

# Unexpected regioselectivity in the coupling of $\pi$ -coordinated trityllallene with an amido ligand in molybdenum complex

Bor-Chen Huang, Ying-Chih Lin,\* Yi-Hong Liu and Yu Wang

Department of Chemistry, National Taiwan University Taipei, Taiwan 106, Republic of China. E-mail: yclin@mail.ch.ntu.edu.tw

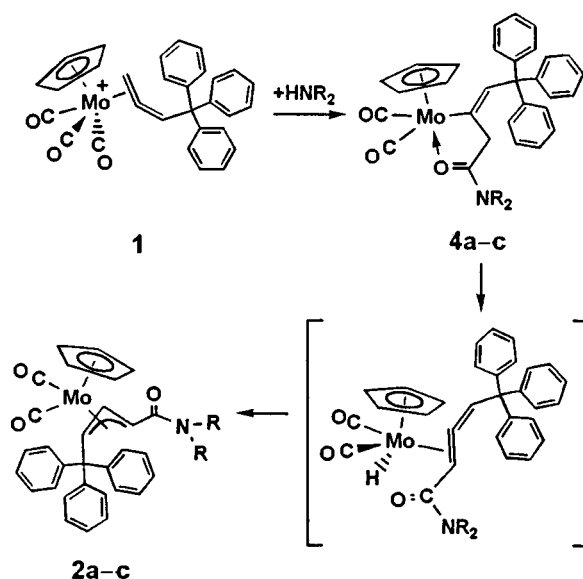
**Coupling of  $\pi$ -coordinated trityllallene with an amido ligand was unexpectedly found to take place at the terminal carbon in the reaction of  $[\text{Cp}(\text{CO})_3\text{Mo}(\eta^2\text{-CH}_2\text{=C=CHCPh}_3)][\text{BF}_4]$  **1**, with three secondary amines (dimethylamine, piperidine, morpholine).**

The synthesis and reactivity of organometallic complexes containing  $\eta^3$ -allyl,<sup>1</sup>  $\eta^1$ -allenyl<sup>2</sup> and  $\eta^1$ -propargyl<sup>3</sup> ligands have attracted a great deal of attention owing to their wide applications in organic synthesis. We recently reported distinctive regioselectivity of C–C bond formation in the reactions of tungsten allenyl and propargyl complexes. In the allenyl system,<sup>4</sup> reactions with amines and with alcohols afforded high yields of azametallacycles and oxametallacycles, respectively. The C–C bond formation takes place solely at  $\text{C}_\alpha$  of the allenyl ligand in both cases. By contrast, the corresponding propargyl complex afforded exclusively the  $\beta$ -coupled allylic complex, the latter regioselectivity was assumed to proceed via a  $\eta^2$ -allene intermediate.<sup>5</sup> In a particular system, the  $\eta^2$ -trityllallene complex  $[\text{Cp}(\text{CO})_3\text{M}(\eta^2\text{-CH}_2\text{=C=CHCPh}_3)]\text{-}[\text{BF}_4]$  ( $\text{M} = \text{Mo}$  **1**,  $\text{M} = \text{W}$  **1'**,  $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ) could be isolated and displays coupling reactivity with the expected regioselectivity in reactions with alcohols and some amines.<sup>6</sup> However, when we studied more reactions of **1** with amines, three amines were found to display different regioselectivity. Herein we report the unexpected regioselectivity in the reaction of **1** with these three amines, yielding the  $\alpha$ -amido substituted allylic complex as the major product and the  $\beta$ -amido allylic complex as the minor product.

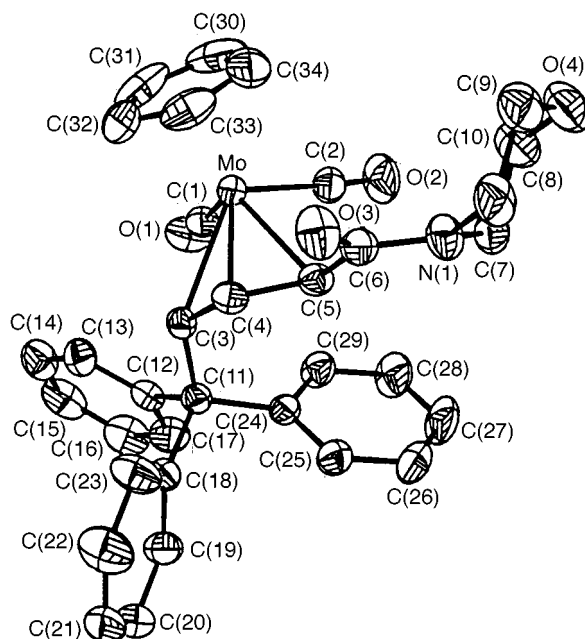
Reaction of **1** with neat piperidine at room temperature for 1 h afforded two amido-substituted allylic products. The major product  $\text{Cp}(\text{CO})_2\text{Mo}[\eta^3\text{-CH}(\text{CONC}_5\text{H}_{10})\text{CHCHCPh}_3]$  **2a**,† has a surprising  $\alpha$ -amido-substituted geometry, and the minor product  $\text{Cp}(\text{CO})_2\text{Mo}[\eta^3\text{-CH}_2\text{C}(\text{CONC}_5\text{H}_{10})\text{CHCHCPh}_3]$  **3a**, a normal  $\beta$ -amido-substituted geometry (Scheme 1). The two isomers can be separated by chromatography over silica gel. Complexes **2a** and **3a** were collected as orange–yellow and light-yellow microcrystalline powders upon re-crystallization from hexane– $\text{CH}_2\text{Cl}_2$  in ca. 65 and 17% yields, respectively. Similar results were found with morpholine and dimethylamine to yield the  $\alpha$ -amido-allylic complexes **2b**, **c**† respectively as the major product and the  $\beta$ -amido-allylic complexes **3b**, **c** as the minor product and an X-ray analysis was carried out on a crystal of **2b**.‡ An ORTEP drawing of **2b** is shown in Fig. 1. The most salient feature of the molecule is the presence of an amido-substituted trityllallyl ligand. The amido substituent is attached to the  $\alpha$ -carbon C(5) of the allyl ligand with a geometry *syn* to the central hydrogen and the trityl moiety is in an *anti* configuration.

Two possible mechanisms are proposed to account for the formation of **2a**. In both cases, it is necessary to consider nucleophilic attack of amine to the terminal carbonyl giving the amido ligand. Deprotonation<sup>7</sup> of the trityllallene ligand in the presence of amine may result in formation of an allenyl ligand and coupling of the amido ligand with the  $\alpha$ -carbon of the  $\sigma$ -allenyl followed by protonation would give the major product.<sup>8</sup> Alternatively, coupling of the amido group with allene leading to C–C bond formation may precede hydrogen

migration and the selectivity would be controlled by the presence of the trityl group. To better understand the detail and with the hope to see an intermediate the reaction was monitored



Scheme 1  $\text{HNR}_2$  = piperidine **a**, morpholine **b** or dimethylamine **c**



**Fig. 1** ORTEP drawing of **2b** with thermal ellipsoids shown at the 50% probability level. Selected bond distances (Å) and angles (°): Mo–C(3) 2.379(2), Mo–C(4) 2.212(2), Mo–C(5) 2.359(2), C(3)–C(4) 1.417(3), C(4)–C(5) 1.409(3), C(5)–C(6) 1.500(3), C(6)–N(1) 1.356(3), C(6)–O(3) 1.228(3); C(4)–C(3)–C(11) 125.1(2), C(4)–C(5)–C(6) 115.4(2), C(1)–Mo–C(2) 77.13(11).

spectroscopically. When the reaction was carried out at  $-60\text{ }^{\circ}\text{C}$ , an intermediate was indeed observed. Upon addition of piperidine at  $-60\text{ }^{\circ}\text{C}$ , the light yellow complex **1** dissolved and the solution turned deep red, to give a mixture of an unstable intermediate **4a** as well as **3a**. In the IR spectrum of the mixture the intermediate displays two peaks at  $1927$  and  $1828\text{ cm}^{-1}$  as well as one amido CO stretching absorption at  $1577\text{ cm}^{-1}$ . The latter suggested the presence of O-coordinated amido carbonyl.<sup>9</sup> Complex **4a**<sup>†</sup> transforms to **2a** in 1 h at room temperature but at lower temperature this process is slowed and the structure of **4a** can be assigned on the basis of the spectroscopic data of the mixture obtained at  $-60\text{ }^{\circ}\text{C}$ . In the  $^1\text{H}$  NMR spectrum, two doublet resonances at  $\delta 2.28$  and  $2.74$  with  $J_{\text{HH}}$   $22.4\text{ Hz}$  indicate the presence of a  $\text{CH}_2$  group while a singlet resonance at  $\delta 6.55$  is assigned to the  $=\text{CH}-$  group for **4a**. Two-dimensional HSQC<sup>10</sup> data confirms the  $\text{CH}_2$   $^{13}\text{C}$  resonance at  $\delta 47.2$  and  $^{13}\text{CH}$  group at  $\delta 147.5$ . In the HMBC<sup>11</sup> spectrum, the cross-peak between the  $\text{CH}_2$  ( $\delta_{\text{H}}$   $2.28, 2.74$ ) and the CON ( $\delta_{\text{C}}$   $180$ ) groups<sup>12</sup> indicate C–C bond formation at the terminal  $\text{CH}_2$  group. These observations imply that the intermediate could be a vinyl<sup>13</sup> complex, (Scheme 1) and the first mechanism is thus ruled out. Hydrogen migration of **4a** may proceed through  $\beta$ -elimination to give the metal hydride allene followed by coupling of the hydride at  $\text{C}_{\beta}$  of the allene to give the final product **2a**.

Reactions of **1** with other amines such as methylamine, ethylamine, propylamine, phenylamine, benzylamine, diethylamine, diisopropyl amine, di-*sec*-butylamine, diisobutyl amine and hydrazine gave only the  $\beta$ -coupled product. The  $pK_{\text{a}}$  values of the three unique amines ( $8.30$  for morpholine,  $10.90$  for  $\text{Me}_2\text{NH}$  and  $11.20$  for piperidine) giving the  $\alpha$ -coupled product are in the range of regular amines ( $4.69$  for aniline to  $11.1$  for diisopropyl amine) while no striking steric effect is seen for these three amines. While we cannot explain their different reactivity, this is the first case where coupling at the  $\alpha$ -position of a  $\eta^2$ -allene has been found. A detailed mechanism for this unusual coupling, the reactivity of compound **1** with other nucleophiles and the corresponding reaction for the tungsten system is currently under investigation.

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## Notes and References

<sup>†</sup> Selected spectroscopic data:  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR were recorded in  $\text{CDCl}_3$  relative to  $\text{SiMe}_4$  and IR in  $\text{CH}_2\text{Cl}_2$ . **2a**: IR,  $1954\text{s}$ ,  $1873\text{s}$ ,  $1605\text{m cm}^{-1}$ .  $^1\text{H}$  NMR,  $\delta 7.28\text{--}7.11$  (m, 15H, aromatic H),  $5.39$  (t,  $J_{\text{HH}}$   $10.0\text{ Hz}$ , 1H,  $\text{H}_{\text{centre}}$ ),  $5.28$  (5H, s, Cp),  $5.06$  (d,  $J_{\text{HH}}$   $10.0\text{ Hz}$ , 1H,  $\text{CH}_{\text{syn}}$ ),  $3.60, 3.24, 2.83$  (m, 4H,  $\text{H}_2\text{CNCH}_2$ ),  $1.52$  (m, 6H,  $\text{CH}_2\text{CNCH}_2\text{C}_3\text{H}_6$ ),  $0.99$  [1H, d,  $J_{\text{HH}}$   $10.0\text{ Hz}$ ,  $\text{HCC}(\text{O})\text{N}$ ].  $^{13}\text{C}\{^1\text{H}\}$  NMR,  $\delta 241.4, 238.4$  (CO),  $169.9$  (C=O),  $130.3, 127.2, 126.1$  (Ph),  $94.1$  (Cp),  $70.1$  ( $\text{CH}_{\text{centre}}$ ),  $68.6$  ( $\text{CH}_{\text{syn}}$ ),  $61.2$  ( $\text{CPh}_3$ ),  $50.2$  ( $\text{CH}_{\text{anti}}$ ),  $46.3, 43.3$  ( $\text{CH}_2\text{NC}_2\text{H}$ ),  $26.8, 25.7, 24.7$  ( $\text{NC}_2\text{H}_4\text{C}_3\text{H}_6$ ). FAB MS:  $m/z$   $614$  ( $\text{M}^+ + 1$ ),  $585$  ( $\text{M}^+ - \text{CO}$ ),  $557$  ( $\text{M}^+ - 2\text{CO}$ ). **2b**: IR (KBr),  $1937\text{s}$ ,  $1858\text{s}$ ,  $1623\text{m cm}^{-1}$ .  $^1\text{H}$  NMR,  $\delta 7.29\text{--}7.15$  (m, Ph),  $5.40$  (t,  $J_{\text{HH}}$   $10.2\text{ Hz}$ , 1H,  $\text{H}_{\text{centre}}$ ),  $5.29$  (s, 5H,  $\text{C}_5\text{H}_5$ ),  $5.07$  (d,  $J_{\text{HH}}$   $10.2\text{ Hz}$ , 1H,  $\text{H}_{\text{syn}}$ ),  $3.57\text{--}2.73$  (m, 8H,  $\text{NC}_4\text{H}_8\text{O}$ ),  $0.88$  (d,  $J_{\text{HH}}$   $10.2\text{ Hz}$ , 1H,  $\text{H}_{\text{anti}}$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR,  $\delta 241.6, 237.8$  (CO),  $170.5$  (C=O),  $130.3\text{--}126.1$  (Ph),  $94.2$  (Cp),  $69.9$  ( $\text{CH}_{\text{centre}}$ ),  $68.8$  ( $\text{CH}_{\text{syn}}$ ),  $66.9$  ( $\text{CH}_2\text{OCH}_2$ ),  $61.2$  ( $\text{CPh}_3$ ),  $49.0$  ( $\text{CH}_{\text{anti}}$ ),  $45.8, 42.5$  ( $\text{CH}_2\text{NC}_2\text{H}$ ). FAB MS:  $m/z$   $616$  ( $\text{M}^+ + 1$ ),  $587$  ( $\text{M}^+ - \text{CO}$ ),  $559$  ( $\text{M}^+ - 2\text{CO}$ ). **2c**: IR (KBr),  $1939\text{s}$ ,  $1855\text{s}$ ,  $1611\text{m cm}^{-1}$ .  $^1\text{H}$

NMR,  $\delta 7.28\text{--}7.15$  (m, Ph),  $5.36$  (t,  $J_{\text{HH}}$   $10.2\text{ Hz}$ , 1H,  $\text{H}_{\text{centre}}$ ),  $5.29$  (s, 5H,  $\text{C}_5\text{H}_5$ ),  $5.05$  (d,  $J_{\text{HH}}$   $10.2\text{ Hz}$ , 1H,  $\text{H}_{\text{syn}}$ ),  $2.81, 2.46$  (s, 2H,  $\text{NCH}_3$ ),  $1.12$  (d,  $J_{\text{HH}}$   $10.2\text{ Hz}$ , 1H,  $\text{H}_{\text{anti}}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR,  $\delta 241.8, 238.3$  (CO),  $171.8$  (C=O),  $130.3\text{--}126.2$  (Ph),  $94.2$  (Cp),  $70.3$  ( $\text{CH}_{\text{centre}}$ ),  $61.1$  ( $\text{CPh}_3$ ),  $50.8$  ( $\text{CH}_{\text{syn}}$ ),  $37.1, 36.1$  ( $\text{NCH}_3$ ). FAB MS:  $m/z$   $574$  ( $\text{M}^+ + 1$ ),  $545$  ( $\text{M}^+ - \text{CO}$ ),  $515$  ( $\text{M}^+ - 2\text{CO}$ ). **4a**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta 7.27\text{--}7.08$  (m, Ph),  $6.55$  (s, 1H,  $=\text{CH}$ ),  $5.33$  (s, 5H,  $\text{C}_5\text{H}_5$ ),  $2.74$  (d,  $J_{\text{HH}}$   $22.4\text{ Hz}$ , 1H,  $\text{CHH}$ ),  $2.28$  (d,  $J_{\text{HH}}$   $22.4\text{ Hz}$ , 1H,  $\text{CHH}$ ),  $3.26\text{--}2.66$  (m, 4H,  $\text{CH}_2\text{NCH}_2$ ),  $1.96$  (m, 6H,  $\text{CH}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2$ ).  $^{13}\text{C}$  NMR [ $(\text{CD}_3)_2\text{CO}$ ],  $\delta 180$  (CON),  $162.5$  (Mo–C),  $147.5$  ( $=\text{CH}-$ ),  $47.2$  ( $\text{CH}_2$ ).

<sup>‡</sup> Crystal data for **2b**:  $\text{C}_{34}\text{H}_{31}\text{O}_4\text{NMo}$ ,  $M = 613.54$ , monoclinic, space group  $P2_1/c$ ,  $a = 13.6809(4)$ ,  $b = 9.8539(3)$ ,  $c = 21.6322(7)\text{ \AA}$ ,  $\beta = 104.061(1)^\circ$ ,  $V = 2828.9(2)\text{ \AA}^3$ ,  $Z = 4$ ,  $D_{\text{c}} = 1.441\text{ g cm}^{-3}$ ,  $\mu = 5.03\text{ cm}^{-1}$ ,  $F(000) = 1264$ ,  $20\ 869$  reflections collected on Smart CCD [ $T = 295(2)\text{ K}$ ],  $6481$  independent reflections ( $R_{\text{int}} = 0.0436$ ) observed with  $I > 2\sigma(I)$ ,  $362$  parameters, no restraints. The final discrepancy indices  $R_1$  and  $wR_2$  were  $0.0357$  and  $0.0734$  respectively. CCDC  $182/980$ .

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