

Phosphanoxyl Complexes

International Edition: DOI: 10.1002/anie.201608169 German Edition: DOI: 10.1002/ange.201608169

Strong Evidence of a Phosphanoxyl Complex: Formation, Bonding, and **Reactivity of Ligated Phosphorus Analogues of Nitroxides**

Tobias Heurich, Vitaly Nesterov, Gregor Schnakenburg, Zheng-Wang Qu,* Stefan Grimme, Khatera Hazin, Derek P. Gates, Marianne Engeser, and Rainer Streubel*

Dedicated to Professor Masaaki Yoshifuji on the occasion of his 75th birthday

Abstract: Facile access to $[W(CO)_5(Ph_2P-OTEMP)]$ is used to initiate a study on the generation, properties, and reactions of transient phosphanoxyl complexes $[ML_n(R_2PO)]$, the first example of which could be trapped via heterocoupling with the trityl radical. It is also demonstrated that the phosphorus nitroxyl complex acts as radical initiator in the polymerization of styrene. The quest for P–O versus O–N bond homolysis, as well as the initial steps of the polymerization were studied by DFT methods.

Over the last decades, stable nitroxides^[1] (or nitroxyls or aminoxyls), such as TEMPO (2,2,6,6-tetramethyl piperidin-1oxyl) and O-bound main-group element derivatives I (Scheme 1) have received increasing attention in molecular and polymer synthesis. For example, the thermally induced reverse homolysis of activated alkoxyamines I (E = C) has recently been recognized as a facile process for the clean generation of C-centered radicals and led to various fundamental radical reactions based on carbon radical/nitroxide pairs^[2] and/or was used in living radical polymerizations,^[3] making use of the persistent radical effect.^[2,4] Despite this long-standing research interest and numerous reports on main-group element derivatives of TEMPO I^[5] (Scheme 1),

[*]	T. Heurich, Dr. G. Schnakenburg, Prof. Dr. R. Streubel Institut für Anorganische Chemie Rheinische Friedrich-Wilhelms-Universität Bonn
	Gerhard-Domagk-Strasse 1, 53121 Bonn (Germany) E-mail: r.streubel@uni-bonn.de
	Dr. V. Nesterov Institut für Siliciumchemie Technische Universität München Lichtenbergstrasse 4, 85748 Garching (Germany)
	Dr. ZW. Qu, Prof. Dr. S. Grimme Mulliken Center for Theoretical Chemistry Rheinische Friedrich-Wilhelms-Universität Bonn Beringstrasse 4, 53115 Bonn (Germany) E-mail: qu@thch.uni-bonn.de
	K. Hazin, Prof. Dr. D. P. Gates Chemistry Department, University of British Columbia 2036 Main Mall, Vancouver, BC, V6T 1Z1 (Canada)
	PrivDoz. Dr. M. Engeser Kekulé-Institut für Organische Chemie und Biochemie Rheinische Friedrich-Wilhelms-Universität Bonn Gerhard-Domagk-Strasse 1, 53121 Bonn (Germany)
D	Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under http://dx.doi.org/10. 1002/anie.201608169.



Scheme 1. Oxygen-bound main-group-element derivatives of TEMPO (I), related phosphorus derivatives (II; R = organic substituent, Z = electron pair, or ML, for a transition-metal complex), and radical species (III, IV) derived from P-O and O-N bond cleavages in II.

stable *P*-OTEMP phosphanes II (Z = electron pair) are unknown.^[6] But there are reports on transient derivatives formed at low temperature. In one case, the intermediate P-OTEMP phosphane generated different radicals via homolytic O-N bond cleavage leading then subsequently to silvl migration to give an O-silvl phosphinate derivative.^[7] We have recently shown that a P^{III} derivative of II (R = Ph, Z = lone pair), obtained at low temperatures by the reaction of diphenylphosphane with TEMPO, yielded the corresponding P^{V} derivative (Z=O) via homolytic O-N bond cleavage as the key reaction step.^[8] Transition-metal complexes II (Z =ML_n) were mentioned only briefly, as a stable Au^{I[9]} or a thermally unstable W⁰ complex.^[10] It was proposed that decomposition of O-phosphano hydroxylamines of the general formula $R_2 NOPR'_2^{[6,11]}$ proceeds via homolytic O-N bond cleavage^[11a] to give rearrangement products R₂NP-(O)R'₂. Therefore, our aim was to develop suitable transitionmetal complexes having P^{III}-II as a ligand to enable the study of homolytic P-O or O-N bond cleavage. In the long term, the hitherto unknown stable κP -phosphanoxyl complexes IV $(Z = ML_n)$, somehow related to functional phosphanyl complexes III $(Z = ML_n)$,^[10,12] could thus become accessible.

Herein, facile methods to synthesize a representative phosphane metal complex II bearing the O-bound TEMPO substituent are reported. A trapping reaction revealed that II is a precursor for a transient phosphanoxyl complex IV as well as a radical initiator for the polymerization of styrene. Stateof-the-art DFT calculations provide insight into reaction mechanisms and molecular properties, such as spin density distributions of various open-shell species.

Starting from pentacarbonyl tungsten(0) complexes 1 and 3, the *P*-nitroxyl substituted phosphane tungsten complex 4 was obtained via two different routes (i, ii): (i) used a lithium/ chlorine exchange of chlorophosphane complex $\mathbf{1}^{[13]}$ with tBuLi to generate the lithium phosphanido tungsten complex

Angew. Chem. Int. Ed. 2016, 55, 1-6

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Scheme 2. Syntheses of complex 4 via routes i and ii.

2 which then reacted at -40 °C with two equivalents of TEMPO to give **4** (Scheme 2). Compound **4** was obtained as a colorless powder after column chromatography at low temperature. Improved results were achieved when phosphanido complex **2** was generated by deprotonation of phosphane complex **3**^[14] with *n*BuLi and reacted in situ with 2 equivalents of TEMPO under otherwise identical conditions (55% isolated yield of complex **4** which exhibited a resonance at 137.9 ppm (¹J_{W,P} = 286.7 Hz) in the ³¹P{¹H} NMR spectrum). The formation of TEMPOLi as by-product suggests a single-electron transfer oxidation reaction by TEMPO (see Scheme S2 in the Supporting Information).

Alternatively, in route (ii) diphenylphosphane complex **3** reacted with 2 equivalents of TEMPO (directly) at ambient temperature (Scheme 2) giving complex **4** in 85 % yield after column chromatography. In this reaction we assumed the intermediacy of the transient diphenylphosphanyl complex^[15a] obtained after hydrogen abstraction and trapped with the second equivalent of TEMPO;^[15b] this proposal was further examined by DFT calculations (see Scheme S1).

The structure of **4**, confirmed by single-crystal X-ray diffraction analysis (Figure 1), showed P–O1 and N–O1 bonds of 1.639(2) Å and 1.482(3) Å, respectively, and a small bond angle sum at phosphorus of about 299.1°.



Figure 1. Molecular structure of complex **4** (thermal ellipsoids set at 50% probability; hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: P–W 2.5194(6), C10–P 1.831(2), C16–P 1.830(2), O1–P 1.639(2), N–O1 1.482(3); O1-P-W 121.66(6), C10-P-W 112.58(8), C16-P-W 119.40(8), N-O1-P 118.9(2), O1-P-C10 99.6(2), O1-P-C16 101.4(2), C16-P-C10 98.2(2).

These data are comparable to those of the *P*-OTEMP phosphane Au^I complex^[9] (d(P-O) and d(N-O) are 1.631(3) Å and 1.490(5) Å, respectively); the bond angle sum at phosphorus is significantly larger (308.3°) than in complex **4**.

To investigate the *P*-nitroxyl phosphane complex **4** as a potential source of free radicals, open-shell species derived after homolytic P–O and O–N bond cleavage were examined by DFT calculations at the TPSS-D3/def2-TZVP + COSMO (THF) level, while better reaction free energies are obtained at the TPSS-D3/def2-QZVP + COSMO-RS (THF) level of theory; the final free energies at 298.15 K and 1 atm are used in our discussion.^[16-24] The initial O–N cleavage (ΔG = 15.0 kcal mol⁻¹) of complex **4** leading to O-centered radical **6** is much more favorable than the P–O cleavage (ΔG = 30.0 kcal mol⁻¹) leading to the P-centered radical **5** (Scheme 3). Though the direct P–O cleavage of complex **4**



Scheme 3. DFT predicted spin densities on $W(CO)_5$, P and O centers for key radical species; the dashed line with a dot indicates a singleelectron dative bond; the radical center is indicated by a bold dot in each structure.

seems less likely under ambient conditions, it can still be induced by a temperature increase of about 300 K (a result of favorable entropy effects) and/or by reactive radicals, such as **6**. Here, the P–O cleavage via the addition of O-centered radical **6** at the P center of **4** is $-21.8 \text{ kcal mol}^{-1}$ exergonic over a free energy barrier of about 24.4 kcal mol⁻¹, thus can be more favorable than the direct P–O cleavage of complex **4**. To gain more insight into the electronic structures of various radical species, the computed spin density values are shown in Scheme 3.

The intermediate $\mathbf{5}^{[15a]}$ is a P-centered radical with only a small spin density population on the adjacent W(CO)₅ moiety, though the spin density is less localized than in its metal-free counterpart **7**. In contrast, the spin density within the κP -phosphanoxyl complex **6** is highly delocalized on both the O center and the W(CO)₅ moiety with only a small spin density population on the central P center, thus it may act as O-centered radical during further reactions. Note that because of such a high spin density population (or reduced electron density) on the W(CO)₅ moiety, the W–P bonding of complex **6** becomes 12.1 kcalmol⁻¹ weaker than that of complex **4** and thus the group could be more easily transferred to other ligands.^[25] Furthermore, the W(CO)₅

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moiety can be easily shifted from the P to the O center within complex **6**, which is 1.6 kcal mol⁻¹ endergonic over a rather low barrier of only 3.5 kcal mol⁻¹. The resultant κO -phosphanoyl (or phosphinoyl^[11c]) complex **8** shows even more delocalized spin density population on the P and O centers as well as the W(CO)₅ moiety, with a stronger P-centered radical nature than **6**. The metal-free counterpart, the phosphinoyl **9**, is clearly dominated by the P-centered radical nature which had been demonstrated in various reactions.^[26]

First solid experimental evidence on the formation of intermediate phosphanoxyl complex $6^{[10b]}$ was obtained via thermal decomposition of complex 4 under mild conditions (50 °C) in the presence of the triphenylmethyl ("trityl") dimer^[27] yielding the corresponding heterocoupling product 10 quantitatively (Scheme 4) according to ³¹P{¹H} NMR



Scheme 4. Reaction of complex 4 in toluene with the Gomberg dimer.

spectra; the product was isolated as a colorless solid in 45% yield. Complex **10** exhibited a resonance in the ³¹P{¹H} NMR spectrum at 112.7 ppm with a tungsten–phosphorus coupling constant of 291.4 Hz.

Single-crystal X-ray diffraction studies confirmed the molecular structure of **10** (Figure 2), showing a P–O1 distance of 1.628(2) Å. The sum of bond angles at phosphorus is about 299.5° (excluding the W(CO)₅ group).



Figure 2. Molecular structure of complex **10** (thermal ellipsoids set at 50% probability; hydrogen atoms are omitted for clarity). Selected bond lengths [Å] and angles [°]: P–W 2.5282(7), C20–P 1.822(3), C26–P 1.833(3), O1–P 1.628(2), C1–O1 1.460(3); O1-P-W 125.56(7), C20-P-W 118.60(8), C26-P-W 108.05(8), O1-P-C20 103.5(2), O1-P-C26 95.6(2), C26-P-C20 100.3(2).

Our DFT calculations show that the cleavage of the Gomberg dimer into trityl radicals in THF solution is exergonic by $-7.3 \text{ kcal mol}^{-1}$ and thus spontaneous, though slight heating is needed for the selective O–N cleavage of complex **4** that is endergonic by 15.0 kcal mol⁻¹ to form the reactive phosphanoxyl complex **6** and TEMP radicals. Further

trapping of **6** and TEMP by the trityl radicals eventually lead to the final products. Direct heterocoupling between the exposed O center of **6** and the central C-atom of the trityl radical (spin densities on the central, *para-* and *ortho-*Catoms: 0.59 *e*, 0.12 *e*, and 0.11 *e*, respectively) is -22.9 kcal mol⁻¹ exergonic to form stable phosphane complex **10** as the main product. In contrast, such direct heterocoupling between N-centered TEMP and trityl is endergonic by 6.8 kcalmol⁻¹ because of the strong steric hindrance, while radical addition of TEMP to the *para-*site of trityl is exergonic by -7.3 kcalmol⁻¹, and to the *ortho-*site endergonic by 4.1 kcalmol⁻¹, leading to the quinoid-type adduct between TEMP and trityl as the other product.

The properties of *P*-nitroxyl complex **4** as a radical initiator were studied for the polymerization of styrene (Scheme 5) under various conditions; for details, see Table 1. In all cases, colorless polystyrene was obtained that was analyzed by various analytical means. In stable free-radical polymerization $(SFRP)^{[28]}$ and more specified in nitroxide-mediated polymerization $(NMP)^{[29]}$ of styrene the temperatures are significantly higher^[30] compared to the route described herein.



Scheme 5. Reaction of complex 4 in toluene with excess of styrene.

Table 1: Reaction conditions for the polymerization of styrene using complex **4** as radical initiator and GPC data of the polymer obtained.

Equiv. styrene	t [h]	$M_{ m w}$ [kg mol ⁻¹]	M_n [kg mol ⁻¹]	PDI
1000 ^[a]	120	143.8	72.0	2.0
500 ^[a]	46	48.7	17.5	2.8
500 ^[a]	96	86.0	23.9	3.6
500 ^[b]	115	42.3	25.6	1.6

[a] In toluene at 60 °C. [b] In *n*-pentane at 40 °C.

¹H and ¹³C¹H NMR experiments revealed that the polystyrene obtained was atactic,^[31] as there was no preconfiguration of the monomer in the chain-growth step that directs the polymerization into a specific orientation therefore preferring a certain tacticity. The ³¹P{¹H} NMR spectrum shows several signals as broad multiplet in the range of 26 ppm to 28 ppm that suggests a phosphane oxide as end group rather than a P-bound tungsten complex; the tungsten complex was also (almost) excluded by the absence of ${}^{1}J({}^{183}W,{}^{31}P)$ satellites. Such a wide range signal distribution in the ³¹P{¹H} NMR spectrum has been observed for a similar polystyrene for which the polymerization was initiated by the Ph₂P radical.^[32] As no carbonyl absorption bands were present in the IR spectra (in the solid state as well as in toluene solution), and in the MALDI-TOF mass spectra the typical isotope pattern of tungsten was absent, we came to the conclusion that the $W(CO)_5$ group was lost during (or before)

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the polymerization. The composition of the polymer was determined as from the MALDI spectra shown by the formula in Scheme 5, that is, having a proton as the other end group. Elemental analysis of the polymer gained by the reaction with 1000 equivalents of styrene revealed a composition of 91.77% carbon and 7.569% hydrogen, but no nitrogen. The phosphorus content in the polymer was further confirmed by energy-dispersive X-ray (EDX) analysis.

As discussed above, both radicals 6 and TEMP can be formed from the initial O-N cleavage of complex 4 upon heating. The reactive radical TEMP may be added directly to styrene in a -1.9 kcalmol⁻¹ exergonic step over a moderate barrier of 17.4 kcal mol⁻¹ and thus induces the polymerization of styrene. Alternatively, TEMP is able to abstract a H atom from toluene, or even a $W(CO)_5$ moiety from 6, which is exergonic by $-3.6 \text{ kcal mol}^{-1}$ and $-0.7 \text{ kcal mol}^{-1}$ to form benzyl and the P-centered radical 9, respectively, which may induce further polymerization of styrene. The radical addition of complex 6 to styrene is $1.2 \text{ kcal mol}^{-1}$ endergonic over a low barrier of only 8.7 kcalmol⁻¹, thus the bond formed in this process may easily dissociate back. Without efficient radical trapping, complex 6 can easily convert into more reactive Pcentered radical form 8, which may lose the $W(CO)_5$ moiety to form phosphinoyl radical 9. The radical additions of 8 and 9 to styrene are both exergonic (by $-9.0 \text{ kcal mol}^{-1}$ and $-14.1 \text{ kcalmol}^{-1}$, respectively) and almost barrierless to form a new P-C bond, which may eventually lead to phosphane oxide as the polymer end group owing to the relatively weak coordination of phosphane oxide to $W(CO)_5$.

Gel permeation chromatography (GPC) investigations on the polymers obtained were conducted to see the influence of different initiator to monomer ratios on the molecular mass distribution and, hence, the chain length (Table 1).

The data of the GPC analysis showed that the average molecular weight of the polystyrene depends on the ratio of styrene to initiator (as expected). Furthermore, the chosen reaction time, temperature, and solvent also affected the polydispersity index (PDI) as well as the molar masses. Thus, it might be possible to open up a new class of initiators from this initial study that works at significantly lower temperatures than in the usual methods used in NMP.

In conclusion, it was demonstrated that a *P*-nitroxyl phosphane complex can be easily accessed and used as an effective source for corresponding transient phosphanoxyl species which can be trapped in the presence of persistent radicals, such as trityl. This initial study also revealed that polymerization of styrene can be achieved at a comparatively low temperature which offers further opportunities for fine tuning by changing substituents, metals, and co-ligands. Transition-metal binding changes the spin-density distribution and, hence, reactivity of open-shell ligands of the general formula R_2PO which otherwise react as P-centered radicals. In the near future, stable phosphanoxyl complexes may come within reach, thus building a bridge to the rich chemistry of nitroxides.

Acknowledgements

We are grateful to the Deutsche Forschungsgemeinschaft (SFB 813 "Chemistry at Spin Centers") for financial support, to M. Kremer for GPC measurements and to Dr. R. Weisbarth for the EDX measurements; G.S. thanks Prof. Dr. A. C. Filippou for support.

Keywords: density functional theory · phosphanoxyl · phosphanyl · spin density · TEMPO

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Received: August 21, 2016

Published online:

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Phosphanoxyl Complexes

Strong Evidence of a Phosphanoxyl Complex: Formation, Bonding, and Reactivity of Ligated Phosphorus Analogues of Nitroxides



Build up to break: *P*-OTEMP phosphane metal complex I preferentially undergoes homolytic O–N bond cleavage forming the transient phosphanoxyl complex II. DFT calculations provide insight into the formation of I as well as into the homolysis processes of I and the trapping reactions of II.

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