ELSEVIER

Journal of Organometallic Chemistry 548 (1997) 191–194

Journal of Organometallic Chemistry

Mechanistic information of substitution reaction of $W(PhC{\equiv}CPh)_3(CO)$ with trimethylphosphine

Wenn-Yann Yeh *, Shu-Min Chien

Department of Chemistry National, Sun Yat-Sen University, Kaohsiung 80424, Taiwan

Received 30 April 1997; received in revised form 1 July 1997

Abstract

Substitution reaction of $W(PhC{\equiv}CPh)_3(CO)$ (**1**) with PMe_3 to give $W(PhC{\equiv}CPh)_3(PMe_3)$ (**2**) has been studied by IR and NMR spectroscopy as well as cross-over experiments. A metastable intermediate $W(CO)(PhC{\equiv}CPh)_2(PMe_3)_2$ (**3**) is produced by adding two PMe_3 moieties into **1** accompanied with loss of a PhC≡CPh ligand. Subsequent conversion from **3** to **2** might involve decarbonylation and PMe_3/PhC≡CPh exchange. © 1997 Elsevier Science S.A.

Keywords: Trimethylphosphine; Spectroscopy; Ligand

Tetrahedral tris(alkyne) complexes of the type $W(RC{\equiv}CR')_3(CO)$ [1–7] have played an important role in developing the chemistry of alkynes to act as two- and four-electron donors [8–12]. In addition, the alkyne ligands themselves can undergo interesting coupling reactions, leading to carbocyclic and metallacyclic complexes [13–19]. The analogous complexes $W(RC{\equiv}CR')_3$(phosphine) can be prepared by treating $W(RC{\equiv}CR')_3(CO)$ with phosphine substrates [20–24]. Since the alkyne moieties are retained, this substitution reaction appears to proceed via either dissociation of the carbonyl ligand before phosphine being incorporated (S_N1), or association of phosphine following by decarbonylation (S_N2) [25]. However, our study on the reaction of $W(PhC{\equiv}CPh)_3(CO)$ (**1**) [1,2] and PMe_3 reveals a multistep pathway, in which reversible dissociation–association of the alkyne and phosphine ligands are also involved.

PMe_3 (2.2 equiv.) was introduced into a dichloromethane solution of **1** at −78°C under N_2. The mixture was slowly warmed up to ambient temperature, leading to a color change from pale-yellow to deep red. The solution color faded away after 24 h, and $W(PhC{\equiv}CPh)_3(PMe_3)$ (**2**) [24] was obtained in 74% yield. Since compound **2** is colorless, the intense red color apparently arises from the reaction intermediates.

One species, formulated as $W(PhC{\equiv}CPh)_2(CO)(PMe_3)_2$ (**3**) [1], is discovered during the reaction, but attempts to isolate **3** in pure form have led to the mixture of **2** and **3**. The $^{31}P\{^1H\}$ NMR spectrum recorded after combining **1** and PMe_3 in CD_2Cl_2 displays a singlet at −5.0 ppm ($^1J(W-P) = 140$ Hz) for **2** and a singlet at −30.2 ppm ($^1J(W-P) = 262$ Hz) for **3** in an approximate 1:1.5 ratio. The IR spectrum of the red solution shows that the CO stretching band for **1** at 2062 cm^{-1} disappears and a new band at 1907 cm^{-1} for **3** grows up. The $^{13}C\{^1H\}$ NMR spectrum of **3** at 213 K (Fig. 1) presents a carbonyl resonance at 246.4 ppm with ^{183}W satellites ($^1J(W-C) = 136$ Hz), indicating that the CO group is still coordinated to the tungsten atom. The four alkyne≡C carbons give rise to a single resonance at 195.2 ppm, which is between those mea-

[1] Compound **3**: IR (CH_2Cl_2): 1907 (νCO) cm^{-1}. ^1H NMR (CD_2Cl_2, 20°C): 7.59–7.10 (m, Ph), 0.85 (t, PMe_3) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 20°C): −30.2 (s; with ^{183}W satellites, $^1J(W-P) = 262$ Hz) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −105°C): 246.6 (s, CO; with ^{183}W satellites, $^1J(W-C) = 136$ Hz), 197.2, 191.3, 173.6 (s, ≡C), 142.1–122.2 (Ph), 18.8 (t, PCH3) ppm.

* Corresponding author.

PII S0022-328X(97)00418-X

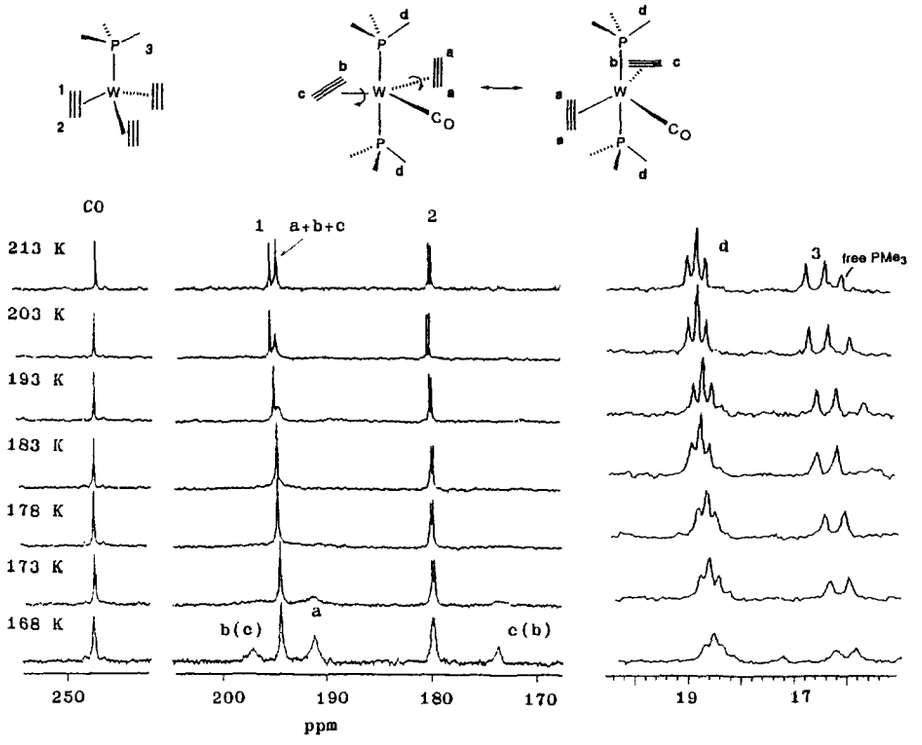


Fig. 1. 75.4 MHz variable-temperature $^{13}C\{^1H\}$ NMR spectra of $W(Ph^*C{\equiv}CPh)_3(PMe_3$ (**2***) and $W(Ph^*C{\equiv}CPh)_2(^*CO)(PMe_3)_2$ (**3***) in CD_2Cl_2. The resonances of CH_3 groups have been magnified for clarity.

sured for four-electron donor (ca. 220 ppm) and two-electron donor (ca. 120 ppm) alkyne ligand [8,26]. The triplet signal at 18.8 ppm for the methyl carbons indicates trans geometry for the two PMe_3 ligands. This pattern is attributed to virtual coupling [25,27] when the methyl group is coupled to both its own and the trans phosphorus nuclear about equally, giving rise to a virtual triplet. The ^1H NMR spectrum of **3** also presents a triplet signal at 0.85 ppm for the methyl protons, and its appearance is invariant with field (200 and 300 MHz).

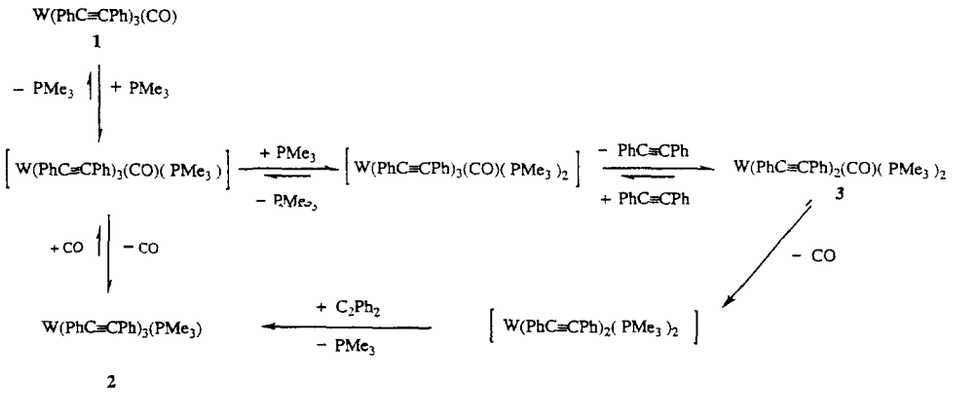
The variable-temperature $^{13}C\{^1H\}$ NMR spectra of a mixture containing $W(Ph^*C{\equiv}CPh)_3(PMe_3)$ (**2***) and $W(Ph^*C{\equiv}CPh)_2(^*CO)(PMe_3)_2$ (**3***) (the star indicating ca. 20% ^{13}C enrichment) in CD_2Cl_2 are displayed in Fig. 1. The resonances for **2*** at 196.3, 179.6 (≡C), and 16.3 (CH_3) ppm remain unchanged at low temperatures. In contrast, the alkyne C≡C resonance of **3*** collapses at 183 K and splits into a 1:2:1 pattern at 197.2, 191.3, and 173.6 ppm below 168 K. It is probable the two alkyne ligands are mutually orthogonal, with one C≡C moiety parallel and the other C≡C moiety perpendicular to the W–P vector, and a dynamic process by rotating the W–alkyne bonds could equilibrate the two C≡C units. Since CO and PMe_3 are two-electron donor, the two alkynes must supply six electrons to satisfy the 18-electron rule. A semi-empirical MO calculation (PM3) [2] based on the proposed structure suggests that the parallel alkyne donates four electrons ($\pi_{\parallel} + \pi_{\perp}$) and the perpendicular alkyne donates two electrons ($\pi_{\parallel}$) to the tungsten atom.

The decay of the CO stretching peak of **1** in IR is found to follow first order kinetics with the concentration of PMe_3. [3] The presence of extra diphenylacetylene does not affect the disappearing rate of **1**, but does inhibit the formation of **3**. Introduction of PMe_2Ph (1 equiv.) into the solution containing **2** and **3** also affords $W(PhC{\equiv}CPh)_3(PMe_2Ph)$ [21] in 10% yield. Furthermore, treating **1** with PMe_3 in the presence of TolC≡CTol leads to mixed products $W(PhC{\equiv}CPh)_{3-n}(TolC{\equiv}CTol)_n(PMe_3)$ (n = 0–3). [4]

[2] MacSPARTAN Plus, Wave function, Inc., Irvine, CA, USA.

[3] The reaction was followed by intermittently withdrawing samples with a hypodermic syringe and monitoring the infrared spectra in the ν(CO) region. The concentration of **1** was determined by measuring the height of the band at 2062 cm^{-1} recorded in absorbance units.

[4] These compounds are not separable by TLC. The mass spectrum of the mixture shows the molecular ions at m/z 878, 850, 822 and 794 (^{184}W) for each components. The $^{31}P\{^1H\}$ NMR spectrum gives four signals for the PMe_3 resonances. The ^1H NMR spectrum displays four doublet signals for the PMe_3 groups and two broad signals for the methyl groups of ditolylacetylene.



Scheme 1.

These require reversible dissociation–association of the alkyne and phosphine ligands to occur during the reaction. Attempts to reform **1** by bubbling CO through a toluene solution of **2** at 100°C give no reaction. Only under harsh conditions (2 atm CO, 120°C, 48 h), **1** is obtained in 6% yield accompanied with considerable decomposition.

A reaction sequence can be drawn (Scheme 1) to rationalize the observations. The kinetic and spectra data have precluded the mechanism of initial CO dissociation. Thus, PMe_3 is incorporated to **1** to produce $W(PhC{\equiv}CPh)_3(CO)(PMe_3)$, which may undergo decarbonylation to account for immediate formation of **2**, or undergo further addition with PMe_3 to yield $W(PhC{\equiv}CPh)_3(CO)(PMe_3)_2$. Since octahedral d^6 metal complexes have no vacant d_π orbitals, a repulsive interaction between the metal filled d_π orbitals and the alkyne $\pi_\perp$ orbitals is anticipated [28]. Elimination of an alkyne ligand from $W(PhC{\equiv}CPh)_3(CO)(PMe_3)_2$ is therefore accessible to provide a vacant metal orbital mate for the filled $\pi_\perp$ alkyne orbitals, forming $W(PhC{\equiv}CPh)_2(CO)(PMe_3)_2$ (**3**). Indeed, free PhC≡CPh is detected by ^{13}C NMR (89.1 ppm), which vanishes when the reaction is completed. It appears that conversion between $W(PhC{\equiv}CPh)_3(CO)(PMe_3)$ and **3** is reversible to meet the crossover results. Subsequent transformation from **3** to **2** apparently follows the reversal pathway. It is also possible that **3** carries out decarbonylation to generate $W(PhC{\equiv}CPh)_2(PMe_3)_2$, and PMe_3/PhC≡CPh exchange to yield **2**. Connor and Hudson [29] has previously reported the reaction of $W(MeSC{\equiv}CSMe)_3(CO)$ with $Me_2PC_2H_4PMe_2$ (dmpe) to produce $W(MeSC{\equiv}CSMe)_2(CO)(\eta^2-$ dmpe), analogous to **3**, and eventually $W(MeSC{\equiv}CSMe)_2(\eta^2-$ dmpe), Jolly and Zakrzewski [30] showed that treating $Cr(PMe_3)_2Cl_2$ with PhC≡CPh in the presence of active-Mg generated $Cr(PhC{\equiv}CPh)_2(PMe_3)_2$, which reacted further to yield $Cr(PhC{\equiv}CPh)_3(PMe_3)$. Recently, Brauers et al. [31] reported the reaction of $(C_2B_9H_{11})Mo(PhC{\equiv}CPh)_2(CO)$ and $P(OMe)_3$ to afford $(C_2B_9H_{11})Mo(PhC{\equiv}CPh)[P(OMe)_3]_2$ and $(C_2B_9H_{11})Mo(PhC{\equiv}CPh)_2P(OMe)_3$.

It is of interest to compare analogous reaction of $W(PhC{\equiv}CPh)_3(NCMe)$ [23] and PMe_3. This reaction to yield **2** (90%) is completed in 2 h at 25°C, while neither reaction intermediates nor solution color change is observed. King [32] has shown that in a $W(alkyne)_3$ unit of either D_{3h} or C_{3v} symmetry, the three alkyne ligands can donate a total of only 10 electrons to the tungsten atom. A pathway dissociating NCMe to generate an unstable, 16-electron species $[W(PhC{\equiv}CPh)_3]$ is plausible. Alternatively, association of PMe_3 to generate $W(PhC{\equiv}CPh)_3(NCMe)(PMe_3)$ is more likely, but consecutive elimination of the labile NCMe ligand seems to override further reaction with PMe_3, leading to **2** predominantly.

Acknowledgements

We are grateful for support of this work by the National Science Council of Taiwan.

References

[1] D.P. Tate, J.M. Augl, J. Am. Chem. Soc. 85 (1963) 2174.
[2] D.P. Tate, J.M. Augl, W.M. Ritchey, B.L. Rose, J.G. Grasselli, J. Am. Chem. Soc. 86 (1964) 3261.
[3] R.B. King, A. Fronzaglia, Inorg. Chem. 7 (1968) 1837.
[4] J.M. Maher, J.R. Fox, B.M. Foxman, N.J. Cooper, J. Am. Chem. Soc. 106 (1984) 2347.
[5] J. Okuda, K.H. Zimmermann, J. Organomet. Chem. 384 (1990) C21.
[6] U. Rosenthal, G. Oehme, V.V. Burlakev, P.V. Petrovskii, V.B. Sur, M.E. Vol'pin, J. Organomet. Chem. 391 (1990) 119.
[7] J.A. Potenza, R.J. Johnson, R. Chirico, A. Efraty, Inorg. Chem. 16 (1977) 2354.
[8] J.L. Templeton, Adv. Organomet. Chem. 29 (1989) 1.

[9] S. Otsuka, A. Nakamura, Adv. Organomet. Chem. 14 (1976) 245.
[10] B.C. Ward, J.L. Templeton, J. Am. Chem. Soc. 102 (1980) 1532.
[11] D.J. Wink, T. Greagan, Organometallics 9 (1990) 328.
[12] E. Sappa, A. Tiripicchio, P. Braunstein, Chem. Rev. 83 (1983) 203.
[13] D.B. Grotjahn, Comprehensive Organometallic Chemistry II, vol. 12, Pergamon, Oxford, 1995, p. 741.
[14] N.E. Shore, Chem. Rev. 88 (1988) 1081.
[15] W.-Y. Yeh, L.-K. Liu, J. Am. Chem. Soc. 114 (1992) 2267.
[16] W.-Y. Yeh, S.-M. Peng, G.-H. Lee, J. Chem. Soc., Chem. Comm., (1993) 1056.
[17] W.-Y. Yeh, S.-M. Peng, L.-K. Liu, Inorg. Chem. 32 (1993) 2965.
[18] W.-Y. Yeh, C.-S. Ting, S.-M. Peng, G.-H. Lee, Organometallics 14 (1995) 1417.
[19] W.-Y. Yeh, C.-L. Ho, M.Y. Chiang, I.-T. Chen, Organometallics 16 (1997) .
[20] K.J. Odell, E.M. Hyde, B.L. Shaw, I. Shepherd, J. Organomet. Chem. 168 (1979) 103.
[21] D.J. Wink, N.J. Cooper, Organometallics 10 (1990) 494.
[22] K.W. Chiu, D. Lyons, G. Wilkinson, M. Thornton-Pett, M.B. Hursthouse, Polyhedron 2 (1983) 803.
[23] W.-Y. Yeh, C.-S. Ting, C.-F. Chih, J. Organomet. Chem. 427 (1991) 257.
[24] W.-Y. Yeh, C.-S. Ting, S.-M. Chien, S.-M. Peng, G.-H. Lee, Inorg. Chim. Acta 255 (1997) 335.
[25] R.H. Crabtree, The Organometallic Chemistry of the Transition Metals, Wiley, New York, 1994.
[26] B.E. Mann, B.F. Taylor, ^{13}C NMR Data for Organometallic Compounds, Academic Press, New York, 1981.
[27] J.C. Green, M.L.H. Green, Comprehensive Organometallic Chemistry, Pergamon Press, Oxford, 1973, p. 355.
[28] K.R. Birdwhistell, T.L. Tonker, J.L. Templeton, J. Am. Chem. Soc. 109 (1987) 1401.
[29] J.A. Connor, G.A. Hudson, J. Organomet. Chem. 185 (1980) 385.
[30] P.W. Jolly, U. Zakrzewski, Polyhedron 10 (1991) 1427.
[31] G. Brauers, S.J. Dossett, M. Green, M.F. Mahon, J. Chem. Soc., Chem. Commun., (1995) 985.
[32] R.B. King, Inorg. Chem. 7 (1968) 1044.