

An Unusual Transition-metal-mediated [2 + 2 + 2] Cyclization of Functionalized Alkenes

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The metal- η^3 -2-methoxycarbonylpentadienyl complexes $(C_5R_5)M(CO)_2(\text{syn-}\eta^3\text{-2-COOMe-C}_6\text{H}_5)$ ($R=H$, $M=W$; $R=H$, Me , $M=Mo$) undergo a novel acid-catalysed cotrimerization with α - and β -unsaturated ketones to afford two products with diastereoisomeric six-membered rings which have been structurally characterized by X-ray diffraction.

Metal-catalysed oligomerization of olefins is recognized to be an important reaction in organic synthesis.^{1,2} Controlled oligomerization of functionalized olefins such as methyl vinyl ketone, acryloyl esters and nitriles is of special interest because of their facile polymerization. Only linear dimerization of these olefins has been proved successful.³ Cocyclooligomerization of these olefins either stoichiometrically or catalytically is known for limited systems, which are manifested by their codimerization with dienes (Diels-Alder reactions), olefins² and strained alkanes.² No precedent case⁴ for the cocyclo-trimerization of these olefins with other alkenes has been reported. Here, we report a novel metal-mediated [2 + 2 + 2] cyclization of a metal- η^3 -pentadienyl ligand with two molecules of α - and β -unsaturated ketones.

Treatment of the η^3 -allyl complex **1**⁵ with two equiv. of methyl vinyl ketone in cold toluene (-40°C), followed by addition of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (1.0 equiv.) led to a yellow suspension. Monitoring of the reaction by a SiO_2 -TLC plate showed the presence of two elutable organometallic species ($R_f = 0.47$ and 0.32 , diethyl ether-hexane = 4) and no cationic precipitate was observed. The two new complexes were isolated as a crystalline solid in reasonable yields [**4a** (42%), **4b** (19%)] after workup. The molecular structures of **4a**[†] and **4b**[‡] have been determined by X-ray diffraction (XRD) measurements with the results given in Figs. 1 and 2, respectively. In the structure of **4a**, each unit cell contains two independent molecules that are structurally related to each other by rotation of the C(4)–C(12) bond by 180° . From the ORTEP drawing, the η^3 -allyl vinyl group has evidently undergone a novel cocyclo-trimerization with methyl vinyl ketone to generate a six-membered ring. The major isomer **4a** adopts a chair-like conformation with the tungsten- η^3 -allyl group occupying the axial position. If the C(3)-carbon on the allyl ligand is defined as R^* configuration, **4a** has the ($3R^*$, $4S^*$, $5R^*$, $7R^*$) configuration. The structure of the minor isomer **4b** (Fig. 2) bears a close resemblance to that of **4a** except that the $(C_5H_5)W(CO)_3$ fragment is situated in the equatorial position of the chair-like ring; *i.e.* the molecule has ($3R^*$, $4S^*$, $5S^*$, $7S^*$) configuration.

Scheme 1 lists the related reactions between the η^3 -allyl compounds **1–3** and α -, β -unsaturated ketones that likewise gave two diastereoisomers **5a, b–7a, b**. Structural assignments

of the two isomers were made upon comparison of their ^1H NMR data to those of **4a** and **4b**. For **4a–7a**, the values of the coupling parameters between the C(4)–H and C(5)–H protons is 2–3 Hz, indicative of axial-equatorial coupling; for **4b–7b**, the corresponding value is 9–10 Hz, consistent with axial-axial proton coupling.

In organic chemistry, nucleophilic attack of organometallic reagents on α , β -unsaturated ketones only gave the 1:1 addition product (Michael reaction).⁶ BF_3 -Catalysed addition of related complexes $\text{Mo}(C_5H_5)(CO)_2$ -(η^3 -1-vinylallyl) and -(η^3 -2-vinylallyl) to methyl vinyl ketone likewise gave only a 1:1 product.⁷ To test the probability of Michael reaction, we

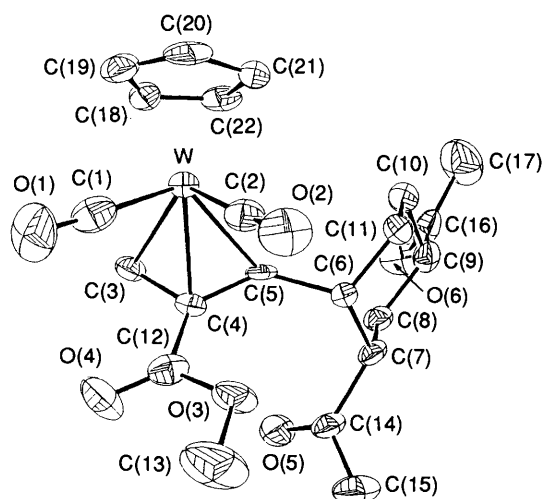


Fig. 1 ORTEP drawing of complex **4a** (one of the two independent molecules). Pertinent bond distances (\AA): W(1)–C(3) 2.27(1), W(1)–C(4) 2.26(1), W(1)–C(5) 2.32(1), C(3)–C(4) 1.42(2), C(4)–C(5) 1.40(2), C(5)–C(6) 1.53(2).

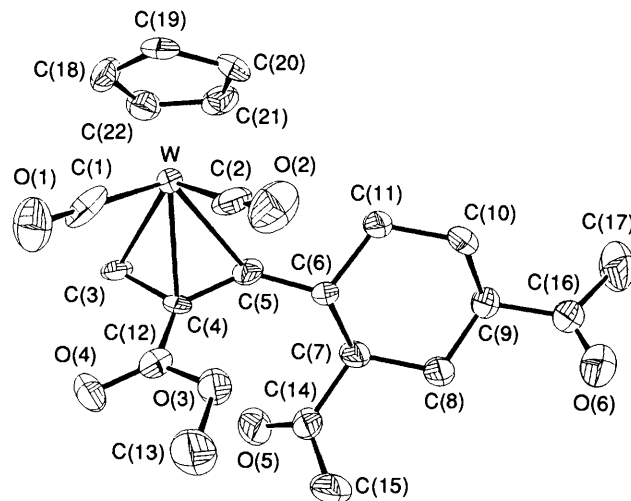
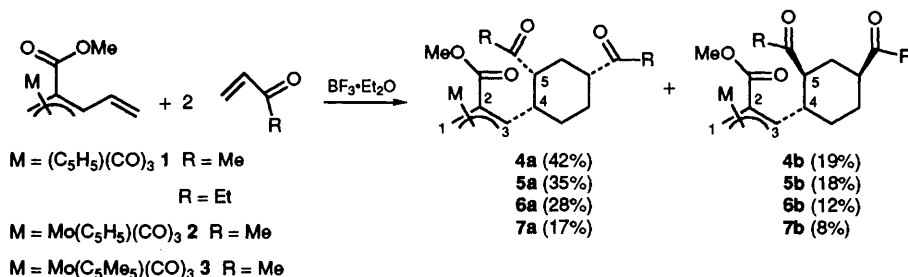


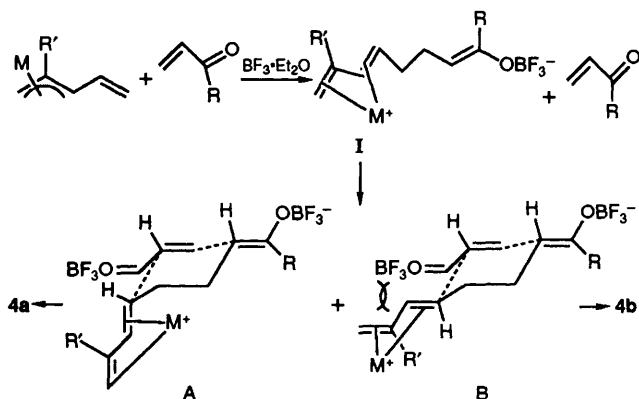
Fig. 2 ORTEP drawing of complex **4b**. Pertinent bond distances (\AA): W–C(3) 2.28(1), W–C(4) 2.27(1), W–C(5) 2.33(1), C(3)–C(4) 1.45(1), C(4)–C(5) 1.44(1), C(5)–C(6) 1.49(1).

[†] Crystal data: complex **4a** crystallizes in the monoclinic space group $P2_1/c$, $a = 10.4725(13)$, $b = 19.995(5)$, $c = 20.723(5)$ \AA , $\beta = 91.693(15)^\circ$, $V = 4337.4(15)$ \AA^3 , $Z = 8$. Each unit cell contains two independent molecules. Data were collected on an Enraf-Nonius CAD-4 diffractometer, using Mo-K α radiation. Final $R = 0.036$ and $R_w = 0.029$ for 3551 reflections ($I > 2\sigma(I)$) out of 5686 unique reflections.

[‡] Crystal data: complex **4b** crystallizes in the triclinic space group $P\bar{1}$, $a = 7.9186(16)$, $b = 11.2986(18)$, $c = 12.8863(20)$ \AA , $\alpha = 67.809(14)$, $\beta = 85.638(15)$, $\gamma = 81.669(15)^\circ$, $V = 1056.0(3)$ \AA^3 , $Z = 2$. Data were collected on an Enraf-Nonius CAD-4 diffractometer, using Mo-K α radiation. Final $R = 0.036$ and $R_w = 0.038$ for 3405 reflections ($I > 2\sigma(I)$) out of 3711 unique reflections. Atomic coordinates, bond lengths and angles, and thermal parameters for both compounds have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



Scheme 1



Scheme 2 ($M = (C_5H_5)W(CO)_2$, $R' = CO_2Me$, $R = Me$; the R group of **A** was omitted for clarity)

slowly added methyl vinyl ketone in an equimolar proportion to an equimolar mixture of **1** and $BF_3 \cdot Et_2O$ in cold toluene which afforded only **4a** (47%) and **4b** (20%).[§] Attempts to quench the reaction by H_2O during its course still gave no sign of a 1:1 product.

The reactions above represent a novel acid-catalysed [2 + 2] cyclization of functionalized alkenes. Scheme 2 is our proposed mechanism which involves a metal η^4 -*s-trans*-diene cationic intermediate **I**,⁷ generated from the BF_3 -mediated addition of **1** to methyl vinyl ketone. We propose a near chair-like transition structure⁸ to account for the stereochemical outcome of the reaction. The states **A** and **B** represent the

[§] The yields were calculated based on the amount of methyl vinyl ketone.

two most likely transition-state structures that have the most bulky complexed $RCO(BF_3)$ groups situated at the equatorial sites to avoid 1,3-diaxial steric hindrance. A further comparison between the structures indicates that **A** is the preferable conformation because it avoids steric hindrance between two neighbouring equatorial substituents as in **B**. Herein, we do not preclude an alternative mechanism which involves a one-step uptake of the two molecules of methyl vinyl ketone by **1** to form an analogous closed transition-state.

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