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

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1. Introduction

phosphines, Complexes of the linear polydentate Ph₂PCH₂PPhCH₂PPh₂ (dpmp) and Ph₂ PCH₂CH₂PPhCH₂CH₂PPh₂ (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 d⁸ and d¹⁰ 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 $[M(CO)_6]$ (M = Cr, Mo, W) gave only [cis-M(CO)₄(dpmp)] in which the central phosphorus atom remains uncoordinated [15].

ABSTRACT

The reaction of [W(CO)₅NH₂Ph] with Ph₂PCH₂PPhCH₂PPh₂ under mild conditions and stoichiometric control leads to two sets of linkage isomers: $[(OC)_5W(\kappa^1-PPh(CH_2PPh_2)_2)]$ **6a** and $[(OC)_5W(\kappa^1-PPh(CH_2PPh_2)_2)]$ PPh₂CH₂PPhCH₂PPh₂)] **6b**; $[(OC)_5W{\mu-PPh_2CH_2PPh(CH_2PPh_2)}W(CO)_5]$ **7a** and $[(OC)_5W(u PPh_2CH_2PPhCH_2PPh_2)W(CO)_5$ 7b. Isomers **6a** and **6b** exist in solution in equilibrium with K = 4.35 for 6b/6a in CDCl₃ 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: $[(OC)_5W{\mu-\kappa^1-, \kappa^2-PPh_2CH_2(PhPCH_2PPh_2)W(CO)_4}$ }] **9a**, $[(OC)_5W{\mu-\kappa^1-}, \kappa^2-PPh (CH_2PPh_2)_2}W(CO)_4$ }] **9b**, and $[(OC)_4W{\kappa^2-(PPh_2CH_2)_2PPh}]$ **10b**. X-ray crystal structures of **6a**, **7b**, and **9b** have been determined.

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Carbonyl complexes of dpep, first synthesized in 1961, have been much more extensively investigated than those of dpmp [1,16,17]. Whereas no M(CO)₅ complexes of dpmp have been reported, all five dpep complexes of W(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.







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Fig. 1. Doubly bridged d⁸ and d¹⁰ 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)₅WNH₂Ph] 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 **10b**, but not **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)₅WNH₂Ph], 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 equivalent 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) 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 $[(\text{OC})_5\text{WNH}_2\text{Ph}]$ with dpmp; 8 and 10a were not observed.



Scheme 2. A flowchart for the reaction of [(OC)₅WNH₂Ph] 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



Fig. 4. Solid state molecular structure of $[(OC)_5W[\kappa^1 - PPh(CH_2PPh_2)_2]$ 6a with 50% probability ellipsoids. Selected bond lengths (Å) and bond angles (deg): W(1)-P(1) = 2.5194(8), P(3)-C(2) = 3.430(4), P(3)-C(3) = 3.925(4); P(1)-C-P(2) = 115.6(1), P(3)-C(3) = 3.925(4); P(3)-C(3); P(3)=3.925(4); P(3)-C(3); P(3)-C(3); P(3)-C(3); P(3)=3.925(4); P(3P(1)-C-P(3) = 114.9(1).



Fig. 5. Solid state molecular structure of [(OC)₅W(µ-PPh₂CH₂PPhCH₂PPh₂)W(CO)₅] 7b with 50% probability ellipsoids. Selected bond lengths (Å) and bond angles (deg): W(1)-P(1) = 2.5424(11), W(2)-P(3) = 2.5209(11), P(2)-C(38) = 3.488(5), P(2)-C(58) = 3.488(5), P(2)-C(58) = 3.488(5), P(2)-C(58) = 3.488(5), P(2)-C(58), P(2)-C(58) = 3.488(5), P(2)-C(58), P(2)-C(58), P(2),C(42) = 3.794(5); P(1)-C-P(2) = 119.1(2), P(2)-C-P(3) = 117.0(3).

proximity to a carbonyl group.

The C-13 spectra of the carbonyl region for complexes 6a, 6b, and **7b** show four-bond P-C coupling, ⁴J_{PC} (2.5, 1.9 and 2.7 Hz, respectively), between the uncoordinated phosphine and a cis carbonyl group. It should be noted that ⁴J_{PC} coupling is not observed for the trans carbonyl groups. Table 1 shows ⁴J_{PC} values and solid state distances between pendant phosphines and the carbon atoms of the closest carbonyl group for several complexes. In addition to

Table 1

Four-bond phosphorus-carbon coupling constants (⁴J_{PC}) and solid state phosphorus-carbon bond distances in W(CO)₅ complexes.



the complexes listed in Table 1, cis $^4J_{PC}$ coupling has been observed in $[(OC)_5W{\kappa^1-PPh_2CH_2P(p-tol)_2}]$ (3.2 Hz), $[(OC)_5W{\kappa^1-P(p-tol)_2}]$ tol)₂CH₂PPh₂] (2.9 Hz), and $[(OC)_5W{\kappa^1-P(p-tol)_2CH_2P(p-tol)_2}]$ (2.8 Hz) [20,21]. An examination of four-bond P-C couplings reported in the literature suggests that our values, while comparable to those involving pi bonds [22], are larger than expected for systems involving sigma bonds. For example, in the compounds Ph2PCH2CH2CH2CH3 and [BuPh2PCH2CH2CH2CH3]⁺, ⁴JP-C(Me) couplings are measured as 0 and 0.7 Hz respectively [23]. In $PhP(CH_2PPh_2)_2$, the ${}^4J_{PC}$ coupling (P-C_{Ph}) is 0.6 Hz. We believe that the larger ${}^4J_{PC}$ values for our pentacarbonyl

complexes result from a favorable structural conformation in

solution and it seems likely that there is a "through-space" component arising from a non-bonded interaction of the uncoordinated central P atom with the cis carbonyl groups. While one would not expect the solid state structure to be the same as that in solution, it does seem that the most probable solution arrangement is similar to that in the solid state with the uncoordinated phosphine on average near a cis carbonyl group. The uncoordinated phosphorus atom in $[(OC)_5W{\kappa^1-PPh_2(C=CH_2)PPh_2}]$ lies away from the carbonyl plane and ${}^4J_{PC}$ is zero (Table 1). In the solid state only one of the two uncoordinated phosphines of **6a** lies near a carbonyl group but in solution it can be imagined that each takes a turn to give an average interaction. Similarly, the central uncoordinated arm of **7b** likely alternates between cis carbonyls of the two W(CO)₅ units.

The complex $[(OC)_5W{\kappa^{1}-PPh_2C(SiMe_3) = PMes}]$ is of special interest (Table 1). It has two features that enhance ${}^{4}J_{PC}$ coupling. First, there is a double bond in the coupling pathway and second, its configuration places the uncoordinated phosphine especially close to a carbonyl group (P–CO distance = 3.203 Å). Thus for this system we find by far the largest ${}^{4}J_{PC}$ coupling (6.4 Hz) [24].

The reaction of pure **6a** with $[(OC)_5WNH_2Ph]$ led to a mixture of **7a**, **7b**, and **9a** (Scheme 3). Evidence for **7a** was given by P-31 NMR in which the three nonequivalent phosphorus atoms give three sets of signals, two downfield and one upfield, corresponding to two coordinated and one uncoordinated phosphine. Coupling constants are consistent with other complexes in which the phosphorus atoms are separated by one carbon [21].

Attempts to prepare **8** from the reaction of **7b** with $[(OC)_5WNH_2Ph]$ led only to formation of **9a**. The presence of two CH₂ groups separating phosphorus atoms in **5** as compared with one in **8** emphasizes the importance of steric requirements for trimetallic systems. The P-31 NMR spectrum of **9a** shows three nonequivalent phosphorus atoms giving rise to two doublets (terminal phosphorus atoms) and one doublet of doublets (central phosphorus atom).

An excess of $[(OC)_5WNH_2Ph]$ with dpmp led to formation of **9b.** Its P-31 NMR spectrum consists of a triplet corresponding to a phosphorus atom bound to W(CO)₅ and a doublet corresponding to two phosphorus atoms coordinated to W(CO)₄. The crystal structure of **9b** reveals a six-membered ring with a distorted chair arrangement (Fig. 6). Two of the five phenyl groups are stacked with less than 3.5 Å separation.

2.2. Kinetics and thermodynamics

The isomerization reaction, **6a** \Rightarrow **6b**, starting with pure **6a** or pure **6b** was monitored with ${}^{31}P{}^{1}H{}$ NMR by taking integrals at



Scheme 3. Formation and subsequent reactions of 7a.



Fig. 6. Solid state molecular structure of $[(OC)_5W{\mu-\kappa^1, \kappa^2-PPh (CH_2PPh_2)_2}W(CO)_4]$ **9b** with 50% probability ellipsoids. Selected bond lengths (Å) and bond angles (deg): W(1)-P(2) = 2.5279(11), W(2)-P(3) = 2.5080(11), W(2)-P(1) = 2.4949(11); P(1)-C(22)-P(2) = 124.3(2); P(2)-C(29)-P(3) = 119.3(3), C(22)-P(2)-C(29) = 107.2(2), P(1)-W(2)-P(3) = 87.22(4).

appropriate time intervals. The concentration of **6a** in CDCl₃ at 55 °C as a function of time is shown in Fig. 7. The decrease in the concentration of **6a** is matched by an increase in the concentration of **6b**. At equilibrium the ratio **6b/6a** is 4.35 ± 0.51 , showing that **6b** is somewhat more stable than **6a** under these conditions.

A plot of $\ln\{[6a]-[6a]e_q\}/\{[6a_{in}]-[6a]e_q\}$ versus time gave a straight line with slope equal to $-(k_1 + k_{-1})$ (Fig. 8) [25]. Rate constants of $(4.32 \pm 0.66) \times 10^{-6} \text{ s}^{-1}$ and $(0.99 \pm 0.12) \times 10^{-6} \text{ s}^{-1}$ were found for the forward and reverse reactions, respectively.

These values may be compared to those for isomerization of other complexes containing pendant phosphines (Scheme 4). Rates of isomerization for **11a**, **12a**, and **13a** vary over four orders of magnitude.



Fig. 7. A plot of concentration versus time for the isomerization of 6a.



Fig. 8. A plot of ln{[6a]-[6a]eq}/[6a]in-[6a]eq versus t (ksec).

Previously we have proposed two mechanistic pathways that account for the observed rate differences. The relatively rapid isomerization of **11a** results because one of the two pendant arms interacts with a bound CO group, leading to dissociation of the coordinated phosphine (Scheme 5). When the ring opens, isomer **11b** could potentially form either by a 1,2-shift or by coordination of the second pendant phosphine followed by dissociation of the carbonyl-attached phosphine. The latter reaction is kinetically more favorable [18a].

Isomerization of **12a** can only proceed by a 1,2-shift because it does not have a second arm for the faster pathway available to isomer **11a** (Scheme 6).

The isomerization of **13a** is faster than that of **12a** but slower than for **11a**. Evidence suggests that **13a**, also lacking a second pendant arm, follows a 1,2-shift mechanism with the intermediate relative rate resulting from the close proximity of its one pendant arm to the carbonyl plane [20].

Isomer **6a**, like **11a**, has two pendant arms and so both mechanistic pathways shown in Scheme 7 are theoretically possible for its isomerization. The rate of isomerization of **6a** is approximately the



Scheme 4. Rates of isomerization at 55 °C.



Scheme 5. Pathways for isomerization of 11a.



Scheme 6. Mechanism for isomerization of 12a.

same as for **13a**, suggesting that a 1,2-shift is the most plausible mechanistic route. If the isomerization parallels that of **11a**, an intermediate seven-membered ring would be required and the rate of its formation may be slow compared to the 1,2-shift.

Conversion of **7a** to **7b** was observed with P-31 NMR, but the position of equilibrium between the two linkage isomers so greatly favored **7b** that it was not possible to determine the equilibrium constant. Overlapping signals in the mixture also prevented determination of a reliable rate constant for the conversion.

3. Conclusions

Under mild reaction conditions and stoichiometric control we have synthesized six new $W(CO)_5$ complexes of dpmp and have obtained X-ray structures of three. This work has broadened the scope of linkage isomers examined and revealed additional structural features that influence isomerization rates.

We have established that the rate of exchange between coordinated and uncoordinated phosphines in W(CO)₅L, follows the order: L = Ph₂PCH₂CH(PPh₂)₂ >> PhP(CH₂PPh₂)₂ ~ Ph₂PCH₂ P(*p*tol)₂ >> Ph₂PCH₂CH₂P(*p*-tol)₂. In all cases the first step is the attack



Scheme 7. Mechanistic pathways for the formation of 6b.

of a carbonyl group by a pendant phosphine leading to dissociation of the coordinated phosphine [26]. For complexes of $Ph_2PCH_2P(p-tol)_2$ and $Ph_2PCH_2CH_2P(p-tol)_2$, the isomerization proceeds by a 1,2shift while for complexes of $Ph_2PCH_2CH(PPh_2)_2$, substitution of the bound phosphine with the second pendant phosphine is faster than a 1,2-shift. Isomerization of the $PhP(CH_2PPh_2)_2$ complex could go either way but reaction rates suggest that a 1,2-shift route is more likely. In our 1998 paper we claimed that "two arms are much better than one" for the acceleration of phosphine exchange [18b]. It is now clear that arm length must also be considered.

Our exchange studies may have broad implications for reactions of phosphines with metal carbonyl complexes. Substitution of CO by a phosphine in group 6 metal carbonyls follows a two-term rate law. There is general agreement that the dominant first-order term arises from a dissociative pathway. There is no clear consensus, however, on the mechanistic origin of the second-order term [27–31]. Phosphine attack on the metal or on a bound carbonyl group have both been considered and largely rejected in favor of an interchange dissociative mechanism in which the incoming PR₃ and the departing CO ligand interact prior to full dissociation. Our work suggests that the phosphine may indeed attack a bound carbonyl group but not the one that is replaced.

4. Experimental section

4.1. General

All reactions were carried out under a dry nitrogen atmosphere using standard Schlenk techniques. The tridentate ligand, Ph₂PCH₂PPhCH₂PPh₂ (dpmp), was prepared by reaction of Ph₂PCH₂SiMe₃ (synthesized from NaPPh₂ in liquid ammonia [32,33] with PhPCl₂ [2]. Our analysis of the AB₂ pattern in the ³¹P NMR spectrum is in agreement with that reported in the literature (δP_{term} –22.7, P_{central} –32.9, J_{PP} = 114.2; lit. –22.5, –32.7, J_{PP} = 115.9 [34]). Mp = 138–139 °C (lit. 122–123 [2]; 140–141 [34]). The aniline complex, [(OC)₅WNH₂Ph], was prepared as described previously [18a]. A 300 MHz instrument was used to obtain phosphorus-31 and carbon-13 NMR spectra from CDCl₃ solutions, referenced to 85% phosphoric acid and TMS, respectively. Infrared spectra of the v_{CO} region were obtained from CHCl₃ solutions; values are reported in cm⁻¹.

4.2. Pentacarbonyl[bis(diphenylphosphinomethyl)

phenylphosphine]ditungsten(0), [(OC)₅W{ κ^1 - P_bPh(CH₂P_{a,c}Ph₂)₂}] **6a** and [(OC)₅W(κ^1 - P_aPh₂CH₂P_bPhCH₂P_cPh₂)] **6b**

To a solution of dpmp (2.00 g, 3.95 mmol) in 30 mL of CH₂Cl₂ was added [(OC)₅WNH₂Ph] (0.590 g, 1.41 mmol). The intense vellow color of the solution slowly dissipated over 24 h after which the solvent was removed. The residue consisted of **6a**. **6b**. unreacted dpmp and a minor amount of **7b.** The mixture was eluted with petroleum ether (90%)/ethyl acetate (10%) through a 1.25" x 18" neutral silica gel (60-200 mesh) column. The free ligand, dpmp, eluted first followed by a band containing both 6a and 6b. Crystallization of the **6a/6b** mixture from CH₂Cl₂/CH₃OH (1:2) at -5 °C gave **6a** (0.35 g, 30%). IR: 1934, 1979, 2070. 31P NMR: $\delta_{a,c}$ -24.8, d, δ_b gave **ba** (0.53 g, 50%). It. 1954, 1973, 2070. Trivin, $o_{a,c} = 24.3$, d, o_b 3.9, t; ${}^2J_{PP} = 86.8$, ${}^1J_{WP} = 250.4$. ${}^{13}C$ NMR: δ_{trans} 1994, d, ${}^2J_{PC(trans)} = 23.6$; δ_{cis} 197.6, dd, ${}^2J_{PC(cis)} = 7.2$ Hz, ${}^4J_{PC(cis)} = 2.5$. Anal. Calc. for $C_{37}H_{29}O_5P_3W$: C, 53.52; H, 3.52. Found: C, 53.89; H, 3.61. The mother liquor was concentrated and at -5 °C 6b precipitated (0.25 g, 21%). IR: 1937, 1981, 2070. 31 P NMR: δ_a 9.3 d, δ_b –34.7 dd, $\delta_{\rm C}$ –23.5 d; ${}^{2}J_{P(a)P(b)}$ = 96.1, ${}^{2}J_{P(b)P(c)}$ = 112.6, ${}^{1}J_{WP}$ = 245.0. 13 C NMR: δ_{trans} 199.5 d, ${}^{2}J_{\text{PC}(\text{trans})} = 23.2$; δ_{cis} 197.0, dd, ${}^{2}J_{\text{PC}(\text{cis})} = 7.2$, ${}^{4}J_{\text{PC}(\text{cis})} = 2.0$. Anal. Calcd. for $C_{37}H_{29}O_{5}P_{3}W$: C, 53.52; H, 3.52. Found: C, 54.13; H, 3.58. The dimetallic complex 7b was not recovered from this reaction.

4.3. [bis(diphenylphosphinomethyl)phenylphosphine] [bis(pentacarbonyl)tungsten(0)], [(OC)₅W(μ-P_aPh₂CH₂P_bPhCH₂P_cPh₂)W(CO)₅] **7b**

A CH₂Cl₂ solution (30 mL) of [(OC)₅WNH₂Ph] (1.00 g, 2.40 mmol) and dpmp (0.570 g, 1.11 mmol) was stirred for 24 h. The residue resulting from removal of solvent was crystallized from a 1:2 volume of CH₂Cl₂/CH₃OH to give a powder consisting principally of **7b** with minor amounts of chelated products, [(OC)₅W{ μ - κ^1 , κ^2 - $P_aPh_2CH_2$ ($P_bPhCH_2P_cPh_2$)}W(CO)₄] **9a** and [(OC)₅W{ μ - κ^1 , κ^2 - P_bPhCH_2 (CH₂ P_a,cPh_2)₂}W(CO)₄] **9b**. No evidence for the formation of [(OC)₅W{ μ - R_1 , κ^2 - P_bPhCH_2 (CH₂ P_a,cPh_2)₂}W(CO)₄] **9b**. No evidence for the formation of [(OC)₅W{ $\{\mu$ - R_1 , κ^2 - P_bPhCH_2 (CH₂ P_a , $P_bPh_2CH_2P_bPh(CH_2P_cPh_2)$)W(CO)₅] **7a** was observed. The powder was dissolved in a minimum of CH₂Cl₂ to which an equal amount of CH₃OH was added. At -5 °C after 120 h, crystals of **7b** were obtained (0.38 g, 29%). IR: 1939, 1981, 2071. ³¹P NMR: $\delta_{P(a,c)}$ 8.8, d, $\delta_{P(b)}$ -37.9, t; ² $_{JPP}$ = 79.3, ¹ $_{JWP}$ = 245.3. ¹³C NMR: δ_{trans} 199.4, d, ² $_{JPC(trans)}$ = 23.3; δ_{cis} 196.9 dd, ² $_{JPC(cis)}$ = 7.2, ⁴ $_{JPC(cis)}$ = 2.7. Anal. Calcd. for C₄₂H₂₉P₃W₂O₁₀: C, 43.70; H, 2.53. Found: C, 44.12; H, 2.58.

4.4. [bis(diphenylphosphinomethyl) phenylphosphine](pentacarbonyl) (tetracarbonyl)ditungsten(0)], [(OC)₅W{ μ - κ ¹, κ ²- $P_aPh_2CH_2$ ($P_bPhCH_2P_cPh_2$)}W(CO)₄] **9a**

A solution of **7b** (0.16 g, 0.14 mmol) and [(OC)₅WNH₂Ph] (0.10 g, 0.24 mmol) in toluene (25 mL) was heated for 24 h at 60 °C. The residue resulting after solvent removal was crystallized from a 1:2 solution of CH₂Cl₂/CH₃OH to give **9a** (0.090 g, 57%). IR: v_{CO} 1898, 1934, 1978, 2019, 2071. ³¹P NMR: $\delta_{P(a)}$ 8.1, d, $\delta_{P(b)}$ –33.1 dd, $\delta_{P(c)}$ –17.9 d; ²J_{P(a)P(b)} = 19.4, ²J_{P(b)P(c)} = 36.3; ¹J_{WP(a)} = 247.9, ¹J_{WP(b)} = 226.4, ¹J_{WP(c)} = 201.7. Anal. Calcd. for C₄₁H₂₉O₉P₃W₂: C, 43.72; H, 2.60. Found: C, 43.95; H, 2.72. The goal of this reaction had been to synthesize [{(OC)₅W}₃dpmp] **8** but there was no evidence for it as a product.

4.5. [bis(diphenylphosphinomethyl) phenylphosphine](pentacarbonyltunsten 0) (tetracarbonyltungsten(0)], [(OC)₅W{ μ - κ ¹, κ ²- P_bPhCH₂ (CH₂P_{a,c}Ph₂)₂}W(CO)₄] **9b**

A solution of [(OC)₅WNH₂Ph] (1.0 g, 2.4 mmol) and dpmp

Table 2

Crystal data and structure refinement for complexes **6a**, **7b**, and **9b**.

| | 6a | 7b | 9b |
|--|--|---|--|
| Empirical Formula | C ₃₇ H ₂₉ WO ₅ P ₃ | $C_{42}W_2P_3H_{29}O_{10}$ | C ₄₁ W ₂ P ₃ O ₉ H ₂₉ |
| Formula Weight | 830.40 | 1154.31 | 1126.30 |
| Crystal Dimensions | $0.31 \times 0.41 \times 0.21 \text{ mm}$ | $0.13 \times 0.24 \times 0.26 \text{ mm}$ | 0.31 \times 0.19 \times 0.26 mm |
| Crystal System | tetragonal | triclinic | Triclinic |
| Lattice Type | I-centered | Primitive | Primitive |
| Lattice Parameters | a = 32.902(3) Å | a = 11.7988(12) Å | a = 9.647(1) Å |
| | c = 12.681(2) Å | b = 13.651(1) Å | b = 11.567(2) Å |
| | $V = 13727.7(22) \text{ Å}^3$ | c = 14.579(2) Å | c = 18.726(3) Å |
| | | $\alpha = 102.148(2)$ Å | $\alpha = 95.383(2) \text{ Å}$ |
| | | eta = 107.335(2) Å | $eta = 94.288(2) \text{\AA}$ |
| | | $\gamma = 106.689(2)$ | $\gamma = 102.280(2)$ Å |
| | | $V = 2031.4(4) \text{ Å}^3$ | $V = 2023.2(5) \text{ Å}^3$ |
| Space Group | <i>I</i> 4 ₁ /a (#88) | P-1 (#2) | P-1 (#2) |
| Z value | 16 | 2 | 2 |
| D _{calc} | 1.607 g/cm ³ | 1.887 g/cm ³ | 1.849 g/cm ³ |
| F ₀₀₀ | 6560.00 | 1108.00 | 1080.00 |
| μ(ΜοΚα) | 35.51 cm ⁻¹ | 58.41 cm $^{-1}$ | 58.60 cm^{-1} |
| No. Observations $(I > 3.00\sigma(I))$ | 6565 | 8025 | 7809 |
| No. Variables | 415 | 514 | 496 |
| Reflection/Parameter Ratio | 15.82 | 15.61 | 15.74 |
| Residuals: R1; wR2 | 0.030; 0.038 | 0.020; 0.041 | 0.023; 0.048 |
| Goodness of Fit Indicator | 1.34 | 1.62 | 1.67 |
| Max Shift/Error in Final Cycle | 0.03 | 0.00 | 0.00 |
| Maximum peak in Final Diff. Map | 1.10 e ⁻ /Å ³ | 1.25 e ⁻ /Å ³ | 1.81 e ⁻ /Å ³ |
| Minimum peak in Final Diff. Map | −0.79 e [−] /Å ³ | $-0.97 \text{ e}^{-}/\text{\AA}^{3}$ | $-0.92 e^{-}/Å^{3}$ |

(0.38 g, 0.75 mmol) was stirred for 24 h. The solvent was removed and the residue was crystallized from a 1:2 ratio of CH₂Cl₂/CH₃OH to give 0.63 g, shown to consist of **9b** and **7b**. Recrystallization of this mixture from a 1:1 solution of CDCl₃/CH₃OH gave light yellow crystals of **9b** (0.090 g, 11%). IR: 1898, 1933, 1982, 2021, 2071. ³¹P NMR: $\delta_{P(ac)}$ 4.7 d, $\delta_{P(b)}$ –2.7 t; ²*J*_{P(a,C)P(b)} = 12.1, ¹*J*_{WP(a,c)} = 237.1, ¹*J*_{WP(b)} = 249.1. Anal. Calcd. for C₄₁H₂₉O₉P₃W₂: C, 43.72; H, 2.60. Found: C, 43.90; H, 2.75.

4.6. Evidence for formation of [bis(diphenylphosphinomethyl) phenylphosphine][bis(pentacarbonyl)ditungsten(0)], [(OC)₅W{ μ - $P_aPh_2CH_2P_bPh(CH_2P_cPh_2)$ }W(CO)₅] }]**7a**

A solution of $[(OC)_5WNH_2Ph]$ (0.050 g, 0.12 mmol) and **6a** (0.080 g, 0.096 mmol) in 20 mL of CH₂Cl₂ was stirred for 24 h. The residue, obtained upon solvent removal, was shown by ³¹P NMR to contain **7a**, **7b**, **9a**, and **9b**. ³¹P NMR assigned to **7a**: $\delta_{P(a)}$ 8.3 d, $\delta_{P(b)}$ 11.9 dd, $\delta_{P(c)} - 20.7$ d; ² $J_{P(a)P(b)} = 57.9$, ² $J_{P(b)P(c)} = 137.5$. This compound could not be separated from **7b**, **9a**, and **10b** by chromatography and is unstable with respect to its linkage isomer **7b**. Overlap of P-31 signals from **7b**, **9a**, and **9b** prevented determination of tungsten-phosphorus satellites for **7a**.

4.7. Formation of tetracarbonyl[bis(diphenylphosphinomethyl) phenylphosphine]tungsten(0), [(OC)₄ $W(\kappa^2$ - $P_aPh_2CH_2P_bPhCH_2P_cPh_2$] **10b**

A 1:1 mol ratio of $[(OC)_5WNH_2Ph]$ and dpmp in CH₂Cl₂ was stirred for 24 h. As identified in the reaction mixture by P-31 NMR, major products were **6a**, **6b**, and **7b**. Minor products were **7a**, **9a**, and **10b**. ³¹P NMR assigned to **10b**: $\delta_{P(a,c)}$ 3.1, d, $\delta_{P(b)}$ –38.4, t; ² $J_{P(a,c)}$ P(b) = 73.6. Complex **10b** was previously prepared by refluxing dpmp with W(CO)₆ in toluene over 30 h [15].

4.8. Equilibrium and kinetic studies

These experiments were performed on a pure sample of each isomer (30-40 mg) dissolved in 0.4–0.5 mL of CDCl₃ and flame-sealed in a standard NMR tube. The samples were placed in a

constant temperature bath of the appropriate temperature. The NMR probe was brought to the same temperature and ³¹P NMR spectra were recorded at selected time intervals until a constant ratio of isomers resulted. A delay time of 18 s was used to insure sufficient relaxation to allow meaningful integrations. The signals from isomers of each spectrum were integrated three times and the average value was used in subsequent calculations.

4.9. X-ray crystallography

X-ray quality crystals of 6a, 7b, and 9b were grown by slow diffusion of methanol into a solution of CH₂Cl₂. Colorless block crystals were mounted on a glass fiber. All measurements were made on a Bruker SMART-1000 CCD plate detector with graphite monochromated Mo-K α radiation. The data were collected at a temperature of -120 ± 1 °C and processed using the SMART-NT AND SAINT-NT programs from Bruker. The data were corrected for Lorentz and polarization effects. The structure was solved using Direct Methods SHELXS, and refined with the SHELXL refinement package using Least Squares minimization [35]. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in idealized positions but not refined. Neutral atom scattering factors were taken from Cromer and Waber [36]. Anomalous dispersion effects were included in Fcalc [37]; the values for Δf^1 and Δf^2 are those of Creagh and McAuley [38]. The values for the mass attenuation coefficients are those of Creagh and Hubbell [39]. Additional crystallographic details are summarized in Table 2.

CCDC 1033877, 1033878, and 1033879 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

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