A Novel Tungsten-mediated Carbonylation Reaction *via* a Tandem 1,3-Metal Sigmatropic Shift through a σ-Hex-2-en-4-yn-1-yl Group

Liang Kwei-Wen,[a] Gene-Hsian Lee,[b] Shie-Ming Peng[b] and Rai-Shung Liu*[a]

[a] *Department of Chemistry, National Tsing Hua University, Hsinchu, 30043 Taiwan, Republic of China*
[b] *National Taiwan University, Taipei, 10764, Taiwan, Republic of China*

Stirring of a THF solution of [W(η-C_5H_5)(CO)$_3$(σ-*trans*-$CH_2CH{=}CHC{\equiv}CMe$)] with RXH (RXH = H_2O, MeOH, NH_2Bu^i) over silica or Florisil gel leads to a new carbonylation reaction to give [W(η-C_5H_5)(CO)$_2$(η^3-3-*syn*-RXCO-3-*anti*-Me-1-vinylallyl)] compounds in moderate yields, providing direct evidence for a tandem 1,3-metal shift across conjugated allyl and alkyne bonds.

Metal–σ-allyl,[1] σ-propynyl[2–4] and σ-allenyl[2–4] compounds are very useful in organic synthesis and their reactions with electrophiles are of extensive interest. One important feature of these compounds is the feasibility of a 1,3-metal sigmatropic shift (1) which has a significant influence on electrophilic regioselectivities.[1–4] Direct evidence of these 1,3-metal shifts has been well documented.[5,6] In a continuing effort to explore the synthetic utility of tungsten σ-propynyl compounds,[7] we report here a novel carbonylation reaction, the mechanism of which involves a tandem 1,3-shift of the W(η-C_5H_5)(CO)$_3$ fragment across conjugated allyl and alkyne bonds. Although zero-valent metals[8] M such as magnesium and zinc are known to react with $BrCH_2CH{=}CHC{\equiv}CH$ to give $CH_2{=}CHCH{=}C{=}CHMBr$, no corresponding σ-pent-2-en-4-yn-1-yl compounds have ever been isolated.

Treatment of 1-chlorohex-2-en-4-yne (*cis*:*trans* = 1:4) with Na[W(η-C_5H_5)(CO)$_3$] in THF (0 °C, 3 h) produces [W(η-C_5H_5)(CO)$_3$(σ-hex-2-en-4-yn-1-yl] **1** in 78% yield (*cis*:*trans* = 1:4) before column separation. Chromatographic elution of this isomeric mixture on a silica column [diethyl ether–hexane (1:4)] at 0 °C allows separation of the *cis*- and *trans*-isomers in 13 and 49% yields, respectively. Compound **1** retains the chemical reactivity expected for σ-allyl compounds as shown by the reaction of its *trans*-isomer with tetracyanoethylene to give the [3 + 2] cycloaddition adduct **2** in 67% yield, the molecular structure of which has been characterized by an X-ray diffraction study.†

We attempted to separate the *cis*/*trans* isomers of **1** using a conventional silica column at higher temperature (30 °C), but only the *cis*-isomer of **1** (11%) and a new compound **3** (38%) were obtained. This implies that **3** is produced from the *trans*-isomer of **1** on silica gel at higher temperatures. Relative to **1**, the NMR and IR spectra of **3** show the presence of vinyl, CO_2H and W(η-C_5H_5)(CO)$_2$(π-allyl) groups, indicative of structural rearrangement in the conversion of **1** to **3**. The structure of **3** has been determined by an X-ray diffraction study‡ and an ORTEP drawing is shown in Fig. 1. This structure of **3** may be envisaged by considering that one of the three carbonyls of its parent compound **1** has been attacked by water to give a W–CO_2H group, and subsequently added to the ≡*C*–Me atom of the ligand; the remaining W(η-C_5H_5)(CO)$_2$ fragment is linked to the acyclic organic moiety by π-allyl bonding with the CO_2H and $CH{=}CH_2$ groups in *syn*-position, and the methyl group in *anti*-position.

Scheme 2 shows the proposed mechanism of formation of **3** involving a double 1,3-metal migration of W(η-C_5H_5)(CO)$_3$ across the enyne ligand to form the intermediate **B** and then **C**. Further CO insertion into the W–σ-allenyl bond of the vinylallen-1-yl intermediate **C**, followed by attack of water is expected to give the carbonylation product **3**. In earlier reports, [W(η-C_5H_5)(CO)$_3$(σ-allen-1-yl)] reacted with water and alcohols to give [W(η-C_5H_5)(CO)$_2$(η^3-1-O_2C-allyl)][9] (R = H, Me) whereas [W(η-C_5H_5)(CO)$_3$(σ-$CH_2C{\equiv}CH$)] reacted with H_2O and MeOH to afford [W(η-C_5H_5)(CO)$_2$(η^3-O_2CCR-allyl)][9,10] (R = H, Me). These reports support the involvement of intermediate **C** but not **B** since no η^3-2-carboxylated allyl is isolated in our case.

We have found alternative reaction conditions for the carbonylation of **1** with water, methanol and isobutylamine. A typical reaction involves the stirring of a THF solution of the *trans*-isomer of **1** with excess water, methanol or isobutylamine over predried Florisil gel (250 °C, 12 h, 10^{-4} Torr) at 30 °C for 4–5 h, which afforded η^3-1-carboxylated allyl compounds **3**, **4** and **5** in 52, 38 and 23% yields, respectively. Spectroscopic data for **4** and **5** are fully consistent with the attributed

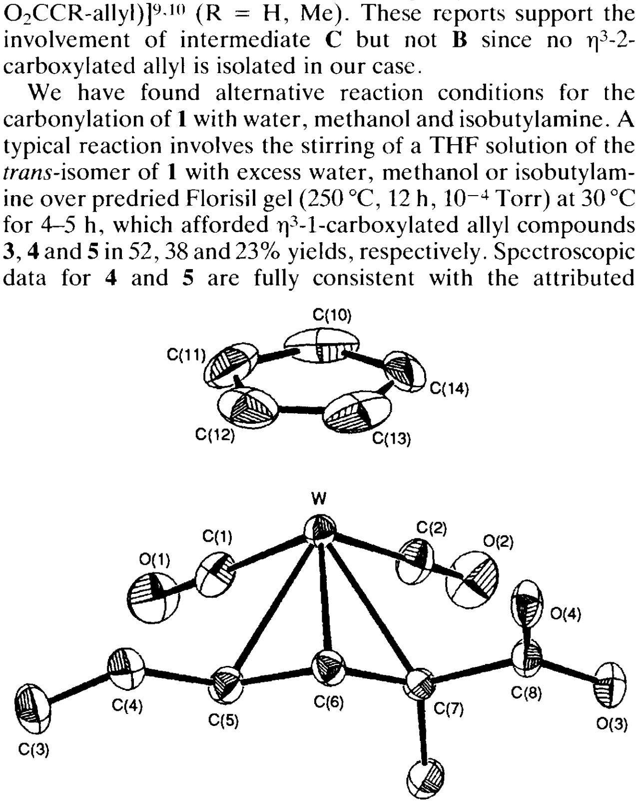
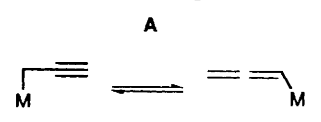
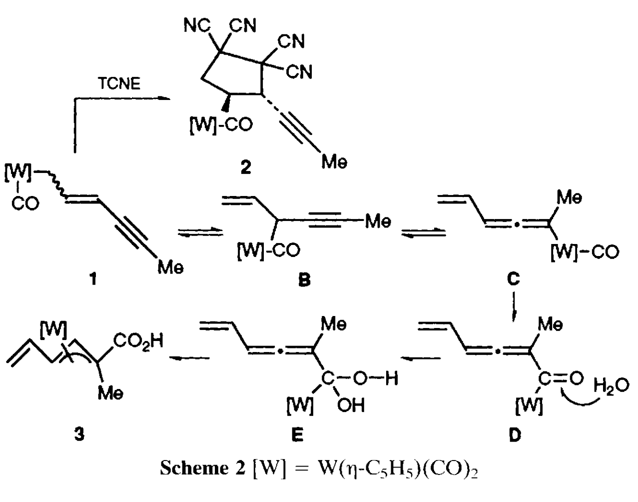


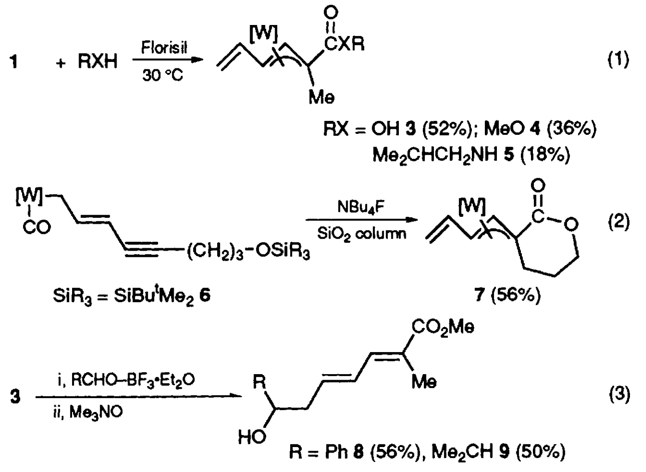
Fig. 1 Molecular structure of **3**



Scheme 1



Scheme 2 [W] = W(η-C_5H_5)(CO)$_2$



Scheme 3 [W] = $W(\eta\text{-}C_5H_5)(CO)_2$

structure. Intramolecular carbonylation *via* this double metal 1,3-shift is also feasible as depicted in Scheme 3 [eqn. (2)]. Desilylation of the σ-*trans*-allyl compound **6** with NBu_4F (2.0 equiv.) in THF (0 °C, 2 h), followed by elution through a silica column (30 °C, 2 h) delivered **7** in 56% yield. The η^3-lactone structure of **7** was confirmed by an X-ray diffraction study.§ Similar to **1**, the desilylated *cis*-isomer of **6** failed to undergo intramolecular cyclization under similar reaction conditions, and was recovered exclusively (*ca.* 58%).

To demonstrate the synthetic utility of this reaction, compound **4** was treated with aldehydes RCHO (R=Ph, Me_2CH) in cold diethyl ether (−40 °C) to yield insoluble η^4-diene precipitates.[11] Further demetallation of this precipitate by Me_3NO (23 °C, 20 h) provided **8** and **9** in 56 and 50% yields respectively.

The *cis*-isomers of **1** and **6** were inactive in the carbonylation reactions. According to theoretical studies,[12] the initial 1,3-metal allyl shift involves a π-allyl-like transition state **A** (Scheme 1), and the inactivity of the *cis*-isomer is attributed to the strong steric interaction between the $W(\eta\text{-}C_5H_5)(CO)_3$ and *anti*-R [R = Me, $(CH_2)_3OSiR_3$] groups of this π-allyl transition state.

Received, 26th September 1994; Com. 4/05880A

Footnotes

† Compound **2** crystallizes in the orthorhombic space group *Pbca*, $a = 8.066(5)$, $b = 25.917(6)$, $c = 18.618(4)$ Å, $V = 3892(3)$, $Z = 8$. Data were collected on an Enraf-Nonius CAD-4 diffractometer, using Mo-Kα radiation. Final $R = 0.032$ and $R_w = 0.020$ for 1728 reflections with $I > 2\sigma(I)$ out of 2541 unique reflections.

‡ Compound **3** crystallizes in the monoclinic space group $P2_1/n$, $a = 7.759(3)$, $b = 14.201(5)$, $c = 12.638(3)$ Å, $\beta = 101.074(24)°$, $V = 1366.5(8)$ Å^3, $Z = 4$. Data were collected on an Enraf-Nonius CAD-4 diffractometer, using Mo-Kα-radiation. Final $R = 0.032$ and $R_w = 0.036$ for 2087 reflections with $I > 2\sigma(I)$ out of 2390 unique reflections.

§ Compound **7** crystallizes in the orthorhombic space group $P2_12_12_1$, $a = 6.830(4)$, $b = 11.862(4)$, $c = 18.112(3)$ Å, $V = 1468.1(12)$ Å^3, $Z = 4$. Data were collected on an Enraf-Nonius CAD-4 diffractometer, using Mo-Kα radiation. Final $R = 0.032$ and $R_w = 0.032$ for 1333 reflections with $I > 2\sigma(I)$ out of 1503 unique reflections.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

References

1 For chemistry and application of metal–allyl compounds, see Y. Yamamoto and N. Asao, *Chem. Rev.*, 1993, **93**, 2207.

2 D. Seyferth, D. Y. Son and S. Shah, *Organometallics*, 1994, **13**, 2105, and references therein.

3 R. L. Danheiser and D. J. Carini, *J. Org. Chem.*, 1980, **45**, 3925; R. L. Danheiser, E. J. Stoner, H. Koyama, D. S. Yamashita and C. A. Clady, *J. Am. Chem. Soc.*, 1989, **111**, 4407.

4 J. A. Marshall and X.-J. Wang, *J. Org. Chem.*, 1991, **56**, 3212; J. A. Marshall and X.-J. Wang, *J. Org. Chem.*, 1991, **56**, 6264.

5 I. D. Gridnev, M. E. Gurskii, A. V. Ignatenko and Y. N. Bubnov, *Organometallics*, 1993, **12**, 2487.

6 R.-S. Keng and Y.-C. Lin, *Organometallics*, 1990, **9**, 289; J. Pu, T. S. Peng, A. M. Arif and J. A. Gladysz, *Organometallics*, 1992, **11**, 3232.

7 S.-H. Wang, L.-H. Shu, H.-G. Shu, Y.-L. Yao, S.-L. Wang, G.-H. Lee, S.-M. Peng and R.-S. Liu, *J. Am. Chem. Soc.*, 1994, **116**, 5967.

8 F. Gerard and P. Miginiac, *J. Organomet. Chem.*, 1978, **155**, 271; J. P. Dulcere, J. Gore and M. L. Roumestant, *Bull. Soc. Chim. Fr.*, 1974, 1119.

9 T.-W. Tseng, I.-Y. Wu, Y.-C. Lin, C.-T. Chen, M.-C. Chen, Y.-J. Tsai, M.-C. Chen and Y. Wang, *Organometallics*, 1991, **10**, 43; M.-H. Cheng, Y.-H. Ho, G.-H. Lee, S.-M. Peng and R.-S. Liu, *J. Chem. Soc., Chem. Commun.*, 1991, 697.

10 J. Collin, C. Charrier, M. J. Pouet, P. Cadiot and J. L. Roustan, *J. Organomet. Chem.*, 1979, **168**, 321; J. L. Roustan, J. Y. Merour, C. Charrier, J. Benaim and P. Cadiot, *J. Organomet. Chem.*, 1979, **169**, 39; C. Charrier, J. Collin, J. Y. Merour and J. L. Roustan, *J. Organomet. Chem.*, 1978, **162**, 57.

11 S.-H. Lin, Y.-J. Yang and R.-S. Liu, *J. Chem. Soc., Chem. Commun.*, 1991, 1004.

12 T. Clark, C. Rohde and P. v. R. Schleyer, *Organometallics*, 1983, **2**, 1344; M. Buhl, P. V. R. Schleyer, M. A. Ibrahim and T. Clark, *J. Am. Chem. Soc.*, 1991, **113**, 2466.