# Reactivity of the Four-Membered Heterometallacycles $CH(3,5\text{-}Me_2Pz)_2(CO)_3WSnAr_3$ (Pz = Pyrazol-1-yl) with $P(OR)_3$: Unexpected P−O/C Exchange Reactions in Phosphite

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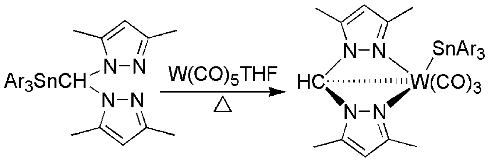
Reactions of $CH(3,5\text{-}Me_2Pz)_2(CO)_3WSnAr_3$ (Pz = pyrazol-1-yl; Ar = phenyl, *p*-tolyl) with $P(OR)_3$ (R = methyl, isopropyl) under solvent-free conditions give the decarbonylated complexes $CH(3,5\text{-}Me_2Pz)_2(CO)_2(P(OR)_3)WSnAr_3$. However, treatment of $CH(3,5\text{-}Me_2Pz)_2(CO)_3WSnAr_3$ with $P(OMe)_3$ at elevated temperature results in unexpected P−O/C exchange reactions with the cleavage of the W−C bond to give the novel reductive elimination product $(MeO)_2PCH(3,5\text{-}Me_2Pz)_2W(CO)_3$. Furthermore, even at low temperature, the reaction of $CH(3,5\text{-}Me_2Pz)_2(CO)_3WSnAr_3$ with $P(OAr)_3$ only yields the similar reductive elimination products $(ArO)_2PCH(3,5\text{-}Me_2Pz)_2W(CO)_3$. In these novel tungsten(0) complexes, the newly formed diaryl or dialkyl bis(3,5-dimethylpyrazol-1-yl)methylphosphonite acts as a neutral tridentate $\kappa^3$-[N,N,P] chelating ligand.

## Introduction

Metallacycles have been extensively investigated for a long time, due to the important roles they play in many catalytic transformations. Furthermore, they are key intermediates in a variety of catalytic C−C bond formation as well as C−C and C−H bond activation reactions.[1] Due to their ring strain, small metallacycles such as metallacyclopropanes[2] and metallacyclobutanes[3] usually have high activity. For example, they undergo easy ring expansion by the insertion of unsaturated small molecules into the M−C bonds. The oxidative addition of the C−C bond to the low-valent transition-metal centers is one of the classic methods for the synthesis of metallacycles.[1] Our recent investigations introduced the reaction of (triarylstannyl)bis(pyrazol-1-yl)methane with $W(CO)_5THF$, which leads to the oxidative addition of the $Sn-C_{sp^3}$ bond to the tungsten(0) atom, yielding the novel heterodinuclear four-membered heterometallacyclic complexes $CH(3,5\text{-}Me_2Pz)_2(CO)_3WSnAr_3$ (**1**) (eq 1).[4] Upon treatment of **1** with electrophilic reagents such as HX (X = Cl, Br), the $W-C_{sp^3}$ bond in the small four-membered metallacycles of **1** shows unusual reactivity, owing to the ring strain and the high polarity of the metal−carbon bond.[5] This result has inspired us to carry out further investigations on whether the reaction of these complexes with nucleophilic reagents also leads to novel reactivity modes. In this paper, we report the distinctive reaction of **1** with $P(OR)_3$, which leads to an unexpected P−O/C exchange reaction with the cleavage of the $W-C_{sp^3}$ bond instead of the simple carbonyl substitution reaction, supplementing the common knowledge that the nucleophilic attack of phosphorus ligands at metal carbonyl complexes results in a carbonyl substitution reaction.

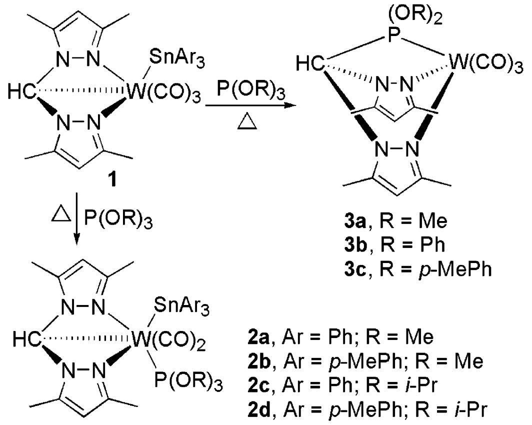


(1)

**1a**, Ar = Ph
**1b**, Ar = *p*-MePh

## Results and Discussion

**Reaction of 1 with $P(OR)_3$ (R = Me, *i*-Pr, Ph, *p*-MePh).** Upon treatment of **1** with trialkyl phosphite under solvent-free conditions and at low temperature, only one carbonyl is displaced to give complexes **2** (eq 2). However, when the reaction of **1** with $P(OMe)_3$ is carried out at elevated temperature, the novel reductive elimination product $(MeO)_2PCH(3,5\text{-}Me_2Pz)_2W(CO)_3$(**3a**) is obtained with an unexpected P−O/C exchange reaction. Furthermore, even at low temperature the reaction of **1** with $P(OAr)_3$ yields only the reductive elimination products $(ArO)_2PCH(3,5\text{-}Me_2Pz)_2W(CO)_3$. On the other hand, even at elevated temperature, treatment of **1** with stronger nucleophiles $PR_3$ (R = phenyl, *n*-butyl) under similar conditions



(2)

**3a**, R = Me
**3b**, R = Ph
**3c**, R = *p*-MePh

**2a**, Ar = Ph; R = Me
**2b**, Ar = *p*-MePh; R = Me
**2c**, Ar = Ph; R = *i*-Pr
**2d**, Ar = *p*-MePh; R = *i*-Pr

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only yields the decarbonylation products CH(3,5-Me$_2$Pz)$_2$(CO)$_2$(PR$_3$)WSnAr$_3$ (see the Supporting Information), with no similar P−C/C exchange reactions taking place.

Complexes **2** and **3** are air-stable in the solid state, and even their solutions can be manipulated in the air without notable decomposition. They have been characterized by elemental analyses and IR and NMR spectroscopy. Complexes **2** and **3** display markedly different IR and NMR spectra. For example, complexes **2** show two strong $\nu$(CO) bands in the range of 1781−1880 cm$^{-1}$, while complexes **3** have three such absorption peaks in the range of 1781−2004 cm$^{-1}$. The proton signal of the CH group in **3** is markedly shifted to lower field in comparison to the signals for **1** and **2** but is very close to those in the ligands Ph$_3$SnCH(3,5-Me$_2$Pz)$_2$ and (*p*-MePh)$_3$SnCH(3,5-Me$_2$Pz)$_2$.[4a] At the same time, the $^{13}$C NMR signals of the CH group in complexes **3a** and **3b** are accordingly shifted to lower field, in comparison with the signal for complex **2c**. All of these complexes display the expected $^{31}$P coupling to the proton and carbon of the CH group. In addition, the $^{31}$P NMR signal in **3a** (204.36 ppm) is also markedly shifted to lower field in comparison with those for complexes **2a** (158.69 ppm) and **2b** (159.75 ppm) as well as for the free P(OMe)$_3$ ligand (130.23 ppm). Furthermore, the $^{31}$P NMR signals of **3b** (182.81 ppm) and **3c** (181.78 ppm) are also markedly different from those for the free ligands P(OPh)$_3$ (127.55 ppm) and P(OPhMe-*p*) (127.57 ppm). These results are consistent with the fact that the CH group in complexes **3** has linked to the phosphorus atom.

The molecular structure of **3b**, presented in Figure 1, has been confirmed further by X-ray single-crystal diffraction analyses, which clearly show that the phosphorus atom is integrated with the bridging carbon of bis(pyrazol-1-yl)methide and the newly formed diphenyl bis(3,5-dimethylpyrazol-1-yl)methylphosphonite acts as a neutral tridentate $\kappa^3$-[N,N,P] chelating ligand. The tungsten atom adopts a six-coordinate distorted-octahedral geometry. The average W−N distance is 2.275 Å, comparable to the corresponding values found in other octahedral W(0) complexes with poly(pyrazol-1-yl)alkanes or poly(pyrazol-1-yl)silane (such as the average values 2.25 Å in Ph$_3$GeCH(3,5-Me$_2$Pz)$_2$W(CO)$_4$,[6] 2.269 Å in Me$_3$SiCH(3,5-Me$_2$Pz)$_2$W(CO)$_4$,[6] 2.2915 Å in (CH$_2$=CH)$_3$SnCH(3,5-Me$_2$Pz)$_2$W(CO)$_3$,[4b] 2.285 Å in MeSi(3,5-Me$_2$Pz)$_3$W(CO)$_3$[7] and 2.265 Å in PhP(3,5-Me$_2$Pz)$_2$W(CO)$_3$[8]). The W−P distance is 2.4269(8) Å, slightly shorter than that reported in other W(0) complexes with phosphorus ligands (such as 2.484(1) Å in (PNN)W(CO)$_3$[9]).

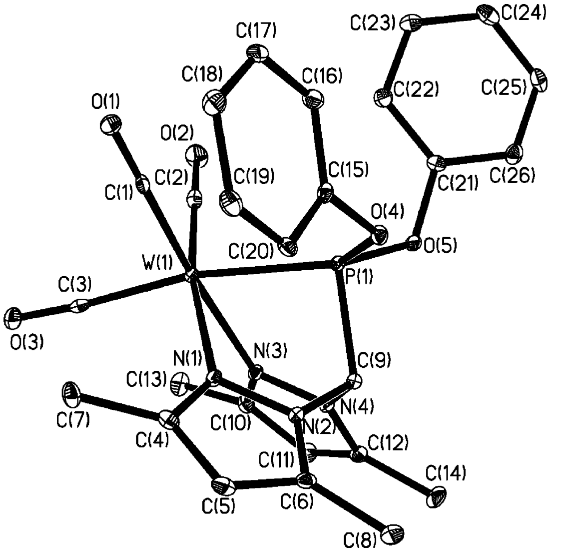

**Figure 1.** Molecular structure of **3b**. The thermal ellipsoids are drawn at the 30% probability level. Selected bond distances (Å) and angles (deg): W(1)−C(1) = 1.961(3), W(1)−C(2) = 1.950(3), W(1)−C(3) = 1.973(3), W(1)−N(1) = 2.287(3), W(1)−N(3) = 2.262(2), W(1)−P(1) = 2.4269(8), P(1)−O(4) = 1.618(2), P(1)−C(9) = 1.876(3), C(9)−N(2) = 1.451(4), C(9)−N(4) = 1.445(4), C(1)−O(1) = 1.173(4), C(2)−O(2) = 1.166(4), C(3)−O(3) = 1.174(4); N(2)−C(9)−N(4) = 110.7(2), N(4)−C(9)−P(1) = 105.5(2), N(2)−C(9)−P(1) = 103.9(1), C(21)−O(5)−P(1) = 122.3(1), O(5)−P(1)−O(4) = 100.5(1), O(5)−P(1)−C(9) = 96.0(1), O(5)−P(1)−W(1) = 129.47(9), C(9)−P(1)−W(1) = 93.65(9), N(1)−W(1)−N(3) = 77.81(9), C(1)−W(1)−N(3) = 173.7(1), C(3)−W(1)−P(1) = 169.56(9), C(1)−W(1)−N(1) = 98.6(1), C(1)−W(1)−C(2) = 88.1(1), W(1)−C(1)−O(1) = 177.0(3), W(1)−C(2)−O(2) = 179.1(3), W(1)−C(3)−O(3) = 175.8(3).

**Possible Pathways of the Formation of 3.** The P−C/X (X = aryl, alkyl, N- or O-base group) exchange reactions in transition-metal−phosphine complexes have been extensively observed.[10] In addition, the P−O/C exchange, through the nucleophilic substitution reaction of triphenyl phosphite with carbanions, has already been widely used in the synthesis of phosphines, phosphinites, and phosphonites.[11] In combination with these known facts, a plausible mechanism for the formation of **3** is depicted as in Scheme 1. Initially, the phosphorus electron lone pair attacks the tungsten atom, leading to the cleavage of the W−C bond. The resulting anion subsequently attacks the phosphorus atom to complete the P−O/C exchange reaction. Finally, the nucleophilic attack of the phenoxide or alkoxide leaving group at the tin atom breaks the Sn−W bond to give the reductive elimination products **3**. In spite of the fact that breaking of the W−C bond can release the ring strain of the four-membered metallacycle in **1** as well as the decarbonylation products CH(3,5-Me$_2$Pz)$_2$(CO)$_2$(PR$_3$)WSnAr$_3$ (see the Supporting Information) and decrease the steric pressure at the tungsten center of the decarbonylation products and the fact that triaryl-

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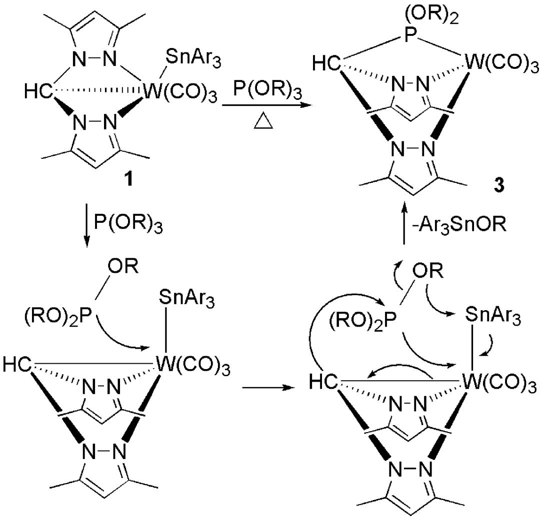
**Scheme 1. Possible Pathways of the Formation of 3**



or trialkylphosphines have stronger nucleophilicities in comparison with triaryl or trialkyl phosphites,[12] no similar P$-$C$_{\mathrm{aryl}}$/C$_{\mathrm{alkyl}}$ exchange reactions[10] take place upon treatment of **1** with PR$_3$. On the other hand, the reaction of **1** with triphenyl phosphite, with a good phenoxide leaving group, only gives the reductive elimination products **3**, even at low temperature. These facts indicate that the P$-$O/C exchange reaction may play a decisive role in the formation process of **3**.

## Experimental Section

**General Considerations.** All reactions were carried out under an atmosphere of argon. Solvents were dried and distilled prior to use according to standard procedures. NMR spectra ($^1$H, $^{13}$C, and $^{31}$P) were recorded on a Bruker AV300 spectrometer, and the chemical shifts were reported in ppm with respect to reference standards (internal SiMe$_4$ for $^1$H NMR and $^{13}$C NMR spectra, external 85% H$_3$PO$_4$ aqueous solution for $^{31}$P NMR spectra) using CDCl$_3$ as solvent unless otherwise noted. IR spectra were recorded as KBr pellets on a Bruker Equinox55 spectrometer. Elemental analyses were carried out on an Elementar Vairo EL analyzer. Complexes **1** were prepared according to the literature methods.[4b]

**Reaction of 1 with P(OR)$_3$ (R = Me, *i*-Pr) To Give Complexes 2.** The mixture of complex **1a** or **1b** (0.5 mmol) and P(OR)$_3$ (4 mmol) was stirred and heated at a suitable temperature for 4 h. After it was cooled to room temperature, the reaction mixture was washed with hexane to remove the excess P(OR)$_3$, and the residue was purified by column chromatography on silica using CH$_2$Cl$_2$/hexane or ethyl acetate/hexane as eluent. The eluate was concentrated to dryness under reduced pressure, and the residual solid was recrystallized from CH$_2$Cl$_2$/hexane to give yellow-green crystals.

**Synthesis of 2a.** This complex was obtained by the reaction of **1a** with P(OMe)$_3$ at 100 °C. The reaction mixture was purified by column chromatography using CH$_2$Cl$_2$/hexane (3/2 v/v) as eluent. Yield: 53%. $^1$H NMR: $\delta$ 1.71, 2.34 (s, s, 6H, 6H, C*H*$_3$), 3.49 (d, 9H, $^3J_{\mathrm{PH}} = 11.4$ Hz, OC*H*$_3$), 4.28 (d, 1H, $^3J_{\mathrm{PH}} = 3.3$ Hz, C*H*), 5.54 (s, 2H, hydrogen in 4-position of pyrazole), 7.10$-$7.12, 7.32$-$7.35 (m, m, 9H, 6H, C$_6$*H*$_5$). $^{31}$P NMR: $\delta$ 158.69. IR (cm$^{-1}$): $\nu_{\mathrm{CO}}$ 1797.9 vs, 1879.0 s. Anal. Calcd for C$_{34}$H$_{39}$N$_4$O$_5$PSnW: C, 44.52; H, 4.29; N, 6.11. Found: C, 44.44; H, 4.45; N, 6.02.

**Synthesis of 2b.** This complex was obtained by the reaction of **1b** with P(OMe)$_3$ at 80 °C. The reaction mixture was purified by column chromatography using CH$_2$Cl$_2$/hexane (2/1 v/v) as eluent. Yield: 45%. $^1$H NMR: $\delta$ 1.79, 2.41 (s, s, 6H, 6H, C*H*$_3$), 2.28 (s, 9H, C*H*$_3$C$_6$H$_4$), 3.56 (d, 9H, $^3J_{\mathrm{PH}} = 8.7$ Hz, OC*H*$_3$), 4.35 (d, 1H, $^3J_{\mathrm{PH}} = 2.1$ Hz, C*H*), 5.60 (s, 2H, hydrogen in 4-position of pyrazole), 6.98, 7.27 (d, d, $^3J_{\mathrm{HH}} = 5.4$ Hz, 6H, 6H, C$_6$*H*$_4$). $^{31}$P NMR: $\delta$ 159.75. IR (cm$^{-1}$): $\nu_{\mathrm{CO}}$ 1806.1 vs, 1877.3 s. Anal. Calcd for C$_{37}$H$_{45}$N$_4$O$_5$PSnW·CH$_2$Cl$_2$: C, 43.71; H, 4.54; N, 5.37. Found: C, 44.14; H, 4.70; N, 5.61.

**Synthesis of 2c.** This complex was obtained by the reaction of **1a** with P(O-*i*-Pr)$_3$ at 80 °C for 3 h. The reaction mixture was purified by column chromatography using CH$_2$Cl$_2$/hexane (1/1 v/v) as eluent. Yield: 40%. $^1$H NMR: $\delta$ 1.19 (d, $^3J_{\mathrm{HH}} = 4.5$ Hz, 18H, OCH(C*H*$_3$)$_2$), 1.78, 2.47 (s, s, 6H, 6H, C*H*$_3$), 4.36 (d, 1H, $^3J_{\mathrm{PH}} = 1.8$ Hz, C*H*), 4.41$-$4.45 (m, 3H, OC*H*(CH$_3$)$_2$), 5.56 (s, 2H, hydrogen in 4-position of pyrazole), 7.17$-$7.20, 7.41$-$7.44 (m, m, 9H, 6H, C$_6$*H*$_5$). $^{13}$C NMR: $\delta$ 8.71, 13.30 (carbons of 3- or 5-*C*H$_3$), 24.26 (OCH(*C*H$_3$)$_2$), 52.12 (d, $^2J_{\mathrm{PC}} = 50.9$ Hz, *C*H), 69.91 (d, $^2J_{\mathrm{PC}} = 8.5$ Hz, O*C*H(CH$_3$)$_2$), 104.58 (carbon of 4-position of pyrazole), 127.31, 127.55, 137.15, 141.19 (*C*$_6$H$_5$), 146.21, 150.81 (carbons of 3- and 5-positions of pyrazole), 228.79, 229.08 (*C*O). The $^{31}$P coupling with carbonyl carbons is not observed, due to the lower signal intensity. $^{31}$P NMR: $\delta$ 143.84. IR (cm$^{-1}$): $\nu_{\mathrm{CO}}$ 1797.1 vs, 1875.6 s. Anal. Calcd for C$_{40}$H$_{51}$N$_4$O$_5$PSnW: C, 47.98; H, 5.13; N, 5.99. Found: C, 47.88; H, 5.26; N, 6.23.

**Synthesis of 2d.** This complex was obtained by the reaction of **1b** with P(O-*i*-Pr)$_3$ at 80 °C for 3 h. The reaction mixture was purified by column chromatography using CH$_2$Cl$_2$/hexane (1/1 v/v) as eluent. Yield: 36%. $^1$H NMR: $\delta$ 1.19 (d, $^3J_{\mathrm{HH}} = 4.5$ Hz, 18H, OCH(C*H*$_3$)$_2$), 1.78, 2.46 (s, s, 6H, 6H, C*H*$_3$), 2.27 (s, 9H, C*H*$_3$C$_6$H$_4$), 4.37 (d, 1H, $^3J_{\mathrm{PH}} = 2.4$ Hz, C*H*), 4.39$-$4.45 (m, 3H, OC*H*(CH$_3$)$_2$), 5.56 (s, 2H, hydrogen in 4-position of pyrazole), 6.70, 7.30 (d, d, $^3J_{\mathrm{HH}} = 5.7$ Hz, 6H, 6H, C$_6$*H*$_4$). $^{31}$P NMR: $\delta$ 144.45. IR (cm$^{-1}$): $\nu_{\mathrm{CO}}$ 1794.5 vs, 1875.7 s. Anal. Calcd for C$_{43}$H$_{57}$N$_4$O$_5$PSnW·0.5CH$_2$Cl$_2$: C, 48.07; H, 5.39; N, 5.16. Found: C, 48.53; H, 5.96; N, 5.53.

**Reaction of 1 with P(OR)$_3$ (R = Me, Ph, *p*-MePh) To Give Complexes 3.** The reaction was carried out as detailed above for complexes **2**. The reaction temperature was higher for P(OMe)$_3$. After a similar workup, yellow-green crystals of **3** were obtained.

**Synthesis of 3a.** This complex was obtained by the reaction of **1a** or **1b** with P(OMe)$_3$ at 120 °C for 3 h. The reaction mixture was purified by column chromatography using ethyl acetate as eluent. Yield: 49% from **1a** and 44% from **1b**. $^1$H NMR: $\delta$ 2.36, 2.40 (s, s, 6H, 6H, C*H*$_3$), 3.48 (d, 6H, $^3J_{\mathrm{PH}} = 13.2$ Hz, OC*H*$_3$), 5.93 (s, 2H, hydrogen in 4-position of pyrazole), 6.00 (d, 1H, $^2J_{\mathrm{PH}} = 4.5$ Hz, C*H*). $^{13}$C NMR: $\delta$ 11.63, 16.11 (carbons of 3- or 5-*C*H$_3$), 57.23 (d, $^2J_{\mathrm{PC}} = 12.5$ Hz, O*C*H$_3$), 71.74 (d, $J_{\mathrm{PC}} = 38.3$ Hz, *C*H), 107.46 (carbon of 4-position of pyrazole), 139.05, 154.33 (carbons of 3- and 5-positions of pyrazole), 214.99, 220.55, 220.66 (*C*O). $^{31}$P NMR: $\delta$ 204.36. IR (cm$^{-1}$): $\nu_{\mathrm{CO}}$ 1781.4 vs, 1805.7 sh, 1908.8 vs. Anal. Calcd for C$_{16}$H$_{21}$N$_4$O$_5$PW: C, 34.06; H, 3.75; N, 9.93. Found: C, 34.04; H, 3.27; N, 9.48.

**Synthesis of 3b.** This complex was obtained by the reaction of **1a** or **1b** with P(OPh)$_3$ at 80 °C for 4 h. The reaction mixture was purified by column chromatography using ethyl acetate/hexane (1/1 v/v) as eluent. Yield: 46% from **1a** and 45% from **1b**. $^1$H NMR: $\delta$ 2.31, 2.39 (s, s, 6H, 6H, C*H*$_3$), 5.98 (s, 2H, hydrogen in 4-position of pyrazole), 6.37 (d, 1H, $^2J_{\mathrm{PH}} = 4.2$ Hz, C*H*), 6.65$-$6.68, 7.11$-$7.14, 7.22$-$7.25 (m, m, m, 4H, 2H, 4H, C$_6$*H*$_5$). $^{13}$C NMR: $\delta$ 11.52, 15.87 (carbons of 3- or 5-*C*H$_3$), 71.58 (d, $J_{\mathrm{PC}} = 46.1$ Hz, *C*H), 107.45 (carbon of 4-position of pyrazole), 120.93, 125.60, 130.03, 152.20 (*C*$_6$H$_5$), 139.11, 154.57 (carbons of 3- and 5-positions of pyrazole), 218.70, 218.81, 228.01 (*C*O). $^{31}$P NMR: $\delta$ 182.81. IR (cm$^{-1}$): $\nu_{\mathrm{CO}}$ 1794.4 vs, 1814.5 vs, 1916.6 vs. Anal. Calcd for C$_{26}$H$_{25}$N$_4$O$_5$PW: C, 45.37; H, 3.66; N, 8.14. Found: C, 45.51; H, 3.48; N, 8.36. In addition, this reaction was also carried out at 60 °C; only **3b** was isolated. At temperatures lower than 60 °C, no evident reaction was observed.

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**Synthesis of 3c.** This complex was obtained by the reaction of **1a** or **1b** with P(O-*p*-MePh)$_3$ at 100 °C for 4 h. The reaction mixture was purified by column chromatography using ethyl acetate/hexane (1/1 v/v) as eluent. Yield: 39% from **1a** and 42% from **1b**, respectively. $^1$H NMR: $\delta$ 2.29 (s, 6H, C$H_3C_6H_4$), 2.39, 2.43 (s, s, 6H, 6H, C$H_3$), 6.03 (s, 2H, hydrogen in 4-position of pyrazole), 6.38 (d, 1H, $^2J_{PH} = 3.0$ Hz, C$H$), 6.60, 7.05 (d, d, 4H, 4H, $^3J_{HH} = 6.0$ Hz, $C_6H_4$). $^{31}$P NMR: $\delta$ 181.78. IR (cm$^{-1}$): $\nu_{CO}$ 1800.8 vs, 1854.9 vs, 2003.8 vs. Anal. Calcd for $C_{28}H_{29}N_4O_5PW$: C, 46.95; H, 4.08; N, 7.82. Found: C, 47.28; H, 4.16; N, 7.86.

**X-ray Crystallographic Determination of 3b.** Yellow-green crystals of **3b** suitable for X-ray analyses were grown by slow diffusion of hexane into its $CH_2Cl_2$ solution at −10 °C. All intensity data were collected with a Rigaku Saturn CCD diffractometer, using graphite monochromated Mo Kα radiation ($\lambda = 0.710\,70$ Å). The structure was resolved by direct methods and refined by full-matrix least squares on $F^2$. All non-hydrogen atoms were refined anisotropically. Crystal data: $C_{26}H_{25}N_4O_5PW$, $M_r = 688.32$, monoclinic, space group $P2_1/c$, $a = 15.739(3)$ Å, $b = 9.6644(14)$ Å, $c = 16.808(3)$ Å, $\beta = 95.225(2)^o$, $V = 2546.1(7)$ Å$^3$, $Z = 4$, $D_{calcd} = 1.796$ g cm$^{-3}$, $T = 113(2)$ K, A total of 6071 unique reflections was used for refinement ($R_{int} = 0.0410$); final $R$ indices ($I \geq 2\sigma(I)$) were R1 = 0.0253 and wR2 = 0.0611.

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**Supporting Information Available:** Text, figures, and tables giving details of the reaction of **1** with PR$_3$ (R = Ph, *n*-Bu), crystallographic data, atom coordinates, thermal parameters, and bond distances and angles for **3b** and the decarbonylation products CH(3,5-Me$_2$Pz)$_2$(CO)$_2$(PR$_3$)WSnAr$_3$, and two ORTEP plots of the decarbonylation products. This material is available free of charge via the Internet at http://pubs.acs.org.

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