

Generalized Synthesis of Pentaco-ordinated Tungsten(IV) Carbene Complexes

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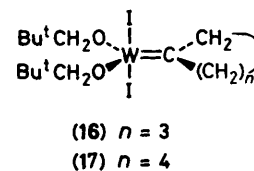
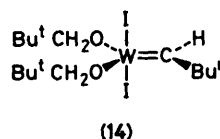
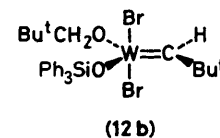
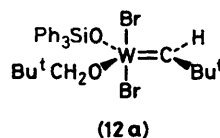
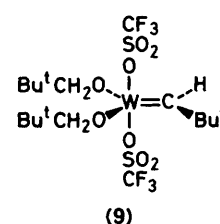
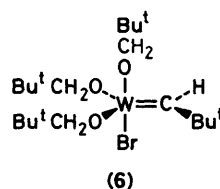
General methods enabling the synthesis of a large variety of pentaco-ordinate tungsten(IV) carbene complexes are described permitting notably the isolation of the first unsaturated (<18e) metal carbenes containing β -hydrogens.

Although several metal carbene complexes have been found to catalyse olefin metathesis,^{1,2} only one type² seems to induce the very high activity found for classical catalyst systems.³ We report here the synthesis of further members of this important family, thus enabling a clearer understanding of their chemical and catalytic properties.

The previously reported complexes (1) and (2) (Table 1) resulted from the reaction of $\text{WO}(\text{OCH}_2\text{Bu}^t)_2(\text{CH}_2\text{Bu}^t)_2$ with AlX_3 .² Although (3)—(5) can be prepared similarly, this synthetic route is not general. Fortunately, we find that ligand substitution reactions can be conveniently carried out on (1)—(5), allowing replacement of the anionic ligands X or OR, as well as of the neopentylidene group.

The stepwise substitution of the *axial* halide ligands X has been achieved in several cases. For example, treatment of (2) with the appropriate number of equivalents of $\text{LiOCH}_2\text{Bu}^t$ (in pentane) or AgSO_3CF_3 (in benzene) yields straightforwardly (6) and (7), or (8) and (9), respectively. The ^1H and ^{13}C n.m.r. chemical shifts (Table 1) are consistent with the expected π -donor strength of the axial ligands, and show clearly that the usually labile trifluoromethanesulphonate anion is strongly co-ordinated to the metal and unfortunately the cationic species such as $[\text{W}(\text{CHBu}^t)(\text{OCH}_2\text{Bu}^t)_2\text{Br}]^+$ which are extremely active in metathesis are not formed.² No changes are observed in the $\text{C}_\alpha\text{—H}_\alpha$ coupling constant, whose high value indicates that only a weak direct W—H_α interaction⁴ occurs in all these compounds, despite their formally unsaturated nature.

The equatorial OR ($\text{R} = \text{CH}_2\text{Bu}^t$, Pri) ligand in (1)—(5) can also be substituted: e.g. (10) and (11) are formed from (2) and (3) by treatment with BX_3 (0.5 equiv.). Certain alcohols e.g. Ph_3SiOH or phenols react with (2), displacing $\text{Bu}^t\text{CH}_2\text{OH}$, to yield complexes such as (12) and (13). Compound (12) exists as two isomers (12a) and (12b) (ca. 3:1 in C_6H_6 at 25 °C) differing by the respective positions of the OCH_2Bu^t and OSiPh_3 ligands in the equatorial plane of the molecule. We find for these complexes that rapid intermolecular alkoxo exchange occurs and hence the (12a):(12b) ratio is under



thermodynamic control. Homologous compounds such as $\text{W}(\text{CHBu}^t)(\text{OCH}_2\text{Bu}^t)(\text{OR})\text{Br}_2$ ($\text{R} = \text{Ph}$, Pri) or $\text{W}(\text{CHBu}^t)(\text{OCH}_2\text{Bu}^t)(\text{OEt})\text{I}_2$ behave similarly. In contrast with axial substitution, the replacement of the equatorial neopentoxo ligands by poorer π -donors is followed by the decrease of the $J(\text{C}_\alpha\text{H}_\alpha)$ value (Table 1) which indicates the strengthening of the direct W—H_α interaction⁴ and explains the high field shift of the $^1\text{H}_\alpha$ n.m.r. signal (Table 1).

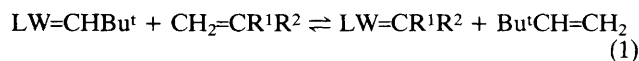
The neopentylidene complexes (1)—(5) react with terminal olefins $\text{CH}_2=\text{CR}^1\text{R}^2$ (10–20 equiv., CH_2Cl_2 , 25 °C, h) in a metathesis reaction ($\text{L} = \text{ligand}$), equation (1). Good yields of the new carbene complexes are obtained by displacement of the equilibrium by vacuum evaporation of the $\text{Bu}^t\text{CH}=\text{CH}_2$. Hence reaction of e.g. (3) with hex-1-ene yields (14), with

Table 1. Characteristic n.m.r. data for the tungsten carbene complexes.

Complexes	δH_α (C ₆ D ₅ Br)	δC_α (C ₆ D ₆)	$^1J(C_\alpha H_\alpha)$ /Hz
W(CHBu ^t)(OCH ₂ Bu ^t) ₂ Cl ₂ (1) ^a	10.78	289.9	136
W(CHBu ^t)(OCH ₂ Bu ^t) ₂ Br ₂ (2) ^a	11.12	297.2 ^b	135
W(CHBu ^t)(OCH ₂ Bu ^t) ₂ I ₂ (3)	11.38	305.2	135
W(CHBu ^t)(OPr ⁱ) ₂ Cl ₂ (4)	10.64	288.6	
W(CHBu ^t)(OPr ⁱ) ₂ Br ₂ (5)	10.99	295.2	135
W(CHBu ^t)(OCH ₂ Bu ^t) ₃ Br (6)	9.76	273.7 ^b	135
W(CHBu ^t)(OCH ₂ Bu ^t) ₄ (7)	7.90	252.6	137
W(CHBu ^t)(OCH ₂ Bu ^t) ₂ (CF ₃ SO ₃)Br (8)	11.50	302.5 ^b	137
W(CHBu ^t)(OCH ₂ Bu ^t) ₂ (CF ₃ SO ₃) ₂ (9)	11.78	306.2 ^b	
W(CHBu ^t)(OCH ₂ Bu ^t)Br ₃ (10) ^a	8.54 ^c	308.2 ^{c,d}	127
W(CHBu ^t)(OCH ₂ Bu ^t)I ₃ (11)	6.66 ^d	321.5 ^{c,d}	114
W(CHBu ^t)(OCH ₂ Bu ^t)(OSiPh ₃)Br ₂ (12a)	10.64	299.2	134
(12b)	10.85	300.4	
W(CHBu ^t)(OSiPh ₃) ₂ Br ₂ (13)	10.21	302.1	
W(CHBu ⁿ)(OCH ₂ Bu ^t) ₂ I ₂ (14)	11.89 ^c	302.1	
W(CHPh)(OCH ₂ Bu ^t) ₂ I ₂ (15)	11.88	285.8	

^a Ref. 2. ^b In C₆D₅Br. ^c At 240 K. ^d In CD₂Cl₂. ^e Triplet, $^3J(CH)$ 8 Hz.

styrene (**15**), and with the exomethylene carbocycles $CH_2=\overline{C}(CH_2)_nCH_2$ ($n = 3, 4$) (**16**) and (**17**).[†] This reaction is quite general and provides for instance the first examples of non-18e metal carbene complexes possessing β -hydrogens, permitting a systematic study of their properties *e.g.* thermal stability, modes of decomposition, reactivity, which differ notably from (**1**)–(**5**).



The combination of the three synthetic methods above provides access to a large number of simple pentaco-ordinate tungsten carbene complexes and further reports will be concerned with studies on their reactivity as metathesis catalysts in the presence or absence of Lewis acids. For example, using (**3**), functionalised olefins such as $CH_2=CH(CH_2)_2CO_2Me$ can be metathesised at 60 °C into C₂H₄ and MeO₂C(CH₂)₂CH=CH(CH₂)₂CO₂Me in chlorobenzene. Further, by such suitable ligand modifications,

[†] Satisfactory analyses of (**17**) were obtained and the mass spectrum showed the expected parent ions and fragmentation, as for most of the reported compounds.

certain of these carbenes show Wittig⁵ type reactivity with carbonyl functional groups (*e.g.* in esters, lactones), the details of which will be reported separately.

We thank the C.N.R.S. for supporting this work. A. A. thanks the Venezuelan Government for financial support.

Received, 25th February 1985; Com. 256

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