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Chemistry of Thermally Generated Transient Phosphanoxyl Complexes

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S Supporting Information

ABSTRACT: Investigations on the reactivity of the transiently formed phosphanoxyl complex $[(CO)_5W(Ph_2PO^{\bullet})]$, thermally generated from $[(CO)_5W(Ph_2PO^{-}TEMP)]$ in toluene, is presented. Apart from self-reactions, trapping of this radical complex was achieved using group 14 hydrides Ph_3EH (E = Si, Ge, Sn), leading to new phosphane complexes possessing a P–O–EPh₃ bonding motif and the corresponding TEMP-H as byproduct. Reaction pathways, derived from DFT calculations, clearly revealed the intermediacy of various openshell complexes; EPR measurements showed the presence of radicals, but unfortunately interpretation was not achieved.

INTRODUCTION

Among the commonly used nitroxides,¹ TEMPO (2,2,6,6-tetramethyl-piperidin-1-oxyl) plays an important role and is largely used in polymer chemistry, especially in living free radical polymerization.² Despite this huge interest and numerous reports on main-group-element derivatives of TEMPO (I)³ (Scheme 1), only a few examples of *P*-nitroxyl-substituted phosphanes and their complexes have been reported so far.

All known compounds of type **II** show the interesting feature of having a labile O–N bond that tends to undergo homolytic bond cleavage, yielding a radical of type **III**.

To date, there are no examples of P^{III} derivatives II (Z = lone pair) that are stable at ambient temperature, but transient

Scheme 1. Main-Group-Element Derivatives of TEMPO (I), Their Related Phosphorus Derivatives (II; R = Organic Substituent, Z = Electron Pair or ML_n for a Transition-Metal Complex), Radical Species (III) Derived from O–N Bond Cleavages in II, and a Phosphane Complex (IV) Trapping Product of III



derivatives formed at low temperature have been reported recently. One example led, after homolytic O–N bond cleavage and silyl migration, to an *O*-silyl phosphinate derivative.⁴ In a more recent study, we showed that a P^{III} derivative of **II** (Z = lone pair, R = Ph) can be obtained at low temperature via the reaction of diphenylphosphane with TEMPO,⁵ which also suffered from homolytic O–N bond cleavage to yield the corresponding P^V derivative (Z = O) as the final product.⁶

The knowledge of transition-metal phosphane complexes having the *P*-TEMPO ligand II $(Z = ML_n)$ is also very scarce, and only a few examples have been described. The first report was on a stable Au^I complex,⁷ shortly followed by an unstable W⁰ complex.⁸ In the case of the latter, hints were obtained that radicals are involved in synthesis and decomposition which seemed to occur through O-N bond homolysis, thus leading to the transient (and at that time unknown) phosphanoxyl complex III ($Z = ML_{n}$). Very recently, we were able to get access to a somewhat more stable complex II $(Z = W(CO)_{5}, R)$ = Ph)⁹ that enabled the first reaction studies. Again, a homolytic O-N bond cleavage led to the transient phosphanoxyl complex III that was trapped with the triphenylmethyl (trityl) radical to give complex IV. Furthermore, the use of this transient phosphanoxyl complex as a radical initiator for styrene polymerization was demonstrated⁹

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and DFT calculations provided information on the reaction mechanism.

Herein, investigations on the decomposition of a tungsten(0) complex having the ligand Ph_2P -OTEMP in the absence of trapping reagents are reported as well as trapping of the transient phosphanoxyl complex using group 14 hydrides Ph_3EH (E = Si, Ge, Sn). The reaction pathways have been studied via DFT calculations.

RESULTS AND DISCUSSION

First, the thermal stability of tungsten complex 1^9 in toluene solutions was investigated. Complex 1, which was stable at ambient temperature, started to decompose at elevated temperature, as monitored by ${}^{31}P{}^{1}H$ NMR spectroscopy: at 50 °C two resonances of products appeared high field of 1 but the conversion was quite slow. The same result with respect to selectivity and product ratio could be obtained by heating complex 1 for 3 h to 80 °C, leading to a much faster conversion into the two main products 2^{10} and 3 (ratio 1:1) (Scheme 2).

Scheme 2. Thermal Decomposition of Complex 1 in Toluene



This reaction pointed strongly to the intermediacy of transient phosphanoxyl complex 4, generated via O-N bond cleavage in complex 1. After column chromatography, 2 and 3 were obtained as beige powders and both compositions were confirmed by X-ray analysis.

Complex 2 showed a resonance in the ${}^{31}P{}^{1}H{}$ NMR spectrum at 128.0 ppm as part of a superposition of A₂, ABX, and AA'XX' spin systems (A, A', B = ${}^{31}P$, X = ${}^{183}W$); viable coupling constants were derived from gNMR^{11a} and the WinDNMR^{11b} simulation program (see the Supporting Information). The molecular structure of 2 is shown in Figure 1.

Complex 3 displayed overlapping AB and ABX spin systems (A, B = ³¹P, X = ¹⁸³W) in the ³¹P{¹H} NMR spectrum, showing two doublets at 126.3 ppm (² $J_{P,P}$ = 38.6 Hz and ¹ $J_{W,P}$ = 296.2 Hz) and at 27.5 ppm, the latter without a tungsten-phosphorus coupling. Figure 2 shows the molecular structure of complex 3, obtained from single-crystal X-ray diffraction studies. The mass spectrometry of 3 did not show the expected molecular ion peak (m/z 726.0) but instead the loss of one carbonyl ligand at the tungsten center (m/z 698.1). A LIFDI mass spectrometric measurement also showed the same result. However, NMR spectra and also elemental analysis prove the compound to be as shown in Figure 2 (and Scheme 2).

The thermal decomposition pathway of tungsten complex 1, involving only neutral closed-shell and radical species, were calculated at the TPSS-D3/def2-QZVP+COSMO-RS-(toluene)//TPSS-D3/def2-TZVP+COSMO(toluene) level of theory (see the Supporting Information for a fuller description of computational details).¹² Briefly, all structures were optimized at the TPSS-D3/def2-TZVP level using the COSMO solvation model for toluene, followed by vibrational frequency analysis to confirm the nature of obtained stationary



Figure 1. Molecular structure of complex 2 (50% probability level; hydrogen atoms omitted for clarity). Selected bond lengths (in Å) and angles (in deg): W1–P1 2.4823(12), W2–P2 2.4920(13) C1–P1 1.811(4), C7–P1 1.810(4), O1–P1 1.652(4), C18–P2 1.805(4), C24–P2 1.818(4), O1–P2 1.636(4); P1–O1–P2 144.04(16), W1–P1–C1 120.19(16), W1–P1–C7 110.61(15), W1–P1–O1 109.95(10), O1–P1–C1 107.09(19), O1–P1–C7 102.6(2), C1–P1–C7 104.9(2), W2–P2–C18 118.68(16), W2–P2–C24 112.69(15), W2–P2–O1 110.74(11), O1–P2–C18 107.0(2), O1–P2–C24 112.69(15), C18–P2–C24 103.6(2).

C18



Figure 2. Molecular structure of complex 3 (50% probability level; hydrogen atoms omitted for clarity). Selected bond lengths (in Å) and angles (in deg): W–P1 2.4894(8), C1–P1 1.812(3), C7–P1 1.818(3), O1–P1 1.657(2), O2–P2 1.473(2), O1–P2 1.605(2), C13–P2 1.799(3), C19–P2 1.790(3); O1–P1–W 118.55(8), P1–O1–P2 127.40(14), O2–P2–O1 113.03(13), W–P1–C1 111.42(10), W–P1–C7 119.08(11), O2–P2–C13 112.37(14), O2–P2–C19 115.28(14), O1–P–C1 97.06(13), C1–P1–C7 105.16(15), C13–P2–O1 106.60(13), C19–P2–O1 100.90(13), C13–P2–C19 107.73(15).

points (true minima and transition structures) and to provide thermal free energy corrections. Spin densities for open-shell radicals were computed according to a Mulliken population analysis. Final free energies (298 K, 1 atm) were computed by combining the TPSS-D3/def2-QZVP electronic energies, the COSMO-RS solvation free energies in toluene, and the aforementioned thermal free energy corrections and are used throughout our discussion.

The computed reaction paths for the decomposition of complex 1 via radical intermediates are depicted in Scheme 3.

Upon moderate heating in toluene, the homolytic O–N cleavage of complex 1 is only 14.8 kcal/mol endergonic to form phosphanoxyl radical 4 and is thus feasible, while P–O cleavage to form phosphanyl radical 5^{13} and direct W(CO)₅ or CO

Scheme 3. DFT Predicted Decomposition Reaction Paths of Tungsten Complex 1^a



"The free energy changes and barriers (ΔG and ΔG^* in kcal/mol) are shown above the arrows for each reaction step, respectively.

elimination are highly endergonic and thus forbidden. The resultant radicals TEMP (2,2,6,6-tetramethylpiperidinyl) and 4 (spin densities on central W, P and O: 0.32, 0.12 and 0.32 e, respectively) are unable to form stable homodimers via covalent N–N and O–O bonds or abstract a $W(CO)_5$ unit from complex 1. On the other hand, the radical 4 may easily convert into its slightly less stable, P-centered radical form 4' (spin densities on central W, P and O: 0.21, 0.31 and 0.22 e, respectively) via a $W(CO)_5$ shift. Without additional trapping reagent, the exergonic O-W and O-P radical couplings between two radicals 4 and between radicals 4 and 4' may form the complexes 2O and 3W, respectively. Note that complex 2O has two relatively loose and weak W...O and W...P bonds bound by only 19.4 and 10.9 kcal/mol, respectively. The sterically less hindered terminal oxygen of 20 and W(CO)₅ moiety of 3W can now easily be removed by the reactive radical TEMP, eventually leading to the observed products 2 and 3, respectively. Alternative complex 2 formation via O··P attack between radical 4 and complex 1 followed by TEMPO release is however kinetically less likely over an estimated barrier of about 24 kcal/mol.

To get further experimental evidence for the existence of the transient phosphanoxyl complex 4 (or other radicals), EPR measurements were performed by heating a solution of 1 in toluene- d_8 and following the decomposition. Unfortunately, we obtained only broad and complex spectra, and interpretations were not achieved (see the Supporting Information for more information), but the presence of radicals could be confirmed. Which role the latter play in the decomposition cannot be judged fully at this stage.

To make use of the transient formation, thermal reactions of *P*-nitroxyl complex 1 with various group 14 hydrides R_3EH (E = Si, Ge, Sn) were investigated. First, we examined the case of tri-*n*-butylstannane on the basis of the ability of the transiently formed tri-*n*-butylstannyl¹⁴ radical to act as an effective trap for (other) radical species (Scheme 4).

Scheme 4. Reaction of Complex 1 in Toluene with Different Group 14 Hydrides



According to the ³¹P{¹H} NMR spectroscopic monitoring the reaction starts slowly at room temperature to give selectively complex **6a** in 63% conversion (according to ³¹P{¹H} NMR integration) after 19 days. Gentle heating to 50 °C led to a faster and full conversion within 36 h, and the product was obtained as an orange oily liquid after extraction with *n*-pentane and washing at -50 °C. The formed amine (TEMP-H) could be detected in the reaction mixture by ¹H NMR spectroscopy. Complex **6a** showed a resonance in the ³¹P{¹H} NMR spectrum at 101.5 ppm with a direct tungstenphosphorus coupling of 278.5 Hz and ²*J* couplings with the tin nuclei: i.e. ²*J*(¹¹⁷Sn,³¹P) and ²*J*(¹¹⁹Sn,³¹P) values of 145.9 and 152.1 Hz, respectively. The ¹¹⁹Sn{¹H} NMR spectrum displayed a doublet at 142.2 ppm.

To obtain a trapping product that might possess a higher tendency to crystallize, the tin substituents were changed to phenyl. Heating a toluene solution of complex 1 to 50 °C with triphenylstannane led selectively to complex **6b** (Scheme 4). The reaction mixture of **6b** appeared as a brownish solution, from which, after solvent removal in vacuo, a brown oily compound was obtained. In the reaction mixture the amine (TEMP-H) could be detected by ¹H NMR spectroscopy. After column chromatography at low temperatures a beige powder was obtained. The ³¹P{¹H} NMR spectrum of **6b** showed a signal at 107.2 ppm with tungsten and tin satellites (¹*J*_{W,P} = 281.3 Hz, ²*J*(¹¹⁷Sn,³¹P) = 157.8 Hz, ²*J*(¹¹⁹Sn,³¹P) = 165.0 Hz). A doublet in the ¹¹⁹Sn{¹H} NMR spectrum showed a resonance at -81.5 ppm. The identity could be confirmed by X-ray single-crystal structure determination, which is shown in Figure 3.



Figure 3. Molecular structure of complex **6b** (50% probability level; hydrogen atoms omitted for clarity). Selected bond lengths (in Å) and angles (in deg): W–P 2.4981(5), C19–P 1.821(2), C25–P 1.832(2), O1–P 1.5822(13), O1–Sn 2.0279(13); P–O1–Sn 139.98(8), W–P–C19 111.97(7), W–P–C25 119.86(6), W–P–O1 111.59(6), O1–P–C19 103.18(8), O1–P–C25 106.56(8), C19–P–C25 102.04(9).

In the same manner as for the tin derivatives, the reaction with the germanium derivative Ph_3GeH was performed as well. Heating a mixture of complex **1** and triphenylgermane in toluene to 50 °C led to very good selectivity (95% according to ${}^{31}P{}^{1}H$ } NMR integration) to complex **6c** (Scheme 4). Here, the amine could be proven to be formed during the reaction by ${}^{1}H$ NMR spectroscopy, as in the reactions before. From the brown reaction mixture a colorless powder could be isolated by low-temperature column chromatography. A signal at 110.7 ppm in the ${}^{31}P{}^{1}H$ NMR spectrum with tungsten satellites (${}^{1}J_{W,P} = 287.4 \text{ Hz}$) could be assigned to the proposed product, from which the identity could be confirmed by an X-ray single-crystal structure determination, shown in Figure S1 in the Supporting Information.

The case of 1 and triphenylsilane (see Scheme 4) showed a different reaction behavior, and here the reaction with 1 equiv of the silane led only to a conversion of 68% ($^{31}P{^{1}H}$ NMR integration) of the desired product after heating to 50 °C. In addition to residual starting material, complexes 2 and 3 (about 10% each) were detected as well. Therefore, and to obtain a higher selectivity, 2 equiv of the silane was used, which yielded a 91% conversion to complex 6d. A ¹H NMR spectrum of the reaction solution showed the existence of the amine that is formed in the reaction as well. After low-temperature column chromatography a colorless powder was obtained showing a resonance signal in the ³¹P{¹H} NMR spectrum at 112.1 ppm with tungsten satellites (${}^{1}J_{W,P} = 293.1$ Hz). In the ²⁹Si{¹H} NMR spectrum a doublet with a resonance signal at -12.7 ppm appeared showing a ²J phosphorus silicon coupling of 19.0 Hz. The composition of 6d could be confirmed by an X-ray singlecrystal structure determination, which is shown in Figure S3 in the Supporting Information.

As all these products 6b-d are related to the lighter homologue complex IV, obtained via trapping the phosphanoxyl complex 4 with the trityl radical,⁹ a comparison of some bond lengths and angles with the group 14 elements from carbon to tin is presented in Table 1. It is clearly seen that the

Table 1. Comparison of Bond Lengths (in Å) and Bond Angles (in deg) of Complexes 6b-d (E = Sn, Ge, Si) and Their Lighter Homologue IV (E = C)

no. (E)	d(O-E)	d(P-O)	d(P-W)	$\angle (P-O-E)$
6b (Sn)	2.0279(13)	1.5822(13)	2.4981(5)	139.98(8)
6c (Ge)	1.809(3)	1.600(3)	2.4945(11)	140.67(17)
6d (Si)	1.662(2)	1.609(2)	2.4866(9)	146.27(17)
IV(C)	1.460(3)	1.6282(18)	2.5282(7)	131.96(16)

O-E (E = Sn, Ge, Si, C) bond lengths evidently decrease in the order of decreasing atomic radii: Sn > Ge > Si > C. The adjacent P−O bond lengths slightly but consistently increase, likely due to increasing steric hindrance from the bulky EPh₃ group from carbon to tin. Though the P−O−E bond angles are increased in the order Sn < Ge < Si, the smallest angle of 132° is found for E = C. DFT calculations showed that this is very likely due to the lack of suitable empty d valence orbitals that are present for heavier group 14 elements to accept π -electron donation from central oxygen 2p lone pairs. Consistent with the largest P−O−Si bond angle, the best O(2p) → E(nd) π -electron donation is expected for E = Si due to both the short O−Si bond length and low lying Si 3d orbital; due to similar O(2p) → P(3d) π -electron donation, the P−O−E moieties show some conjugated π -system nature, as evidenced by their

large bond angles. Consistent with such a subtle difference between C and its heavier analogues, slightly decreasing P-W bond lengths are also observed in the order from Sn over Ge to Si except for E = C.

Further extensive DFT calculations were also performed to understand the observed selectivity and reactivity trends for the trapping of phosphanoxyl complex 4 using the group 14 hydrides Ph_3EH (E = Si, Ge, Sn). The predicted reaction paths are compared in Scheme 5 for the tin and silicon derivatives.

Scheme 5. DFT Predicted Reaction Pathways for the Reaction between Tungsten Complex 1 and Group 14 Hydrides $Ph_3EH (E = Si, Sn)^a$



^{*a*}The free energy changes and barriers (ΔG and ΔG^* in kcal/mol) are shown above the arrows for each reaction step, respectively, with red italic numbers for E = Si.

Initiated by the O-N bond cleavage of complex 1, the resultant radicals 4 and TEMP turn out to be reactive with respect to hydrogen atom abstraction from the E-H bond of hydrides Ph_3EH (E = Si, Sn). Both H abstractions from Ph₃SnH by 4 and TEMP are exergonic over a rather low barrier to form the transient radical Ph₃Sn[•], with the latter being kinetically less but thermodynamically more favorable. The temporarily formed complex 4H ((CO)₅W(Ph₂POH)) can be easily removed by another TEMP radical via H abstraction from the O-H site to regenerate 4, which is -7.0 kcal/mol exergonic and almost barrierless. The transient radical Ph₃Sn[•] can be easily coupled with radicals 4 and TEMP to form complexes 6b and TEMP-SnPh₃, respectively, with the latter being easily removed by another radical 4 via radical replacement at the tin center to form complex 6b. The overall reaction is thus initiated by the O–N bond cleavage of complex 1, followed by formally selective H abstraction by TEMP from Ph₃EH and radical coupling between transient 4 and Ph₃Sn[•]. A very similar mechanism is also found for the reaction between complex 1 and Ph₃SiH, except for more difficult H abstractions from the stronger Si-H bond that eventually leads to a 6.3 kcal/mol higher overall barrier at the rate-limiting H abstraction

step. This fact is consistent with the observed reactivity trend for group 14 hydrides as radical trapping reagents.

CONCLUSION

It was shown that *P*-nitroxyl phosphane complexes undergo homolytic bond cleavage upon gentle heating. The transient phosphanoxyl complex, formed preferentially via O–N bond cleavage, can be trapped effectively with group 14 hydrides, giving the corresponding product complexes having a P–O–E motif (E = Si, Ge, Sn). In the absence of any trapping reagent two complexes are formed in a 1:1 ratio which are (mainly) derived from phosphanyl and phosphanoxyl complexes and/or rearranged species, which was analyzed via state of the art DFT calculations. Furthermore, insights into the bond-breaking and -forming processes of different transient radical species were obtained. EPR measurements also showed that open-shell molecules are formed during the thermolysis, but a satisfactory assignment of their role was not achieved.

EXPERIMENTAL SECTION

All manipulations involving air- and moisture-sensitive compounds were carried out under an atmosphere of purified argon by using standard Schlenk-line techniques or in a glovebox. Solvents were dried with appropriate drying agents and degassed before use. The ¹H, ¹³C{¹H}, and ³¹P{¹H} NMR spectroscopic data (δ in ppm) were recorded unless otherwise noted at 25 °C on a Bruker DMX 300 or a Bruker AV III 500 MHz Prodigy NMR spectrometer. The standard for ¹H, ¹³C, and ²⁹Si NMR is tetramethylsilane (Me₄Si), for ³¹P NMR 85% phosphorus acid (H_3PO_4), and for ¹¹⁹Sn NMR tetramethylstannane (Me₄Sn). Mass spectra were recorded on a MAT 95 XL Thermo Finnigan spectrometer and a MAT 90 Thermo Finnigan sector instrument equipped with a LIFDI ion source (Linden CMS) (selected data given). Infrared spectra were recorded on a Thermo Nicolet 380 FT-IR or a Bruker Alpha Diamond ATR FTIR spectrometer (selected data given). Melting points were determined using a Buchi Type S apparatus with samples sealed in capillaries under argon and are uncorrected. Elemental analyses were performed using an ElementarVarioEL instrument.

Complexes 2 and 3. Complex 1 (665 mg, 1 mmol) was dissolved in toluene (5 mL) and the solution heated to 80 °C for 3 h. Volatiles were removed under reduced pressure $(3 \times 10^{-2} \text{ mbar})$ from the dark brown solution. The residue was purified by column chromatography at -20 °C (SiO₂, h = 6 cm, ø = 4 cm; eluent petroleum ether/Et₂O 4/ 1). Evaporation of the first fraction gave 2 as a beige solid after washing with Et_2O and *n*-pentane. Mp: 189 °C. Yield: 140 mg (0.14 mmol, 28%). ¹H NMR (300.13 MHz, CDCl₃): δ 7.31–7.51 (m, 20 H, o-, m- and p-H_{Ph}). ¹³C{¹H} NMR (75.48 MHz, CDCl₃): δ 128.6 ("t", ${}^{3}J_{P,C} = 4.9$ Hz, m-C_{Ph}), 131.1 ("t", ${}^{2}J_{P,C} = 7.1$ Hz, o-C_{Ph}), 131.4 (s, p- C_{Ph}), 139.0 ("t", ¹ $J_{P,C}$ = 20.4 Hz, *ipso*- C_{Ph}), 196.5 ("t" _{sav} ² $J_{P,C}$ = 7.6 Hz, ¹ $J_{W,C}$ = 126.3 Hz *cis*-CO), 221.0 ("t", ² $J_{P,C}$ = 14.3 Hz, *trans*-CO). ³¹P{¹H} NMR (121.51 MHz, CDCl₃): δ 128.0 (s_{Sat} ¹J_{W,P} = 301.0 Hz_n ${}^{2}J_{\rm P,P} = 64.7$ Hz, ${}^{3}J_{\rm W,P} = 1.4$ Hz). IR (ν (CO), neat): $\tilde{\nu}/{\rm cm}^{-1}$ 2072 (s), 1996 (w), 1904 (s), 857 (s, $\nu(P-O-P)$). MS: calcd for $C_{34}H_{20}O_{11}P_2^{184}W_2$, m/z 1034.2; found (EI, 70 eV, ¹⁸⁴W) m/z (%) 1034.1 $[M]^{\bullet+}$ (27). Anal. Calcd for $C_{34}H_{20}O_{11}P_2W_2$: C, 39.49; H, 1.95. Found: C, 39.45; H, 1.92.

Evaporation of the third fraction gave **3** as a beige solid after washing with Et₂O and *n*-pentane. Mp: 128 °C. Yield: 80 mg (0.11 mmol, 22%). ¹H NMR (500.13 MHz, C_6D_6): δ 6.90–6.95 (m, 10 H, *m*- and *p*-H_{Ph} of [W]PPh and *m*-H_{Ph} of (O)PPh), 6.95–7.00 (m, 2 H, *p*-H_{Ph} of (O)PPh), 7.66–7.72 (m, 4 H, *o*-H_{Ph} of [W]PPh), 7.72–7.78 (m, 4 H, *o*-H_{Ph} of (O)PPh). ¹³C{¹H} NMR (125.77 MHz, C_6D_6): δ 128.4 (d, ³*J*_{P,C} = 10.3 Hz, *m*-C_{Ph} of [W]PPh), 128.7 (d, ³*J*_{P,C} = 13.5 Hz, *m*-C_{Ph} of (O)PPh), 131.4 (d, ²*J*_{P,C} = 10.6 Hz, *o*-C_{Ph} of (O)PPh), 131.5 (d, ⁴*J*_{P,C} = 1.9 Hz, *p*-C_{Ph} of [W]PPh), 132.0 (d, ²*J*_{P,C} = 14.8 Hz, *o*-C_{Ph} of [W]PPh), 132.1 (d, ⁴*J*_{P,C} = 2.9 Hz, *p*-C_{Ph} of (O)PPh), 133.2 (d, ¹*J*_{P,C} = 137.5 Hz, *ipso*-C_{Ph} of (O)PPh), 138.4 (dd, ¹*J*_{P,C} = 41.0 Hz, ³*J*_{P,C} = 2.0

Hz, *ipso*-C_{Ph} of [W]PPh), 196.8 $(d_{Sav}{}^{2}J_{P,C} = 7.8 \text{ Hz}, {}^{1}J_{W,C} = 126.0 \text{ Hz},$ $cis-CO), 199.5 <math>(d_{Sav}{}^{2}J_{P,C} = 28.2 \text{ Hz}, {}^{1}J_{W,C} = 138.7 \text{ Hz}, trans-CO).$ ${}^{31}P{}^{1}H} \text{NMR} (202.48 \text{ MHz}, C_6D_6): \delta 27.5 <math>(d_{Sav}{}^{2}J_{P,P} = 38.6 \text{ Hz}, {}^{1}J_{P,C} = 137.5 \text{ Hz}, P(O)), 126.3 <math>(d_{Sav}{}^{2}J_{P,P} = 38.6 \text{ Hz}, {}^{1}J_{W,P} = 296.2 \text{ Hz},$ [W]P). IR (ν (CO), neat): $\tilde{\nu}/\text{cm}^{-1}$ 2073 (m), 1993 (w), 1917 (vs), 1233 (s, ν (O–P(O))), 893 (vs, ν (P–O–P)). MS: calcd for C₂₉H₂₀O₇P₂¹⁸⁴W, *m/z* 726.0; found (EI, 70 eV, {}^{184}W), *m/z* (%) 698.1 [M – CO]^{\bullet+} (10), 92.1 [toluene]^{+\bullet} (98). Anal. Calcd for C₂₉H₂₀O₇P₂W: C, 47.96; H, 2.78. Found: C, 48.02; H, 2.74.

Complex 6a. Complex 1 (665 mg, 1 mmol) was dissolved in toluene (5 mL), and tri-n-butylstannane (292 mg,1 mmol) was added. The solution was then heated to 50 °C for 36 h, and volatiles were removed under reduced pressure $(3 \times 10^{-2} \text{ mbar})$ from the yellow solution. The oily dark orange residue was extracted with *n*-pentane and recrystallized from *n*-pentane at -50 °C to yield a light orange oil (at room temperature). Yield: 312 mg (0.38 mmol, 38%). ¹H NMR (300.13 MHz, CDCl₃): δ 0.88 (t, 9 H, CH₃), 0.99–1.12 (m, 6 H, Sn-CH₂),), 1.19-1.34 (m, 6 H, CH₂-CH₃), 1.40-1.55 (m, 6 H, CH₂-CH2-CH2), 7.37-7.49 (m, 6 H, m- and p-HPh), 7.50-7.64 (m, 4 H, o- H_{ph}). ¹³C{¹H} NMR (75.48 MHz, CDCl₃): δ 13.7 (s, CH₃), 17.6 (s_{Sat}) ${}^{1}J_{\text{Sn,C}} = 334.2 \text{ Hz}, {}^{1}J_{\text{Sn,C}} = 349.7 \text{ Hz}, \text{ Sn-CH}_{2}$, 27.1 (s, CH₂-CH₃), 27.7 (s, CH₂-CH₂-CH₂), 128.3 (d, ${}^{3}J_{P,C} = 9.4$ Hz, m-C_{Ph}), 130.1 (d, ${}^{4}J_{P,C} =$ 1.9 Hz, p-C_{Ph}), 130.4 (d, ${}^{2}J_{P,C} = 13.7$ Hz, o-C_{Ph}), 144.8 (d, ${}^{1}J_{P,C} = 37.0$ Hz, *ipso*-C_{Ph}), 198.1 ($d_{Sat}^{2}J_{P,C} = 8.5$ Hz, ${}^{1}J_{W,C} = 126.0$ Hz, *cis*-CO), 201.3 ($d_{1}^{2}J_{P,C} = 22.0$ Hz, *trans*-CO). ${}^{31}P{}^{1}H$ NMR (121.51 MHz, CDCl₃): δ 101.5 (s_{Sat} , ${}^{1}J_{W,P}$ = 278.5 Hz, ${}^{2}J_{Sn,P}$ = 145.91 Hz, ${}^{2}J_{Sn,P}$ = 152.1 Hz). ${}^{119}Sn{}^{1}H{}$ NMR (111.87 MHz, CDCl₃): δ 142.2 (d, ${}^{2}J_{Sn,P}$ = 152.1 Hz). IR (ν (CO), neat): $\tilde{\nu}/cm^{-1}$ 2066 (m), 1977 (w), 1900 (vs). MS: calcd for $C_{29}H_{37}O_6P^{118}Sn^{184}W$, m/z 814.0; found (EI, 70 eV, ¹¹⁸Sn, ¹⁸⁴W), m/z (%) 814.1 [M]^{•+} (2).

Complex 6b. Complex 1 (665 mg, 1 mmol) was dissolved in toluene (5 mL), and triphenylstannane (352 mg, 0.26 mL, 1 mmol) was added. The solution was then heated to 50 °C for 36 h, and volatiles were removed under reduced pressure $(3 \times 10^{-2} \text{ mbar})$ from the brown solution. Column chromatography was performed at -20°C (Al₂O₃, h = 3 cm, $\emptyset = 2$ cm; eluent, petroleum ether/CH₂Cl₂ 1/1), yielding the product as a beige powder after evaporation of the solvent and recrystallization from toluene and *n*-pentane at lower temperature. Mp: 107 °C. Yield: 325 mg (0.37 mmol, 37%). ¹H NMR (500.13 MHz, C₆D₆): δ 6.86-6.96 (m, 6 H, m- and p-H_{Ph} of PPh), 7.05-7.14 (m, 9 H, m- and p-H_{Ph} of SnPh), 7.33–7.49 (m_{Sat} , ${}^{3}J_{Sn,H}$ = 52.9 Hz, (III, $j = 11, m^2$ and $p = 11p_h$ of Sin II, j = 52.5, j = 12.5, j = 12. $(s_{Sav}^{2}J_{Sn,C} = 47.0 \text{ Hz}, ^{2}J_{Sn,C} = 48.7 \text{ Hz}, o-C_{Ph} \text{ of SnPh}), 137.6 (s_{Sav}^{2})$ ${}^{1}J_{\text{Sn,C}} = 611.2 \text{ Hz}, {}^{1}J_{\text{Sn,C}} = 639.2 \text{ Hz}, ipso-C_{\text{Ph}} \text{ of SnPh}), 144.41(d, {}^{1}J_{\text{P,C}})$ = 37.1 Hz, *ipso*-C_{Ph} of PPh), 198.3 $(d_{Sav}^{2}J_{P,C} = 8.4 \text{ Hz}, {}^{1}J_{W,C} = 125.8 \text{ Hz}$, *cis*-CO), 201.3 $(d_{Sav}^{2}J_{P,C} = 22.6 \text{ Hz}, {}^{1}J_{W,C} = 139.8 \text{ Hz}$, *trans*-CO). ³¹P{¹H} NMR (202.48 MHz, C₆D₆): δ 107.2 (s_{Sat} ¹J_{W,P} = 281.3 Hz, ${}^{2}J_{\text{Sn,P}} = 157.8 \text{ Hz}, {}^{2}J_{\text{Sn,P}} = 165.0 \text{ Hz}). {}^{119}\text{Sn}{}^{1}\text{H}$ inverse gated NMR (186.50 MHz, C₆D₆): δ -81.5 (d_{Sat}, ²J_{Sn,P} = 165.0 Hz, ¹J_{Sn,C} = 639.2 Hz). IR (ν (CO), neat): $\tilde{\nu}$ /cm⁻¹ 2067 (m), 1974 (s), 1907 (vs). MS: calcd for $C_{35}H_{25}O_6P^{118}Sn^{184}W$, m/z 874.0; found (EI, 70 eV, ¹¹⁸Sn, ¹⁸⁴W), m/z (%) 874.0 [M]^{•+} (11). Anal. Calcd for $C_{35}H_{25}O_6PSnW$: C, 48.04; H, 2.88. Found: C, 48.00; H, 2.92.

Complex 6c. Complex 1 (665 mg, 1 mmol) was dissolved in toluene (5 mL), and triphenylgermane (305 mg, 1 mmol) was added. The solution was then heated to 50 °C for 41 h, and volatiles were removed under reduced pressure (3×10^{-2} mbar) from the brown solution. The oily brown residue was purified by column chromatography at -20 °C (Al₂O₃, h = 3 cm, $\theta = 2$ cm; eluent, petrol eumether/CH₂Cl₂ 1/0.2). Evaporation of the first fraction gave a beige powder that was recrystallized from toluene and *n*-pentane at lower temperature. Mp: 146 °C. Yield: 300 mg (0.36 mmol, 36%). ¹H NMR (500.13 MHz, C₆D₆): δ 6.87–6.94 (m, 6 H, *m*- and *p*-H_{Ph} of PPh), 7.03–7.12 (m, 9 H, *m*- and *p*-H_{Ph} of GePh), 7.44–7.51 (m, 6 H,

o-H_{Ph} of GePh), 7.51–7.57 (m, 4 H, o-H_{Ph} of PPh). ¹³C{¹H} NMR (125.77 MHz, C₆D₆): δ 127.9 (d, ³J_{P,C} = 9.6 Hz, *m*-C_{Ph} of PPh), 128.5 (s, *m*-C_{Ph} of GePh), 130.1 (d, ⁴J_{P,C} = 1.8 Hz, *p*-C_{Ph} of PPh), 130.4 (s, *p*-C_{Ph} of GePh), 130.8 (d, ²J_{P,C} = 13.9 Hz, o-C_{Ph} of PPh), 130.9 (s, *ipso*-C_{Ph} of GePh), 134.4 (s, *o*-C_{Ph} of GePh), 142.1 (d, ¹J_{P,C} = 38.2 Hz, *ipso*-C_{Ph} of PPh), 197.6 (d_{Sav} ²J_{P,C} = 8.2 Hz, ¹J_{W,C} = 125.9 Hz, *cis*-CO), 200.1 (d_{Sav} ²J_{P,C} = 24.0 Hz, ¹J_{W,C} = 138.9 Hz, *trans*-CO). ³¹P{¹H} NMR (202.48 MHz, C₆D₆): δ 110.7 (s_{Sav} ¹J_{W,P} = 287.4 Hz). IR (ν (CO), neat): $\tilde{\nu}/cm^{-1}$ 2070 (s), 1917 (vs). MS: calcd for C₃₅H₂₅⁷²GeO₆P¹⁸⁴W, *m*/z 828.0; found (EI, 70 eV, ⁷²Ge, ¹⁸⁴W), *m*/z (%) 827.9 [M]^{*+} (13). Anal. Calcd for C₃₅H₂₅GeO₆PW: C, 50.71; H, 3.04. Found: C, 50.75; H, 3.06.

Complex 6d. Complex 1 (665 mg, 1 mmol) was dissolved in toluene (5 mL), and triphenylsilane (520 mg, 2 mmol) was added. The solution was then heated to 50 °C for 46 h, and volatiles were removed under reduced pressure (3 \times 10⁻² mbar) from the brown solution. The brown oily residue was further purified by column chromatography at -20 °C (SiO₂, h = 2 cm, $\theta = 2$ cm; eluent, petroleum ether/CH₂Cl₂ 1/0.5). Evaporation of the first fraction gave a beige powder that was further recrystallized from toluene and npentane at lower temperature. Mp: 159 °C. Yield: 350 mg (0.45 mmol, 45%). ¹H NMR (500.13 MHz, C₆D₆): δ 6.88–6.95 (m, 6 H, m- and p-H_{Ph} of PPh), 7.07-7.13 (m, 6 H, m- and p-H_{Ph} of SiPh), 7.13-7.19 (m, 3 H, p-H_{Ph} of SiPh), 7.52-7.68 (m, 10 H, o-H_{Ph} of SiPh and PPh). ¹³C{¹H} NMR (125.77 MHz, C_6D_6): δ 128.4 (s, *m*- C_{Ph} of SiPh), 128.5 $(d_1 J_{PC} = 10.0 \text{ Hz}, m-C_{Ph} \text{ of PPh}), 130.8 (s, p-C_{Ph} \text{ of SiPh}), 130.9 (d, m-C_{Ph} \text{ of SiPh}), 130.9 (d, m-C_{$ ${}^{4}J_{P,C}$ = 1.8 Hz, *p*-C_{Ph} of PPh), 131.0 (d, ${}^{2}J_{P,C}$ = 14.6 Hz, *o*-C_{Ph} of PPh), 133.4 $(s_{Sav}^{-1}J_{C,Si} = 83.1 \text{ Hz}, ipso-C_{Ph} \text{ of SiPh}), 135.9 (s, o-C_{Ph} \text{ of})$ 135.4 (s_{sav}) $_{C,Si}$ = 05.1 Hz, $\mu_{por-Cph}$ of Sin H₂, 155.7 (s, c C_{Ph} or GePh), 141.6 (d, $^{1}J_{P,C}$ = 41.5 Hz, $ipso-C_{Ph}$ of PPh), 197.3 (d_{sav} $^{2}J_{P,C}$ = 8.0 Hz, $^{1}J_{W,C}$ = 125.8 Hz, cis-CO), 199.5 (d_{sav} $^{2}J_{P,C}$ = 25.5 Hz, $^{1}J_{W,C}$ = 137.9 Hz, trans-CO). $^{29}Si{}^{1}H$ DEPT20 NMR (99.36 MHz, $C_{6}D_{6}$): δ -12.7 (d_{sav} $^{2}J_{P,Si}$ = 19.0 Hz, $^{1}J_{C,Si}$ = 83.1 Hz). $^{31}P{}^{1}H$ NMR (202.48 MHz, $C_{6}D_{6}$): δ 112.1 (s_{sav} $^{1}J_{W,P}$ = 293.1 Hz). IR (ν(CO), neat): $\tilde{\nu}/$ cm⁻¹ 2073 (m), 1983 (w), 1921 (vs). MS: calcd for C₃₅H₂₅O₆PSi¹⁸⁴W, m/z 784.1; found (EI, 70 eV, ¹⁸⁴W), m/z (%) 784.1 [M]^{•+} (13). Anal. Calcd for C35H25O6PSiW: C, 53.59; H, 3.21. Found: C, 53.60; H, 3.29.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.7b00347.

Crystallographic information for complexes 2, 3, and 6b-d, NMR simulation of complex 2, NMR spectra of the obtained compounds, information on the EPR results, and details of the theoretical calculations (PDF)

Cartesian coordinates of the calculated molecules, transition states and intermediates(PDF)

Accession Codes

CCDC 1545939–1545942 and 974093 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/ cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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Article

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