Tetramerization of Alkynes on a Tungsten(0) Centre to Form a Cyclopentadienylvinylcarbene Complex; Crystal Structure of [W(CO)(PhC≡CPh){η5-C3Ph3(C5Ph5)}]

Wen-Yann Yeh,*[a] Shie-Ming Peng[b] and Gene-Hsiang Lee[b]

[a] Department of Chemistry, National Sun Yat-Sen University, Kaohsiung, Taiwan 80424, Republic of China
[b] Department of Chemistry, National Taiwan University, Taipei, Taiwan 10764, Republic of China

Heating [W(CO)3(MeCN)3] or [W(CO)(PhC≡CPh)3] with an excess of diphenylacetylene produces [W(CO)(PhC≡CPh){η5-C3Ph3(C5Ph5)}], which contains a novel cyclopentadienylvinylcarbene group through coupling of four alkyne ligands on the tungsten(0) centre.

One of the most fascinating aspects pertaining to organo-metallic chemistry concerns the cyclooligomerization of alkynes.[1] It has been shown that reactions of alkynes with transition metal compounds can lead to di-, tri- or tetra-merization of the alkyne ligands, and in doing so lose their individuality, forming metallacyclic systems or carbocycles.[2] Nevertheless, an isolable metal complex, which would confirm the linking of acetylene units, is not formed in all cases. We previously described[3] an alkyne–alkyne coupling reaction with [W(L)(PhC≡CPh)3], where L = CO or MeCN, to yield cyclobutadiene complexes, [W(L)(PhC≡CPh)2(η4-C4Ph4]. Now we report that reaction of [W(CO)3(MeCN)3] or [W(CO)(PhC≡CPh)3] with an excess of diphenylacetylene forms a novel η5-cyclopentadienylvinylcarbene complex

[W(CO)(PhC≡CPh){η5-C3Ph3(C5Ph5)}]. This result is in contrast to previous studies, where tetramerization of alkynes leads mainly to cyclooctatetraene derivatives.[2]

Typically, [W(CO)(PhC≡CPh)3][4] (500 mg, 0.67 mmol) or [W(CO)3(MeCN)3] (250 mg, 0.64 mmol) and an excess amount of diphenylacetylene (1.2 g, 10 equiv.) were sealed in a glass tube under vacuum and heated to 130 °C for 20 min. The mixture was then separated by TLC (silica gel), eluting with dichloromethane–hexane (1:4 v/v). The known [W(CO)(PhC≡CPh)2(η4-C4Ph4)] (40%) was isolated from the orange band. Crystallization of the materials forming the red band from dichloromethane–methanol yielded air-stable,
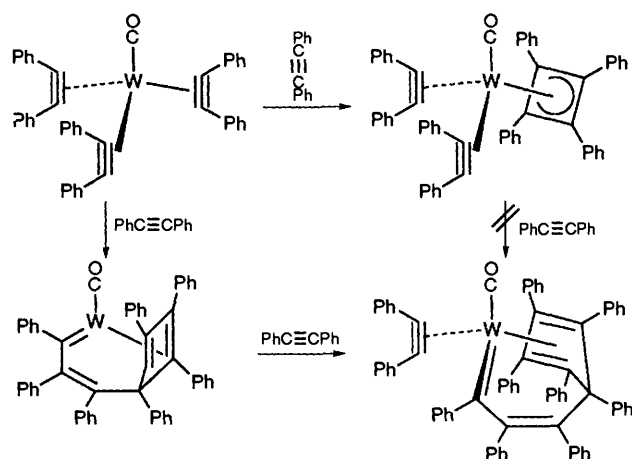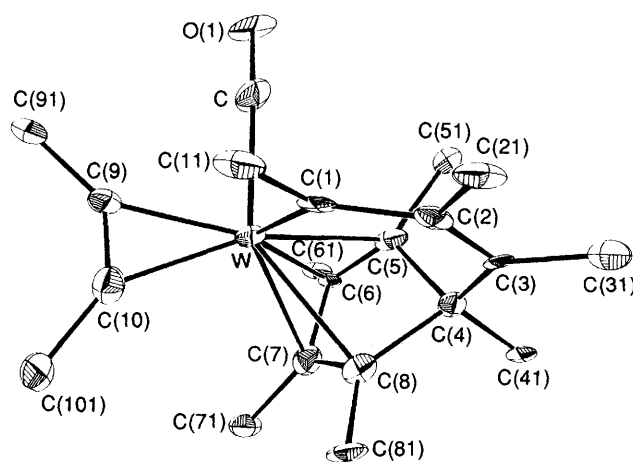

Scheme 1

Fig. 1 Molecular structure of [W(CO)(PhC≡CPh){(η5-C3Ph3-(C5Ph5)}] showing the atomic labelling scheme used in the text. The Ph rings have been omitted for clarity.

dark-red crystals of [W(CO)(PhC≡CPh){η⁵-C₃Ph₃(C₅Ph₅)}] (14%),† whereas, only low yields of [W(CO)(PhC≡CPh){η⁵-C₃Ph₃(C₅Ph₅)}] (<2%) were obtained in refluxing toluene or xylene solution.

The molecular structure of [W(CO)(PhC≡CPh){η⁵-C₃Ph₃(C₅Ph₅)}]‡ is illustrated in Fig. 1. The carbonyl groups is terminally bonded to the tungsten atom with W–C 2.13(2), C–O(1) 1.06(2) Å and ∠W–C–O(1) 178(2)°. The diphenyl-acetylene ligand is eclipsed but slightly tilted (4.6°) with respect to the WCO group. The W–C(9), W–C(10) and C(9)–C(10) distances are 2.06(2), 2.09(2) and 1.22(3) Å, respectively, and the phenyl groups are bent away back from the C≡C axis by angles averaging 138°. The η⁵-C₃Ph₃(C₅Ph₅) group appears to have a tungsten–carbon double bond to C(1) [2.01(2) Å]. The butadiene fragment [C(5) to C(8)] is planar and bonded to the tungsten atom asymmetrically, such that W–C(5) 2.22(2) and W–C(6) 2.23(1) Å are significantly shorter than W–C(7) 2.30(2) and W–C(8) 2.41(2) Å. The geometry of cyclopentadiene ring appears as an opened envelope with the C(4) atom being bent away from the diene plane by angle of 32(1)°. The alkene fragment [C(1) to C(4)] is coplanar to within ±0.03(2) Å, and the dihedral angle between the alkene and the diene planes is 92.8(8)°. The remaining bond lengths and angles around the C₃Ph₃(C₅Ph₅) skeleton are illustrated in Fig. 2.

Formation of a W=C double bond is further evidenced by ¹³C NMR, which shows a low field signal at δ 300.8 characteristic of an alkylidene type carbon.⁵ Since the terminal CO and the η⁵-C₃Ph₃(C₅Ph₅) ligand can be considered as a two- and six-electron donor, respectively, the remaining alkyne ligand must supply four electrons, presumably from the π∥ and π⊥ orbitals,⁶ to the neutral tungsten atom to satisfy the 18-electron rule.⁷ The results are reflected in the ¹³C NMR shifts, which give rise to two resonances at δ 197.4 and 190.0 characteristic of four-electron donor alkyne ligands.⁸

As treating [W(CO)(PhC≡CPh)₂(η⁴-C₄Ph₄)] with diphenyl-acetylene does not give [W(CO)(PhC≡CPh){η⁵-C₃Ph₃-(C₅Ph₅)}], the two compounds are obviously formed by separate routes. Based on the molecular structure of [W(CO)(PhC≡CPh)₃] in which the three alkyne C≡C axes are parallel to the W–CO group, two pathways can be envisaged in response to the observed products (Scheme 1). Presumably, if the C≡C axis of the incoming diphenylacetylene is parallel to the coordinated PhC≡CPh ligands, then dimeriza-
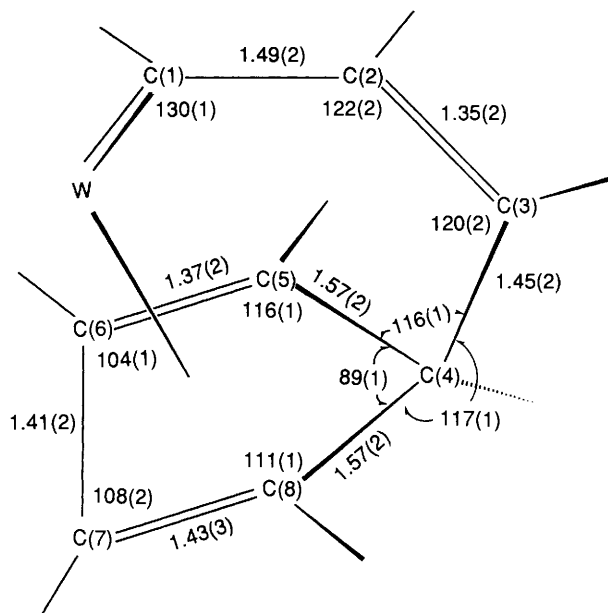
Fig. 2 Bond distances (Å) and bond angles (°) around the [η⁵-C₃Ph₃(C₅Ph₅)] skeleton

tion of the alkynes would give the cyclobutadiene species. On the other hand, the added diphenylacetylene in the perpendicular position could bridge the three-coordianted alkyne ligands which would then couple to form the substituted cyclopentadiene moiety. However, it remains uncertain whether stepwise coupling occurs after all four are linked, or, alternatively, completely concerted bond formation precedes about the metal atom; the details are currently under investigation.

References

1 N. E. Schore, *Chem. Rev.*, 1988, **88**, 1081; P. M. Maitlis, *Acc. Chem. Res.*, 1976, **9**, 93; T. Masuda and T. Higashimura, *Acc. Chem. Res.*, 1984, **11**, 51; K. P. C. Vollhardt, *Acc. Chem. Res.*, 1977, **10**, 1.

2 J. P. Collman, L. S. Hegedus, J. R. Norton and R. G. Finke, *Principles and Applications of Organotransition Metal Chemistry*, University Science Books, Mill Valley, CA, 1987; P. W. Jolly, in *Comprehensive Organometallic Chemistry*, ed. G. Wilkinson, F. G. A. Stone and E. W. Abel, Pergamon, Oxford, 1982, vol. 8, p. 649; W. Keim, A. Behr and M. Röper in *Comprehensive Organometallic Chemistry*, ed. G. Wilkinson, F. G. A. Stone and W. Abel, Pergamon, Oxford, 1982, vol. 8, p. 371; H. Reinheimer, J. Moffat and P. M. Maitlis, *J. Am. Chem. Soc.*, 1970, **92**, 2285; J. Okuda, K. H. Zimmerman and E. Herdtweck, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 430.

3 W.-Y. Yeh and L.-K. Liu, *J. Am. Chem. Soc.*, 1992, **114**, 2267.

4 R. M. Lane, R. E. Moriarty and R. Bau, *J. Am. Chem. Soc.*, 1972, **94**, 1402; D. P. Tate and J. M. Augl, *J. Am. Chem. Soc.*, 1963, **85**, 2174; D. P. Tate, J. M. Augl, W. M. Ritchey, B. L. Rose and J. G. Grasselli, *J. Am. Chem. Soc.*, 1964, **86**, 3261.

5 B. E. Mann and B. F. Taylor, *¹³C NMR Data for Organometallic Compounds*, Academic Press, New York, 1981.

6 D. J. Wink and T. Greagan, *Organometallics*, 1990, **9**, 328, and references therein.

7 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Wiley, New York, 5th edn., 1988; R. B. King, *Inorg. Chem.*, 1968, **7**, 1044.

8 M. H. Chisholm, H. C. Clark, L. E. Manzer and J. B. Stothers, *J. Am. Chem. Soc.*, 1972, **94**, 5087; J. L. Templeton and B. C. Ward, *J. Am. Chem. Soc.*, 1980, **102**, 3288; J. L. Templeton, *Adv. Organomet. Chem.*, 1989, **29**, 1, and references therein.