

Formation of Molybdenum- η^4 -Trimethylenemethane Cations Through Carbon-Carbon Bond Formation

Gin-Ming Su,^a Gene-Hsian Lee,^b Shie-Ming Peng^b and Rai-Shung Liu*^a

^a Department of Chemistry, National Tsing Hua University, Hsinchu, 30043, Republic of China

^b Department of Chemistry, National Taiwan University, Taipei, 10764, Republic of China

In the presence of $\text{BF}_3 \cdot \text{Et}_2\text{O}$, the molybdenum- η^3 -allyl complex $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\{\eta^3\text{-anti-1-Me, 2-(CH}_2\text{=CPh)C}_3\text{H}_3\}]$ reacts with benzaldehyde, methyl vinyl ketone and acetone to give the corresponding η^4 -trimethylenemethane cations; the crystal structure of a pyran complex generated from such cations and of a related complex are reported.

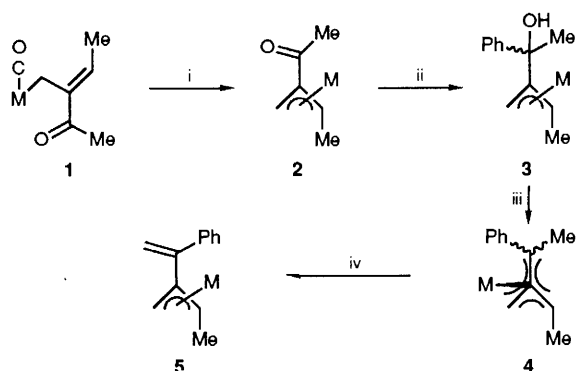
Although numerous transition metal- η^4 -trimethylenemethane compounds^{1,2} have been reported, only the (η^4 -trimethylene) PdL_2 system² has proved useful in organic synthesis. A general method for synthesis of these compounds involves the reaction between an unsaturated metal fragment and methylenecyclopropane¹ or $\text{CH}_2=\text{CCH}_2\text{XCH}_2\text{Y}$ ^{1,2} (X = Y = halide; X = halide, Y = Me_3Si). It is recognized that metal-mediated carbon-carbon bond formation is an important method in modern synthetic chemistry.³ Hence, we now report the generation of molybdenum- η^4 -trimethylenemethane cations⁴ through a carbon-carbon bond forming process.

Complex **2** is readily synthesized through Me_3NO -promoted decarbonylation of **1** under ambient conditions (CH_2Cl_2 , 23 °C, 6 h). The key compound **5** is produced from **2** via a sequence of reactions with an overall yield of 54% (Scheme 1). Complexes **3** and **4** were each obtained as a ca. 1 : 1 mixture of diastereoisomers.

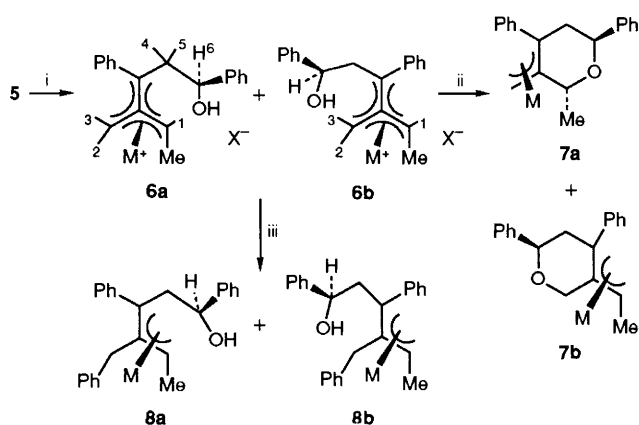
Treatment of **5** with PhCHO in benzene in the presence of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ immediately deposited a fine yellow precipitate which is a 2 : 3 mixture of the trimethylenemethane cations **6a** and **6b**. The salts were obtained in pure form and fully characterized by 2D NMR, IR and FAB mass spectrometry, and elemental analysis.[†] In the ¹H NMR spectra,[‡] the H¹

[†] Satisfactory analytical and/or spectroscopic data were obtained for all new compounds.

[‡] Selected spectroscopic data for **6a** and **6b**: IR(Nujol): **6a** + **6b**, $\nu(\text{CO})/\text{cm}^{-1}$ 2060s and 2011s. ¹H NMR (400 MHz, CD_3CN): **6a** δ 1.45 (d, 3H, Me), 2.41 (dd, 1H, H⁴), 2.96 (dd, 1H, H⁵), 3.42 (d, 1H, H²), 3.71 (d, 1H, H³), 3.87 (q, 1H, H¹), 4.31 (dd, 1H, H⁶), 5.70 (s, 5H, C_5H_5), 7.3–7.8 (m, 10H, Ph); $J_{1,\text{Me}}$ 6.5, $J_{2,3}$ 2.5, $J_{4,5}$ 12.8, $J_{4,6}$ 3.6 Hz; **6b** δ 1.87 (d, 3H, Me), 2.38 (dd, 1H, H⁴), 3.07 (dd, 1H, H⁵), 2.71 (d, 1H, H²), 3.22 (d, 1H, H³), 4.21 (q, 1H, H¹), 4.35 (dd, 1H, H⁶), 5.81 (s, 5H, C_5H_5), 7.3–7.8 (m, 10H, Ph); $J_{1,\text{Me}}$ 6.2, $J_{2,3}$ 3.4, $J_{4,5}$ 13.4, $J_{4,6}$ 3.6, $J_{5,6}$ 4.8 Hz. MS m/z (FAB): 483 (M – BF_4), 455 (M – BF_4 – CO).



Scheme 1 M = $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2$. Reagents and conditions: i, Me_3NO (3.0 equiv.), CH_2Cl_2 , 52%; ii, $\text{BF}_3\cdot\text{OEt}_2$ (1.2 equiv., Et_2O), PhLi (2.0 equiv.), 23 °C, 85%; iii, $\text{CF}_3\text{SO}_3\text{H}$ (1.2 equiv.), Et_2O , 86%; iv, $\text{LiN}(\text{SiMe}_3)_2$ (1.5 equiv.), Et_2O , 23 °C, 75%.



Scheme 2 M = $(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2$, X = BF_4^- . Reagents and conditions: i, $\text{BF}_3\cdot\text{OEt}_2$ (1.2 equiv.), PhCHO (1.2 equiv.), benzene, 23 °C, 85%; ii, NaH-THF (23 °C, 1 h), H_2O , 60%; iii, Ph_2CuLi (5.0 equiv., THF, -40 °C, 1 h), 72%.

proton resonance at δ 4.21 is assigned to **6b**, whereas the H¹ resonance at δ 3.87 is assigned to **6a**. The stereochemistry of **6a** and **6b** was deduced from the X-ray structures of the derivatives **7a** and **8b**, resulting from reactions ii and iii in Scheme 2. Treatment of the cations with NaH in tetrahydrofuran (THF), followed by hydrolysis, afforded a ca. 1:2 mixture of the pyrans **7a** and **7b** (60%) which were separated by preparative TLC. In the structure of **7a**,[¶] each unit cell contains two independent molecules which have different pyran conformations, *i.e.* boat and chair forms respectively.

§ The ¹H NMR assignments of **6a** and **6b** are made from comparison of the NMR data of **8a** with **8b** or **9a** with **9b**. The CHMe resonances of **8b** and **9b** are more downfield (δ 3.5–4.0) than those (δ 1.4–1.6) of **8a** and **9a**.

¶ Crystal data: **7a**: monoclinic, space group $P2_1/c$, $a = 19.510(5)$, $b = 10.2723(18)$, $c = 21.810(6)$ Å, $\beta = 93.58(3)^\circ$, $V = 4362.5(18)$ Å³, $Z = 8$. The unit cell contains two independent molecules. Final $R = 0.032$, $R_w = 0.037$ for 4371 reflections with $I > 2\sigma(I)$ out of 5675 unique reflections; 542 parameters.

Crystal data: **8b**: triclinic space group, $P\bar{1}$, $a = 10.579(3)$, $b = 11.588(2)$, $c = 13.105(6)$ Å, $\alpha = 111.95(3)$, $\beta = 100.60(3)$, $\gamma = 110.31(2)^\circ$, $V = 1303.3(7)$ Å³, $Z = 2$; final $R = 0.031$, $R_w = 0.039$ for 4246 reflections with $I > 2\sigma(I)$ out of 4576 unique reflections; 326 parameters.

For both structures, atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

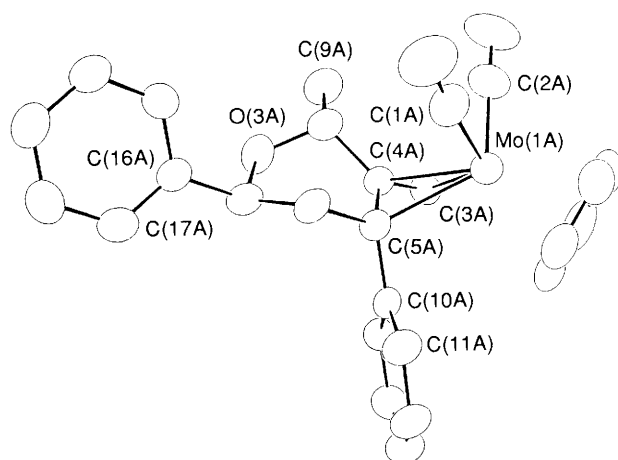


Fig. 1 ORTEP drawing of complex **7a** (boat form). Pertinent bond distances: Mo(1A)–C(3A) 2.299(4), Mo(1A)–C(4A) 2.303(4), Mo(1A)–C(5A) 2.418(4), C(3A)–C(4A) 1.394(6), C(4A)–C(5A) 1.425(6) Å.

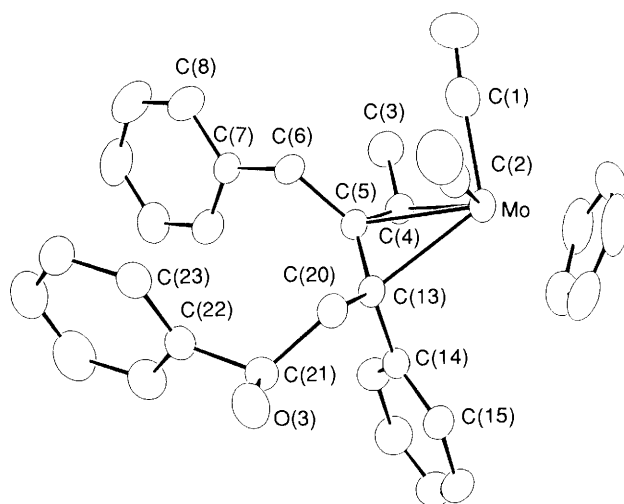
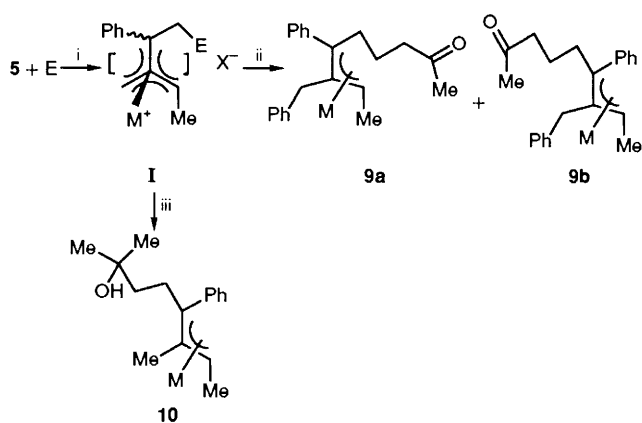


Fig. 2 ORTEP drawing of complex **8b**. Pertinent bond distances: Mo–C(4) 2.295(3), Mo–C(5) 2.330(3), Mo–C(13) 2.414(6) Å.

The ORTEP drawing of the boat conformation is given in Fig. 1. The formation of **7a** seems to involve the intramolecular attack of the CHPhO^- terminus at the CHMe carbon opposite the $(\text{C}_5\text{H}_5)\text{W}(\text{CO})_2$ fragment. Notably, the pyrans **7a** and **7b** represent examples of a novel $2\pi + 2\pi + 2\text{allyl}\pi$ cyclization of **5** and PhCHO . The cations are reactive towards Ph_2CuLi (THF, -40 °C) which added regioselectively at the CH_2 end to give **8a** and **8b** in a 2:3 ratio. The two diastereoisomers were separated by fractional crystallization. The X-ray structure[¶] of **8b** (Fig. 2) clarifies the stereochemistry of **6b**. It is evident that the two conformations of **5** are responsible for generation of the cations. Interestingly, each conformation reacts with PhCHO with preferred diastereofacial selectivity to give only one product.

A cationic precipitate was formed when **5** was treated with methyl vinyl ketone and acetone under similar conditions. Characterization of this cation **I** by NMR spectroscopy is hindered by severe contamination with **4**. The structure of the ion **I** was, however, confirmed by the isolation of **9a** and **9b** as a 3:4 mixture (42%) in a subsequent reaction with Ph_2CuLi . The mixtures were separated by preparative TLC. NaBH_3CN reduction of the cation generated from acetone gave **10** in 6% yield (Scheme 3).



Scheme 3 $M = (\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_2$, $X = \text{BF}_4$, $E = \text{CH}_2=\text{CHCOMe}$ or Me_2CO . Reagents and conditions: i, $\text{BF}_3 \cdot \text{OEt}_2$ (1.2 equiv., benzene, 23°C), electrophile (**E**, 1.2 equiv.); ii, $E = \text{CH}_2\text{CHC}=\text{OMe}$, Ph_2CuLi (5.0 equiv., -40°C , THF, 1 h), 42%; iii, $E = \text{acetone}$ (1.2 equiv.), NaBH_3CN (10 equiv., THF, -40°C , 1 h), 6%.

We are extending this new method for carbon–carbon bond formation to related molybdenum compounds. Our preliminary results⁶ indicate that the corresponding trimethylenemethane cation can be generated from aldehydes and

$[\text{Mo}(\text{C}_5\text{H}_5)(\text{CO})_2(\eta^3\text{-2-vinylallyl})]$.⁶ The fact that these cations are easily transformed to the synthetically valuable Mo– π -allyls^{7,8} by nucleophilic additions should make this reaction of much use in organic synthesis.

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