Isomerization of $(OC)_5WPPh_2CH_2CH(PPh_2)_2$[1]

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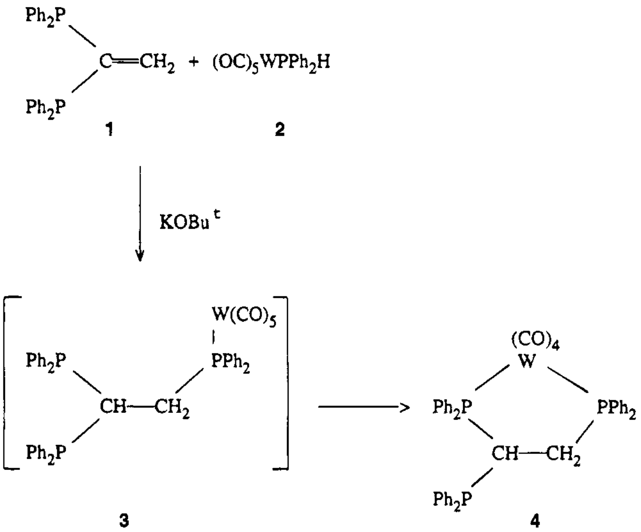
*Summary: It has been found that $(OC)_5WPPh_2CH_2CH(PPh_2)_2$ (**3**) and $(OC)_5WPPh_2CH(PPh_2)CH_2PPh_2$ (**9**) exist in equilibrium in solution at room temperature. This isomerization is the first experimental evidence for the exchange of terminal and coordinated phosphorus groups in pentacarbonyl complexes of group 6 metals.*

The syntheses of complexes in which potentially chelating phosphorus ligands are coordinated as monodentate ligands were greatly facilated by the discovery that it is possible to add a free secondary phosphine across the carbon–carbon double bond of a *coordinated* vinylphosphine.[2] Subsequently, this method was used to prepare a variety of bimetallic and trimetallic complexes in which metal atoms are bridged by polydentate phosphines.[3]

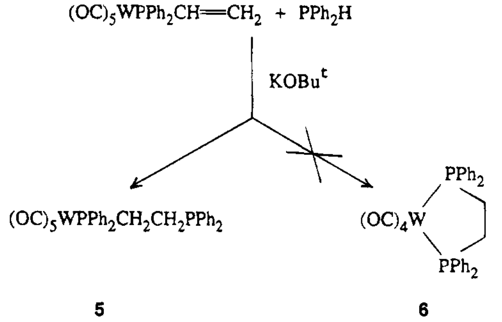
Recently, it was shown that the reaction of $(Ph_2P)_2C{=}CH_2$ (**1**) with $(OC)_5WPPh_2H$ (**2**), in refluxing thf in the presence of potassium *tert*-butoxide, affords complex **4** in which 1,1,2-tris(diphenylphosphino)ethane (tppe) is bound as a bidentate ligand (Scheme 1).[4] It was proposed that this reaction proceeds through intermediate **3**, which was postulated to be unstable with respect to chelation under the conditions of the reaction.

Scheme 1



Previous work of ours[2b] and others[5] has shown, however, that complexes such as $(OC)_5WPPh_2(CH_2)_xPPh_2$ ($x = 1, 2$) do not readily undergo chelation. For example, $(OC)_5WPPh_2CH{=}CH_2$ reacts with PPh_2H to give $(OC)_5W(dppe)$ (**5**) (dppe = $Ph_2PCH_2CH_2PPh_2$) in refluxing thf without the formation of the chelated complex, $(OC)_4W(dppe)$ (**6**) (Scheme 2).[2b] These results led us to question **3** as an intermediate in the formation of **4**.

Scheme 2



Furthermore, it is known that $(OC)_5WPPh_2H$ reacts with $PPh_2CH{=}CH_2$ to give the chelated product, **6**, exclusively.[2b] For several reasons we proposed an intramolecular pathway to account for the formation of **6** (Scheme 3). First, anionic carbonyl complexes such as $[(OC)_5WPPh_2]^-$ readily lose CO in the presence of phosphine ligands.[6] For example, **2**, upon deprotonation, reacts with PPh_3 to give *cis*-$(OC)_4W(PPh_3)(PPh_2H)$ as the principal product.[6d] Further support for the intramolecular route has been provided by the demonstration that *cis*-$W(CO)_4(PPh_2H)(PPh_2CH{=}CH_2)$ reacts with base to give **6**.[7]

In this work we have synthesized **3** by an alternate route and shown that it is stable with respect to chelation when subjected to the reaction conditions described in ref 4.[8] Therefore, **3** cannot be an intermediate in the formation of **4** as shown in Scheme 1. In the course of this investigation, however, we discovered

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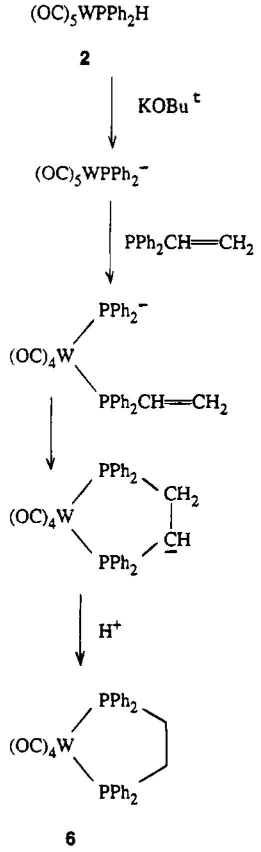
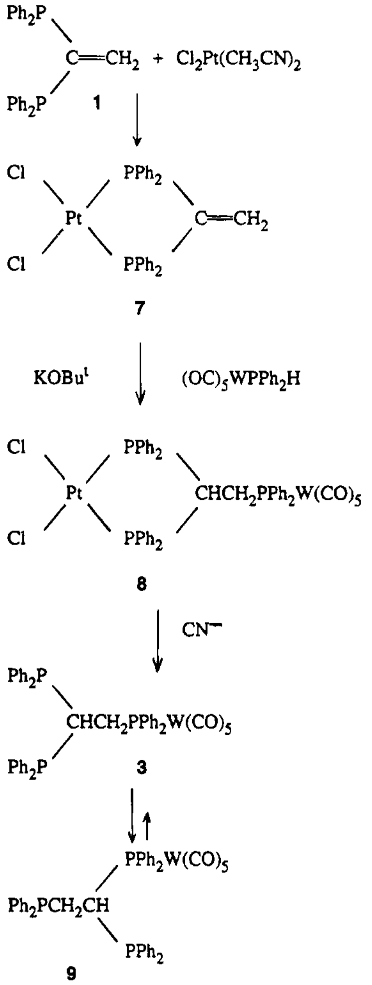
Scheme 3



Scheme 4



that **3** is *unstable with respect to isomerization.* We report here the details of the synthesis of **3** and its unprecedented isomerization.[9]

In order to prevent chelation of tppe in the preparation of **3**, a $PtCl_2$ protecting group was employed (Scheme 4). Complexes **7** and **8** were isolated in good yield prior to their next reactions.[10] In our first attempt to displace **3** from **8** with a stoichiometric quantity of cyanide, carried out over 72 h at ambient temperature in ethanol, **9** and **3** were obtained as predominant and minor products, respectively.[11] When the same reaction was carried out for 4 h, however, the predominant product was **3** while **9** appeared as the minor product. Monitoring the product mixture with ^{31}P NMR spectroscopy revealed that **3**, which formed first, slowly converted to **9**. After 72 h a constant ratio (5:1) of **9** to **3** was observed. Examination of the same mixture periodically over a period of 51 days showed no further change in the ratio. The less soluble **9**, which can be precipitated from this solution by the addition of methanol, was isolated in pure form. When it was placed back into solution, a slow partial conversion to **3** took place. It is apparent that an equilibrium exists between **3** and **9** in solution and that it significantly favors **9**.[12] These results may account for the fact that previous workers could not separate a 4:1 mixture of **9** and **3** obtained from the reaction of tppe with $(OC)_5W(thf)$.[4]

Intimate mechanisms for ligand substitution processes have been classified as dissociative (D), associative (A), or interchange (I_d or I_a).[14] Isomerization of **3** to **9** takes place without the formation of phosphine-bridged dimetallic complexes such as $(OC)_5WPPh_2CH_2CH(PPh_2)PPh_2W(CO)_5$. The absence of such a complex would argue against a dissociative mechanism. The results of two additional experiments support this view. First, when the reaction of **8** with cyanide was carried out in the presence of a 5-fold excess of Ph_3P over 72 h, Ph_3P was not incorporated into the coordination sphere of tungsten. In a separate experiment a 5-fold excess of Ph_3P was added to an equilibrium mixture of **3** and **9** and monitored with ^{31}P NMR for 5 days. There was no evidence in either experiment for the formation of $(OC)_5WPPh_3$ ($^{31}P\{^1H\}$ δ 21 ppm),[13] a product that would

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(8) Formation of **4** was not observed when an equilibrium mixture of **3** and **9** was heated under reflux in thf with potassium *tert*-butoxide for 0.5 h.

(9) Linkage isomers of the type $(OC)_5WP'-P$ and $(OC)_5WP-P'$ have been previously observed, but no evidence for them existing in equilibrium has been reported. Grim, S. O.; Del Gaudio, J.; Molenda, R. P.; Tolman, C. A.; Jesson, J. P. *J. Am. Chem. Soc.* **1974**, *96*, 3416.

(10) **8** (78%): IR ($CHCl_3$) $E + A_1^{(1)}$, 1940 cm^{-1}; $A_1^{(2)}$, 2073 cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 17.7 ($^1J_{WP} = 245$ Hz, $^3J_{PP} = 37.4$ Hz), −37.7 ($^1J_{PtP} = 3072$ Hz, $^3J_{PP} = 37.4$ Hz). Anal. Calcd for $C_{43}H_{33}Cl_2O_5P_3PtW$: C, 44.05; H, 2.84; P, 7.92. Found: C, 44.14; H, 2.88; P, 7.77. Complex **7** (74%) was prepared previously: Higgins, S. J.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1989**, 1527.

(11) Our spectroscopic characterization of **9** and **3** is in agreement with that reported in ref 4.

(12) Kinetics, equilibrium, and mechanistic studies of this isomerization are in progress.

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be expected if a five-coordinate intermediate, as required by a D mechanism, formed in the course of the isomerization.

Several azo complexes, $(OC)_5WL$ (L = pyridazine, 3-methylpyridazine, 4-methylpyridazine, benzo[*c*]cinnoline), have been shown to be fluxional and involve 1,2-metal–nitrogen shifts.[15] The transition state of the pyridazine complexes, in agreement with theoretical calculations,[16] is thought to have a substantial dissociative character. Results for the benzo[*c*]cinnoline complex are more consistent, however, with either a bidentate 20-electron transition state, in agreement with the theoretical studies on monocoordinated diimines and azines,[17] or a π-bonded transition state. Abel and coworkers have examined a number of fluxional dithioether complexes, $(OC)_5W(RSCH_2SR)$ (R = alkyl), with variable-temperature NMR and have proposed a pseudo-seven-coordinate transition state for the observed 1,3-shift.[18] It would seem that a 1,4-metal–phosphorus shift that involves a similar transition state would be consistent with our observed isomerization.

The results of this study lead us to believe that it is probable that complex **4** of Scheme 1 forms via an intramolecular pathway similar to that shown in Scheme 3. Of greater significance is the observation that coordinated and terminal phosphine groups in 18-electron carbonyl complexes can undergo exchange, even under mild conditions. Whether complexes such as $(OC)_5MPPh_2(CH_2)_xPPh_2$ (x = 1, 2; M = Cr, Mo, W) undergo slow exchange remains unclear.[19] Experiments are underway to clarify this point.

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Supplementary Material Available: Text giving details of the synthesis and characterization of **8** and its reaction with cyanide, equilibration studies of **3** and **9**, and a table of ^{31}P NMR data (4 pages). Ordering information is given on any current masthead page.

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