



Dangling phosphine complexes: Phosphine exchange in pentacarbonyl tungsten complexes of bis(diphenylphosphinomethyl) phenylphosphine



Chaminda P. Gamage^a, Ryan C. Bailey^a, Ellen A. Keiter^a, John R. Kuczynski^a, Kraig A. Wheeler^a, Charlotte L. Stern^c, Douglas E. Brandt^b, Richard L. Keiter^{a,*}

^a Department of Chemistry, Eastern Illinois University, Charleston, IL 61920, USA

^b Department of Physics, Eastern Illinois University, Charleston, IL 61920, USA

^c Department of Chemistry, Northwestern University, Evanston, IL 60208, USA

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ABSTRACT

The reaction of $[\text{W}(\text{CO})_5\text{NH}_2\text{Ph}]$ with $\text{Ph}_2\text{PCH}_2\text{PPhCH}_2\text{PPh}_2$ under mild conditions and stoichiometric control leads to two sets of linkage isomers: $[(\text{OC})_5\text{W}\{\kappa^1\text{-PPh}(\text{CH}_2\text{PPh}_2)_2\}]$ **6a** and $[(\text{OC})_5\text{W}(\kappa^1\text{-PPh}_2\text{CH}_2\text{PPhCH}_2\text{PPh}_2)]$ **6b**; $[(\text{OC})_5\text{W}\{\mu\text{-PPh}_2\text{CH}_2\text{PPh}(\text{CH}_2\text{PPh}_2)_2\}\text{W}(\text{CO})_5]$ **7a** and $[(\text{OC})_5\text{W}(\mu\text{-PPh}_2\text{CH}_2\text{PPhCH}_2\text{PPh}_2)\text{W}(\text{CO})_5]$ **7b**. Isomers **6a** and **6b** exist in equilibrium with $K = 4.35$ for **6b/6a** in CDCl_3 at 55°C . Under the same conditions, the rate of isomerization of **6a** to **6b** is $4.32 \times 10^{-6} \text{ s}^{-1}$. Isomerization is thought to proceed by an initial attack of a carbonyl group by a pendant phosphine followed by ring opening and a 1,2-phosphine shift. At higher temperatures, chelated complexes with four- and six-membered rings are formed: $[(\text{OC})_5\text{W}\{\mu\text{-}\kappa^1\text{-}, \kappa^2\text{-PPh}_2\text{CH}_2(\text{PhPCH}_2\text{PPh}_2)\text{W}(\text{CO})_4\}]$ **9a**, $[(\text{OC})_5\text{W}\{\mu\text{-}\kappa^1\text{-}, \kappa^2\text{-PPh}(\text{CH}_2\text{PPh}_2)_2\}\text{W}(\text{CO})_4\}]$ **9b**, and $[(\text{OC})_4\text{W}\{\kappa^2\text{-}(\text{PPh}_2\text{CH}_2)_2\text{PPh}\}]$ **10b**. X-ray crystal structures of **6a**, **7b**, and **9b** have been determined.

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1. Introduction

Complexes of the linear polydentate phosphines, $\text{Ph}_2\text{PCH}_2\text{PPhCH}_2\text{PPh}_2$ (dpmp) and $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPhCH}_2\text{CH}_2\text{PPh}_2$ (dpep), have been known for many years [1]. A convenient synthesis for dpmp first appeared in 1979 [2] but attracted notable attention only after Balch and coworkers demonstrated its remarkable capacity to form trimetallic complexes of linked d^8 and d^{10} metals (Fig. 1) [3,4]. Among the many chelated and bridged complexes of dpmp are those in which one [5–11] or, in rare instances, two [12,13] of the phosphine groups remain uncoordinated.

Few studies have been reported for reactions of dpmp with metal carbonyls other than those of Rh and Ir [3,14]. The one report of reactions with $[\text{M}(\text{CO})_6]$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) gave only $[\text{cis-M}(\text{CO})_4(\text{dpmp})]$ in which the central phosphorus atom remains uncoordinated [15].

Carbonyl complexes of dpep, first synthesized in 1961, have been much more extensively investigated than those of dpmp [1,16,17]. Whereas no $\text{M}(\text{CO})_5$ complexes of dpmp have been reported, all five dpep complexes of $\text{W}(\text{CO})_5$ have been prepared selectively from vinyl phosphines (Fig. 2). These consist of two sets of linkage isomers (**1**, **2** and **3**, **4**) with uncoordinated phosphines and one complex in which dpep is fully coordinated (**5**) [17].

The stability of metal carbonyl complexes of dpep suggested that syntheses of similar complexes of dpmp should be possible. That and our continuing interest in dangling phosphine carbonyl complexes and their exchange of coordinated and uncoordinated phosphine groups led us to initiate this study.

In our previous work we have shown that rates of intramolecular exchange of coordinated and uncoordinated phosphines at 55°C vary over a wide range for rather similar ligands [18–20]. In this work we further examined the mechanism of the exchange process by determining the rates of isomerization of **6a** and **6b** (Scheme 1). Two mechanistic possibilities are discussed.

* Corresponding author.

E-mail address: rlkeiter@eiu.edu (R.L. Keiter).

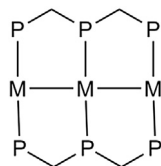


Fig. 1. Doubly bridged d^8 and d^{10} dpmp complexes.

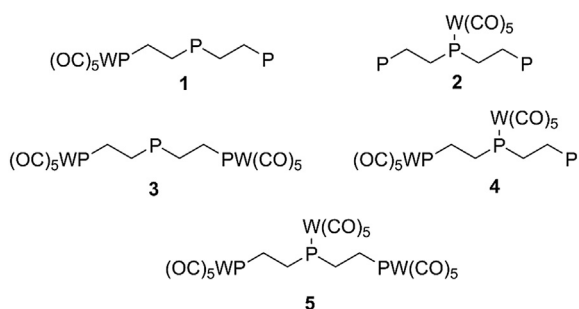
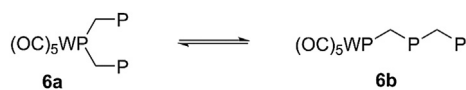


Fig. 2. Non-chelated $W(CO)_5$ complexes of dpep.



Scheme 1. Isomerization of isomers **6a** and **6b**.

2. Results and discussion

2.1. Synthesis and characterization

Although selective methods for synthesizing dpmp complexes analogous to those for dpep are not known, we have succeeded in non-selectively preparing the target compounds by traditional substitution reactions. The reaction of $[(OC)_5WNH_2Ph]$ with dpmp under various conditions gave $W(CO)_5$ products **6a**, **6b**, **7a**, and **7b** but not **8**. In addition, chelated products **9a**, **9b**, and **10a**, were characterized (Fig. 3).

To maximize the formation of **6a** and **6b**, an excess of dpmp was used. Even so, some **7b** was seen in these reactions as both **6a** and **6b** are also ligands competing for vacant tungsten sites. Complex **7a** was seldom observed in these reactions because its precursor **6a** is less abundant than **6b** in the reaction mixtures and because **7a** is unstable with respect to **7b**. With an excess of $[(OC)_5WNH_2Ph]$, only dimetallic complexes (**7b**, **9a**, and **9b**) were found. These results are summarized in Scheme 2.

The P-31 NMR spectrum of linkage isomer **6a** shows a downfield triplet with W-183 satellites for the coordinated central phosphine and a doublet for the two uncoordinated phosphines, confirming that the two are inequivalent in solution. The P-31 NMR spectrum of **6b** shows three nonequivalent phosphorus atoms. That the $W(CO)_5$ is bound to a terminal phosphine rather than the central one of dpmp is confirmed by the presence of a simple downfield doublet with W-183 satellites. The two uncoordinated phosphine groups give an upfield doublet of doublets (central phosphine) and doublet (terminal phosphine). For **7b**, the P-31 spectrum consists of an upfield triplet corresponding to the unbound central phosphorus atom and a doublet (with W satellites) for the two equivalent coordinated terminal phosphines.

The crystal structure of **6a** (Fig. 4), shows that one of the dangling phosphines is directed toward an equatorial carbonyl while the other is directed away from the carbonyl plane. The

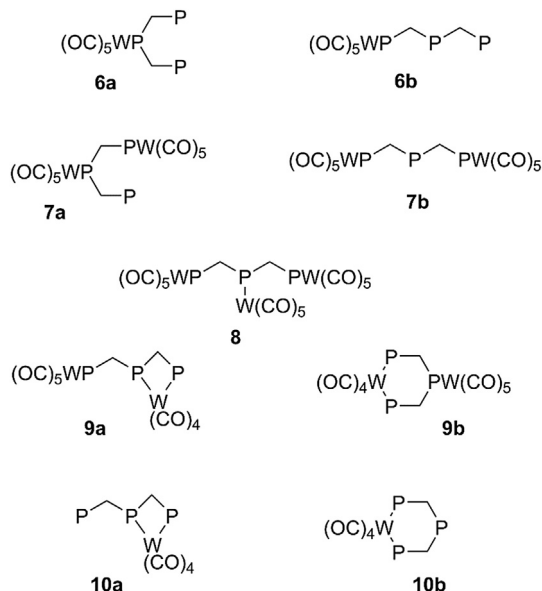
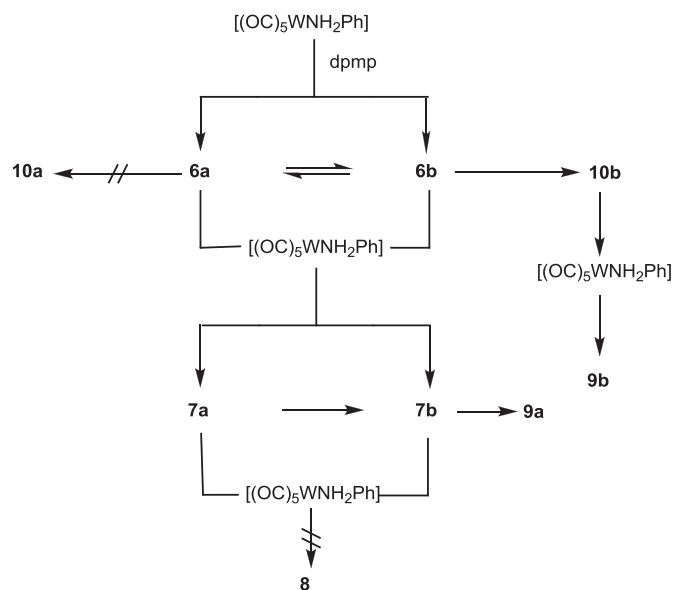


Fig. 3. Targeted products from the reaction of $[(OC)_5WNH_2Ph]$ with dpmp; **8** and **10a** were not observed.



Scheme 2. A flowchart for the reaction of $[(OC)_5WNH_2Ph]$ with dpmp.

observed solid state configuration appears to be partially driven by two sets of intramolecular, face-to-face stacked phenyl groups, each separated by less than 3.5 Å. The arrangement of these pairs of phenyl groups is nearly parallel, with a mutual angle of less than 6°. Intermolecular stacking is not observed.

For **7b**, the crystal structure (Fig. 5) shows that the two coordinated phosphines P(1) and P(3) are nonequivalent as the uncoordinated phosphine P(2) is directed toward an equatorial carbonyl of W(2) and away from the carbonyls of W(1). Just as in **6a**, intramolecular, face-to-face stacking is observed with, in this case, three phenyl groups each separated from another by less than 3.5 Å. The groups are almost parallel with a mutual angle of less than 6° and, as in **6a**, intermolecular stacking is not observed. A second feature to note for both **6a** and **7b** is that the smaller of the two P–C–P angles is the one in which the uncoordinated phosphine is in close

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