).

The origin of the new carbene complexes (5) and (7) could be demonstrated in the following way: (i) irradiation of

$W(CO)_6$ in dichloromethane or hexane, in the presence of (2) ($R = SiMe_3$) for 4 hours leads, after treatment with $MeOH/SiO_2$, to complex (6)[†] in a 32% yield with respect to $W(CO)_6$. The same result could be obtained in the absence of SiO_2 , albeit with a lower yield of (6) (19%). Similar results were observed by modifying either the structure of the alkyne or the nature of the alcohol $R'OH$ (see Table 1). Interestingly, under the same conditions, but-3-ynol leads, by an intramolecular reaction, to the carbene complex (7)[†] in a 10% yield. (ii)



Scheme 1

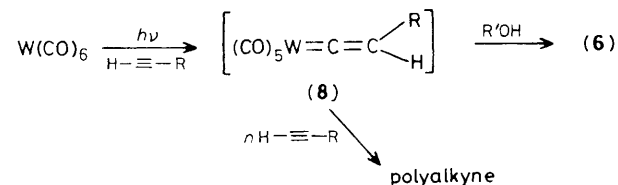
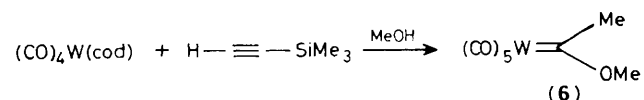
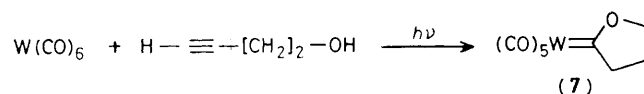
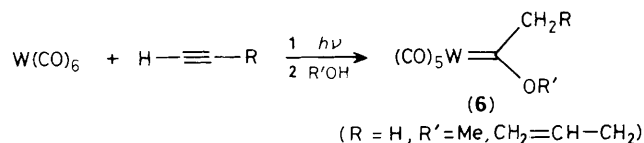
Table 1. Yields of carbene complexes with respect to the starting materials.

Complex ^a	Alkyne	$R'OH$	SiO_2	% Yield
$W(CO)_6$	$H-C\equiv C-H$	$MeOH$	+	16
$W(CO)_6$	$H-C\equiv C-SiMe_3$	$MeOH$	-	19
$W(CO)_6$	$H-C\equiv C-SiMe_3$	$MeOH$	+	32
$W(CO)_6$ ^b	$H-C\equiv C-SiMe_3$	$MeOH$	+	22
$W(CO)_6$	$H-C\equiv C-SiMe_3$	\nearrow/OH	+	10
$W(CO)_4(cod)$	$H-C\equiv C-SiMe_3$	$MeOH$		10

^a Solvents: CH_2Cl_2 or C_6H_{14} . ^b Solvent: $MeOH$.

[†] Complex (6) ($R = H$, $R' = CH_2=CH-CH_2$), yellow oil; i.r. (cyclohexane): 2060, 1975, 1935 cm^{-1} (ν_{CO}); 1H n.m.r. ($CDCl_3$), δ : 6.3, 5.65, 5.45 (m, 3H, $-CH=CH_2$), 5.4 (d, J 6 Hz, 2H, OCH_2), 2.9 (s, 1H, CH_3); ^{13}C n.m.r. ($CDCl_3$), δ : 331.8 (carbene), 203 (*trans* CO), 197.1 (*cis* CO), 130.7 ($-CH=CH_2$), 120.4 ($-CH=CH_2$), 84.4 (OCH_2), 52.0 (CH_3).

Complex (7), yellow solid, m.p. 61–62 °C; i.r. (cyclohexane): 2060, 1955, 1935 cm^{-1} (ν_{CO}); 1H n.m.r. ($CDCl_3$), δ : 4.9 (t, J 8 Hz, 2H, OCH_2), 3.45 (t, J 8 Hz, 2H, $W=C-CH_2$), 1.95 (quintet, J 8 Hz, 2H, $CH_2CH_2CH_2$); ^{13}C n.m.r. (C_6D_6), δ : 314.4 (carbene), 203 (*trans* CO), 197.0 (*cis* CO), 85.6 (OCH_2), 63.2 ($C-CH=CH_2$), 20.8 ($CH_2CH_2CH_2$).



(CO)₄W(cod), which contains a labile ligand, reacts also with (2) (R = SiMe₃) and then with MeOH, at room temperature, to give complex (6) in 10% yield. Taken together, these results show that in the case of the reaction depicted in Scheme 1, it is presumably W(CO)₄ which reacts with the excess of alkyne, then with EtOH formed by hydrolysis of the enol ether on SiO₂, to give complex (5). A common intermediate in all these reactions could be a vinylidene complex (8) which might lead, after an R'OH treatment to the new carbene complexes. It is indeed known,⁸⁻¹² that such unstable complexes can be formed by the interaction of alkynes with transition metals. It is also known that such species contain an electrophilic carbon atom in the α -position with respect to the carbene function.

As a conclusion, these results show that the formation of carbene complexes from co-ordinatively unsaturated tungsten species is easy and can explain the formation of polymers induced by such species. Moreover, these observations show that Fischer-type carbene complexes can be prepared easily, yet until now in moderate yield, from W(CO)₆ and monosubstituted alkynes.

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