Regio- and Stereo-selective Formation of Methylenecyclopropane Complexes from Allenes and Benzylidenepentacarbonyl Tungsten

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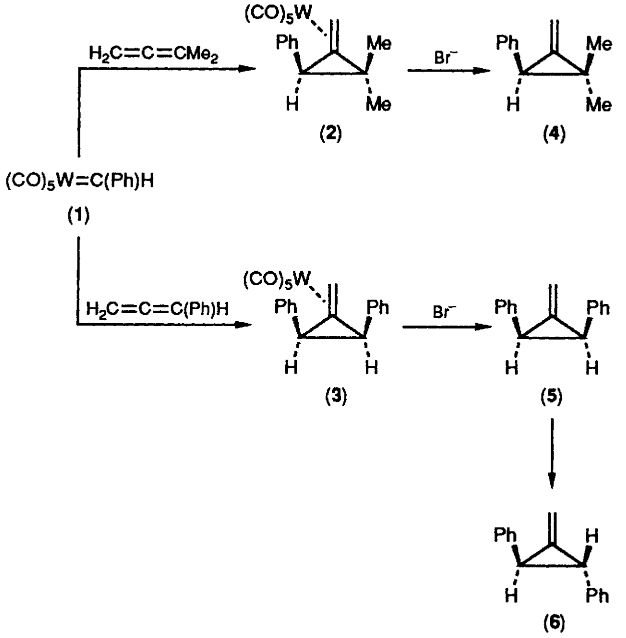
Benzylidenepentacarbonyl tungsten reacts with dimethylallene and phenylallene, respectively, by regiospecific and stereoselective transfer of the benzylidene group to the allene and co-ordination of the product methylenecyclopropane which can be cleaved almost quantitatively from the metal by Br^-; the structure of the 2-phenyl-3,3-dimethylmethylenecyclopropane complex is established by an *X*-ray structure analysis.

Electrophilic transition metal carbene complexes, $L_nM{=}C(Ph)R$, react with allenes to give either trimethylenemethane complexes, by coupling of the carbene ligand with the allenes [R = OEt; L_nM = $(CO)_4Fe$, $(CO)_5M$ (M = Cr, Mo, W)],[1] or alkene scission products [R = Ph, L_nM = $(CO)_5W$].[2] Both reactions were proposed to proceed by initial CO elimination from the complex. We now report the first formation of methylenecyclopropane complexes by transfer of a co-ordinated carbene to allenes and complexation of the resulting methylenecyclopropane.

Benzylidenepentacarbonyl tungsten (**1**)[3] reacts with an excess of 1,1-dimethylallene and phenylallene in pentane–dichloromethane even at −50 °C to form, within several hours, the methylenecyclopropane complexes (**2**) and (**3**), respectively (Scheme 1). After purification by column chromatography and recrystallization from pentane–dichloromethane (**2**) and (**3**) are obtained as yellow crystals in *ca.* 35% yield. According to the ^1H NMR spectra of the crude reaction mixture, only one isomer of (**2**) and (**3**) is formed. The formation of more than 3% of another isomer would have been detected. The complexes were characterized by elemental analysis and by spectroscopic means.† The structure of (**2**) was additionally established by an *X*-ray structure analysis (Figure 1).‡

The carbene ligand is exclusively transferred to the substituted double bond of the allene and the resulting methylenecyclopropane co-ordinates to the pentacarbonyl tungsten fragment *via* the exocyclic double bond. The phenyl group and $(CO)_5W$ occupy *anti* positions. The distances and angles of the methylene cyclopropane framework correspond to those of η^2-(*cis*-2,3-bismethoxycarbonylmethylenecyclopropane)(tetracarbonyl) iron[4] obtained from Feist's ester and $Fe_2(CO)_9$.[5] The ^1H NMR spectrum of (**3**) exhibits in addition to the resonances of the aromatic protons two singlets, one for the ring CH_2 and one for the $=CH_2$ protons. Therefore the phenyl groups must be *cis* and the *cis/trans* stereoselectivity for 'C(Ph)H' addition to the allene must be higher than 30. A pronounced preference for the formation of the thermodynamically less stable *cis* cyclopropanes is also observed in the reactions of (**1**) with monoalkenes (except for alkenes with very bulky substituents),[3a,6] and with conjugated dienes.[7]



Scheme 1

When similar conditions are employed, (**1**) does not react with tetraphenylallene, tetraphenylbutatriene, and tetraphenylhexapentene. Therefore, the formation of methylenecyclopropanes seems to be restricted to mono- and di-substituted allenes, possibly for steric reasons.

The uncomplexed methylenecyclopropanes (**4**) and (**5**) (both yellow oils) are obtained almost quantitatively when solutions of (**2**) and (**3**) are treated at room temperature with NEt_4Br in dichloromethane (4 h).§ In a succeeding reaction (**5**) isomerizes in the course of several days to give the *trans* isomer (**6**) (Scheme 1).

In the reactions of carbenes or carbenoids with allenes double-addition to give spiropentane derivatives is generally difficult to avoid.[8] A similar transfer of two benzylidene

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† *Selected spectroscopic data* for (**2**): IR ν(CO) (pentane) 2085m, 2002w, 1973s, 1961vs cm^{-1}; ^1H NMR δ ($CDCl_3$, −25 °C) 1.11 (s, Me), 1.67 (s, Me), 3.52 (s, br, 6-H), 3.63 (d, *J* 1.2 Hz, 6-H), 3.74 (s, br, 8-H), 7.2 (m, Ph); ^{13}C NMR δ ($CDCl_3$, −30 °C) 21.1 (Me), 27.4 (Me), 31.0 (C-9), 39.3 (C-8), 44.5 (C-6), 92.0 (J_{WC} 15.2 Hz, C-7), 196.4 (J_{WC} 125.6 Hz, *cis*-CO), 201.7 (J_{WC} 143.6 Hz, *trans*-CO). For (**3**): IR ν (CO) (pentane) 2086m, 2005w, 1974s, 1961vs cm^{-1}; ^1H NMR δ ($CDCl_3$, −30 °C) 3.85 (s, $=CH_2$), 3.94 (s, CH_2), 6.8—7.2 (m, Ph); ^{13}C NMR δ ($CDCl_3$, −23 °C) 34.8 (C-8, C-9), 42.8 (C-6), 80.9 (J_{WC} 13.8 Hz, C-7), 126.5, 127.9, 129.2, 135.7 (Ph), 196.1 (J_{WC} 125.2 Hz, *cis*-CO), 201.9 (J_{WC} 144.2 Hz, *trans*-CO).

‡ *Crystal data* for (**2**): $C_{17}H_{14}O_5W$, *M* = 482.15, triclinic, space group $P\bar{1}$, *a* = 9.289(2), *b* = 9.393(2), *c* = 10.058(2) Å, α = 87.44(2), β = 85.23(2), γ = 73.75(2)°, *U* = 839.4 Å^3, D_c = 1.9 g cm^{-3}, *Z* = 2, μ (Mo-K_α) = 70.5 cm^{-1}, 3507 unique reflections were recorded, of which 3292 were 'observed' with $I \geqslant 1\sigma(I)$ (ω-scan, Δω 1°) using Mo-K_α radiation (λ = 0.71069 Å), graphite monochromator, on a Syntex P3 diffractometer. Solution by SHELXTL. *R* (R_w) = 0.029 (0.033). Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

§ *Selected spectroscopic data* for (**4**): ^1H NMR δ ($CDCl_3$, −25 °C) 0.85 (s, Me), 1.34 (s, Me), 2.57 [t, br, C(Ph)H], 5.54 (s, br, $=CH$), 5.57 (dd, *J* 0.9, 2.4 Hz, $=CH$), 7.2 (m, Ph); ^{13}C NMR δ ($CDCl_3$, −30 °C) 17.3 (Me), 22.6 (Me), 25.0 (C-9), 30.9 (C-8), 102.3 (C-6), 144.2 (C-7). For (**5**): ^1H NMR δ ($CDCl_3$) 3.23 [t, *J* 2.3 Hz, C(Ph)H], 5.89 (t, *J* 2.3 Hz, $=CH_2$), 7.3 (m, Ph). For (**6**): ^1H NMR δ ($CDCl_3$) 2.61 [t, *J* 2.3 Hz, C(Ph)H], 5.82 (t, *J* 2.3 Hz, $=CH_2$), 7.3 (m, Ph).

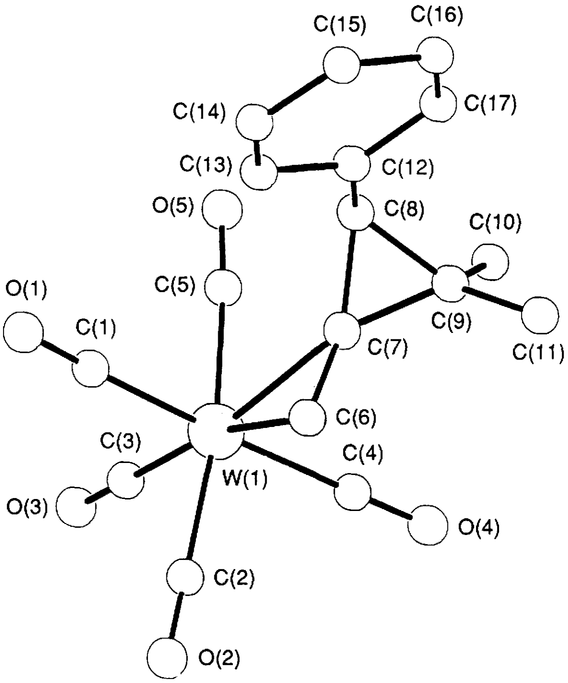

Figure 1. Molecular structure of (**2**). Important distances (Å) and angles (°) are: W–C(6) 2.386(5), W–C(7) 2.376(5), C(6)–C(7) 1.381(9), C(7)–C(8) 1.482(8), C(7)–C(9) 1.483(8), C(8)–C(9) 1.544(7); C(6)–W–C(7) 33.7(2), W–C(6)–C(7) 72.7(3), C(6)–C(7)–C(8) 135.7(5), C(6)–C(7)–C(9) 133.4(4), C(8)–C(7)–C(9) 62.8(4), C(7)–C(8)–C(9) 58.6(4).

ligands from (**1**) to the allenes was not observed. Obviously, the $(CO)_5W$ fragment acts as a protecting group for the methylenecyclopropane. Thus, the reaction of carbene complexes with allenes constitutes a new route for the regiospecific and highly stereoselective synthesis of methylenecyclopropane complexes as well as of methylenecyclopropanes.

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