

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

Wenn-Yann Yeh<sup>\*</sup>, Shu-Min Chien

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

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### Abstract

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

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Tetrahedral tris(alkyne) complexes of the type  $W(\text{RC}\equiv\text{CR}')_3(\text{CO})$  [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  $W(\text{RC}\equiv\text{CR}')_3(\text{phosphine})$  can be prepared by treating  $W(\text{RC}\equiv\text{CR}')_3(\text{CO})$  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  $W(\text{PhC}\equiv\text{CPh})_3(\text{CO})$  (**1**) [1,2] and  $\text{PMe}_3$  reveals a multistep pathway, in which reversible dissociation–association of the alkyne and phosphine ligands are also involved.

$\text{PMe}_3$  (2.2 equiv.) was introduced into a dichloromethane solution of **1** at  $-78^\circ\text{C}$  under  $\text{N}_2$ . 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

$W(\text{PhC}\equiv\text{CPh})_3(\text{PMe}_3)$  (**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  $W(\text{PhC}\equiv\text{CPh})_2(\text{CO})(\text{PMe}_3)_2$  (**3**)<sup>1</sup>, is discovered during the reaction, but attempts to isolate **3** in pure form have led to the mixture of **2** and **3**. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum recorded after combining **1** and  $\text{PMe}_3$  in  $\text{CD}_2\text{Cl}_2$  displays a singlet at  $-5.0$  ppm ( $^1J(\text{W}-\text{P}) = 140$  Hz) for **2** and a singlet at  $-30.2$  ppm ( $^1J(\text{W}-\text{P}) = 262$  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  $2062\text{ cm}^{-1}$  disappears and a new band at  $1907\text{ cm}^{-1}$  for **3** grows up. The  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **3** at 213 K (Fig. 1) presents a carbonyl resonance at 246.4 ppm with  $^{183}\text{W}$  satellites ( $^1J(\text{W}-\text{C}) = 136$  Hz), indicating that the CO group is still coordinated to the tungsten atom. The four alkyne  $\equiv\text{C}$  carbons give rise to a single resonance at 195.2 ppm, which is between those mea-

<sup>1</sup>Compound **3**: IR ( $\text{CH}_2\text{Cl}_2$ ):  $1907(\nu\text{CO})\text{ cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $20^\circ\text{C}$ ): 7.59–7.10 (m, Ph), 0.85 (t,  $\text{PMe}_3$ ) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $20^\circ\text{C}$ ):  $-30.2$  (s; with  $^{183}\text{W}$  satellites,  $^1J(\text{W}-\text{P}) = 262$  Hz) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $-105^\circ\text{C}$ ): 246.6 (s, CO; with  $^{183}\text{W}$  satellites,  $^1J(\text{W}-\text{C}) = 136$  Hz), 197.2, 191.3, 173.6 (s,  $\equiv\text{C}$ ), 142.1–122.2 (Ph), 18.8 (t, PCH3) ppm.

<sup>\*</sup> Corresponding author.

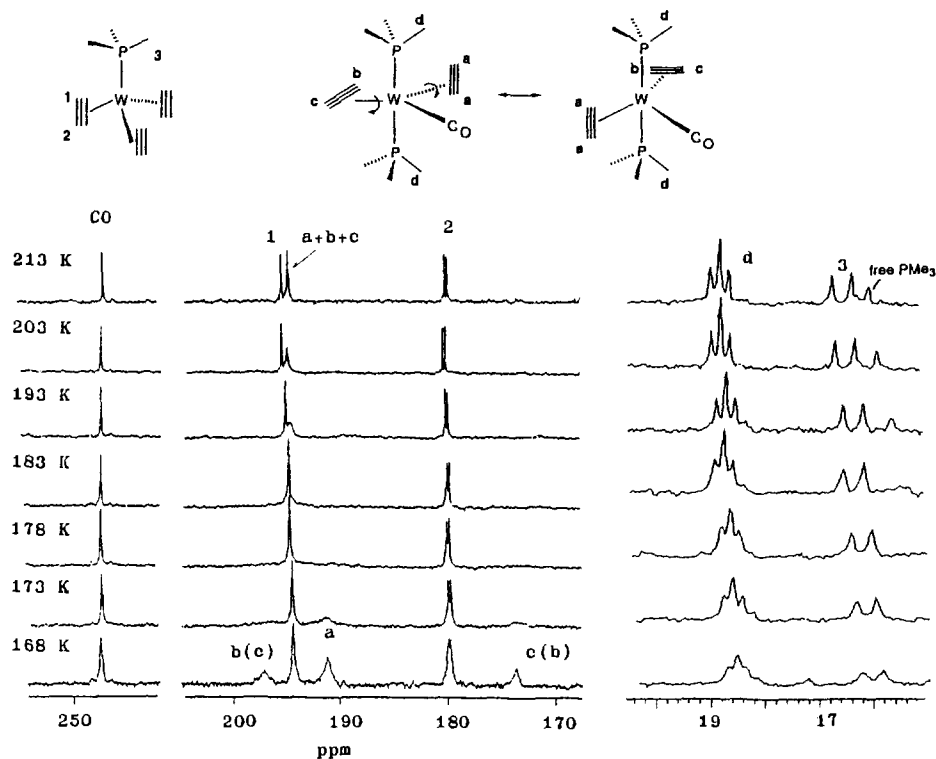


Fig. 1. 75.4 MHz variable-temperature  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of  $\text{W}(\text{Ph}^* \text{C}\equiv\text{CPh})_3(\text{PMe}_3)_2$  ( $2^*$ ) and  $\text{W}(\text{Ph}^* \text{C}\equiv\text{CPh})_2(^* \text{CO})(\text{PMe}_3)_2$  ( $3^*$ ) in  $\text{CD}_2\text{Cl}_2$ . The resonances of  $\text{CH}_3$  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  $\text{PMe}_3$  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  $^1\text{H}$  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  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of a mixture containing  $\text{W}(\text{Ph}^* \text{C}\equiv\text{CPh})_3(\text{PMe}_3)_2$  ( $2^*$ ) and  $\text{W}(\text{Ph}^* \text{C}\equiv\text{CPh})_2(^* \text{CO})(\text{PMe}_3)_2$  ( $3^*$ ) (the star indicating ca. 20%  $^{13}\text{C}$  enrichment) in  $\text{CD}_2\text{Cl}_2$  are displayed in Fig. 1. The resonances for  $2^*$  at 196.3, 179.6 ( $\equiv\text{C}$ ), and 16.3 ( $\text{CH}_3$ ) ppm remain unchanged at low temperatures. In contrast, the alkyne  $\text{C}\equiv\text{C}$  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  $\text{C}\equiv\text{C}$  moiety parallel and the other  $\text{C}\equiv\text{C}$  moiety perpendicular to the  $\text{W}-\text{P}$  vector, and a dynamic process by rotating the  $\text{W}-\text{alkyne}$  bonds could equilibrate the two  $\text{C}\equiv\text{C}$  units. Since  $\text{CO}$  and  $\text{PMe}_3$  are two-electron donor, the two alkynes must supply six electrons to satisfy the 18-electron rule. A semi-em-

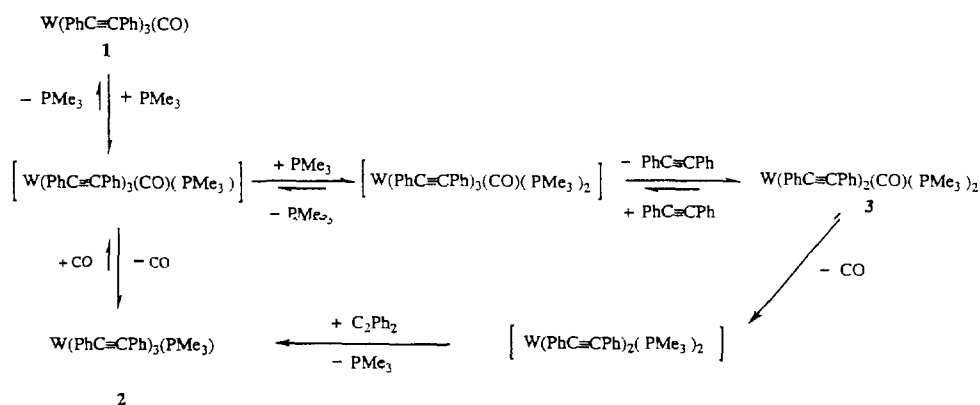
pirical MO calculation (PM3)<sup>2</sup> based on the proposed structure suggests that the parallel alkyne donates four electrons ( $\pi_{\parallel} + \pi_{\perp}$ ) and the perpendicular alkyne donates two electrons ( $\pi_{\parallel}$ ) to the tungsten atom.

The decay of the  $\text{CO}$  stretching peak of  $1$  in IR is found to follow first order kinetics with the concentration of  $\text{PMe}_3$ .<sup>3</sup> The presence of extra diphenylacetylene does not affect the disappearing rate of  $1$ , but does inhibit the formation of  $3$ . Introduction of  $\text{PMe}_2\text{Ph}$  (1 equiv.) into the solution containing  $2$  and  $3$  also affords  $\text{W}(\text{PhC}\equiv\text{CPh})_3(\text{PMe}_2\text{Ph})$  [21] in 10% yield. Furthermore, treating  $1$  with  $\text{PMe}_3$  in the presence of  $\text{TolC}\equiv\text{CTol}$  leads to mixed products  $\text{W}(\text{PhC}\equiv\text{CPh})_{3-n}(\text{TolC}\equiv\text{CTol})_n(\text{PMe}_3)$  ( $n = 0-3$ ).<sup>4</sup>

<sup>2</sup> MacSPARTAN Plus, Wave function, Inc., Irvine, CA, USA.

<sup>3</sup> The reaction was followed by intermittently withdrawing samples with a hypodermic syringe and monitoring the infrared spectra in the  $\nu(\text{CO})$  region. The concentration of  $1$  was determined by measuring the height of the band at  $2062\text{ cm}^{-1}$  recorded in absorbance units.

<sup>4</sup> 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 ( $^{184}\text{W}$ ) for each component. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum gives four signals for the  $\text{PMe}_3$  resonances. The  $^1\text{H}$  NMR spectrum displays four doublet signals for the  $\text{PMe}_3$  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  $100^\circ C$  give no reaction. Only under harsh conditions (2 atm  $CO$ ,  $120^\circ C$ , 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  $d_\pi$  orbitals, a repulsive interaction between the metal filled  $d_\pi$  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  $PhC\equiv CPh$  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  $PMe_3/PhC\equiv CPh$  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  $PhC\equiv CPh$  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  $25^\circ C$ , 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.

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