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ARTICLE TYPE

Selective Phosphanyl Complex Trapping using TEMPO. Synthesis and Reactivity of *P*-Functional *P*-Nitroxyl Phosphane Complexes†‡

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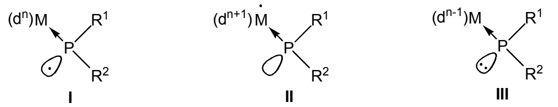
Open-shell phosphanyl complexes $(OC)_5W\{(Me_3Si)_2HCP(X)\}$ (X = F, H), obtained by one-electron oxidation of lithium phosphanido complexes, were trapped by TEMPO to yield novel thermally labile *P*-nitroxyl phosphane complexes. First experimental evidence for an open-shell *P*-F phosphanoxyl complex $(OC)_5W\{(Me_3Si)_2HCP(O)F\}$, formed upon thermolysis of corresponding *P*-nitroxyl derivative, is reported; reaction pathways are also theoretically investigated.

Redox non-innocent ligands represent an important tool in modern transition metal chemistry to modify the reactivity of transition metal complexes.[1] Therefore, the understanding of fundamental principles of transition metal open-shell ligand interactions and the resulting reactivity is important for the design of new effective chemical processes and/or to understand the mechanisms of complex radical reactions present in nature.[2]

Despite the fact that phosphanes are among the most common and well investigated ligands in coordination chemistry, information about open-shell phosphanyl ligands[3] is still very scarce. In this case and *a priori*, spin density can be localized at phosphorus (**I**)[4] (Scheme 1), the transition metal (**II**[5] and **III**[6]) or delocalized, which in total is critical for the reactivity.[7]

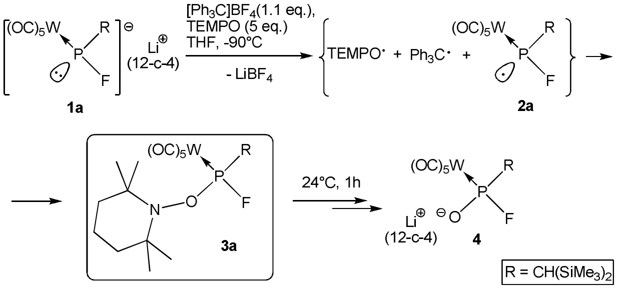


Scheme 1. Formal electron distribution in phosphanyl complexes **I-III**.

Recently, we have demonstrated that Li/Hal phosphinidenoid ligands (Hal = F, Cl) undergo one-electron oxidation with triarylcarbenium tetrafluoroborates to yield highly reactive *P*-functional phosphanyl tungsten(0) complexes of type **I** ($R^1 = CH(SiMe_3)_2$, R^2 = Cl, F or R^1 = Cp*, R^2 = Cl) together with triarylmethyl radicals.[8,9] In the case of the *P*-Cl phosphanyl complexes[8] heterocoupling in *para position* of the trityl unit occurred. In the case of *P*-F derivative[9] even coupling at the central carbon atom of the triarylmethyl radical was possible, when *tris*(*p*-methylphenyl)methyl tetrafluoroborate was employed as an oxidant. When TEMPO has been used in the same vein, first ^{31}P NMR evidence for a transient *P*-F functional *P*-nitroxyl complex $(OC)_5W\{(Me_3Si)_2HCP(F)TEMPO\}$ was obtained,[10] but rapid decomposition *via* an unknown mechanism occurred.

Therefore the quest emerged if trapping of such highly reactive phosphanyl complexes with TEMPO[11,12] could be achieved and, hence, exploited to access novel non-innocent phosphane ligands.

When Li/F phosphinidenoid complex **1a**,[13] generated *in situ* by lithiation of the corresponding fluorophosphane complex using *n*BuLi, was reacted at –90 °C with a mixture of triphenylcarbenium tetrafluoroborate (1.1 eq.) and TEMPO (5 eq.), the *P*-nitroxyl phosphane complex **3a** was obtained quantitatively below –20 °C, but decomposition occurred upon warming to ambient temperature to give the lithium fluorophosphinite complex **4**[10] within about 1 hour (Scheme 2).



Scheme 2. Trapping of *P*-F phosphanyl complex **2a** using TEMPO.

In the $^{31}P\{^1H\}$ NMR spectrum **3a** displayed a doublet with satellites at 216.6 ppm ($^1J_{P,W}$ = 338.5 Hz, $^1J_{P,F}$ = 997.4 Hz). Decreasing the amount of TEMPO in this reaction led to the formation of varying amounts of the coupling product of **2a** with triphenylmethyl as described beforehand, thus pointing to the importance of relatively high concentrations of TEMPO to favour the formation of the trapping product **3a**. Under the described reaction conditions, but without triphenylcarbenium tetrafluoroborate, no reaction between **1a** and an excess of TEMPO was observed below 4 °C.

The structure of **3a** was confirmed by single-crystal X-ray diffraction analysis (Fig. 1). The P–O and O–N distances of complex **3a** are 1.6256(18) and 1.504(3) Å, respectively, thus lying within the normal range of such bond distances;[14] the sum of bond angles at phosphorus is 300.96 ° (ligand only).

To get a more convenient access to such phosphane complexes, we further explored the phosphanyl complex generation/trapping sequence by the use of oxoammonium tetrafluoroborate $[TEMPO]BF_4$,[15,16] thus combining the one-electron oxidation with *in situ* reaction of TEMPO formed.

Complexes **1a**,**b** completely reacted with $[TEMPO]BF_4$ at temperatures even below –50 °C to give selectively the corresponding *P*-nitroxyl phosphane complexes **3a**,**b** (Scheme 3).

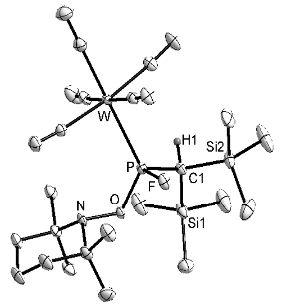
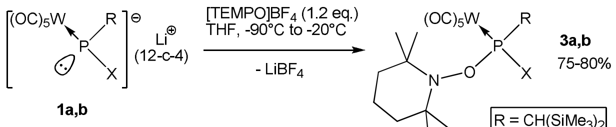


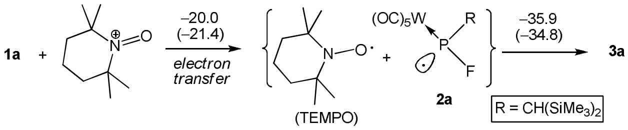
Fig. 1 Molecular structure of complex **3a** (50% probability level; hydrogen atoms except H1 are omitted for clarity). Selected bond lengths [Å] and angles [°]: W–P 2.5034(7), P–O 1.6256(18), O–N 1.504(3), P–F 1.5989(15), P–C(1) 1.814(2), N–O–P 117.52(13), O–P–W 123.79(7), F–P–W 108.65(6), C(1)–P–W 119.15(9).



Scheme 3. Reactions of complexes **1a**,**b** with $[TEMPO]BF_4$.

In contrast to **3a**, complex **3b** appeared to be stable at ambient temperature in reaction solution for days (for the X-ray structure, see Supporting Information).

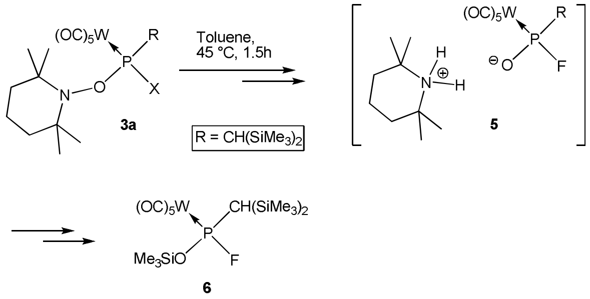
To provide mechanistic insight into the formation of *P*-nitroxyl phosphane complexes **3a**,**b**, state-of-the-art dispersion-corrected DFT calculations were performed.[17] It was found (Scheme 4) that one-electron oxidation of *P*-F phosphinidenoid complex **1a** by $TEMPO^+$ to form radicals **2a** and TEMPO is exergonic by 20 kcal/mol. This is followed by an even more exergonic radical recombination step (trapping) to form complex **3a** (Scheme 4); both processes being not very much solvent dependent.



Scheme 4. DFT-computed free energy changes (in kcal/mol) for one-electron oxidation of phosphinidenoid complex **1a** in THF and in toluene (in parentheses for comparison).

While *P*(III)-nitroxyl phosphanes derivatives are a known class of compounds,[18] TEMPO-derived *P*-nitroxyl phosphane complexes deserve special interest as decomposition through O–N bond homolysis may lead to unknown phosphanoxyl, *i.e.* phosphorus analogues of nitroxyl radicals, impossible to access from analogous P(III) derivatives due to the preferred formation of *P*-centered phosphanoyl radicals.[19] Preliminary theoretical studies[10] had provided first insights into the bonding of **3a**, showing the preference of homolytic O–N over P–O bond cleavage (by ca. 27 kcal/mol), thus prompting us to investigate the thermal stability of this compound experimentally.

Heating of complex **3a** in toluene (0.1 M) to about 50 °C (1–1.5 h) led to the color change from colorless to dark-brown and to selective formation of complex **6** as the single phosphorus-containing product (according to ^{31}P NMR spectroscopy) (Scheme 5). In case of more diluted solutions formation of an additional product was observed. This product, assigned as **5**,[20] formed as a single reaction product (in 0.02 M solutions of **3a**), is unstable and yields selectively complex **6** (^{31}P NMR monitoring).

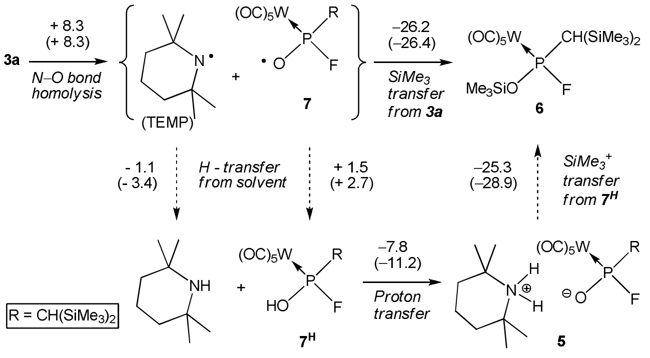


Scheme 5. Thermal decomposition of *P*-nitroxyl complex **3a** in toluene.

Complex **6** was isolated as a pure compound and characterized. The ^{31}P NMR spectrum displayed a doublet with satellites at 191.3 ppm ($^1J_{P,W}$ = 342.1 Hz, $^1J_{P,F}$ = 989.3 Hz). Three different trimethylsilyl groups of **6** were distinguished in the ^{1}H and ^{13}C NMR spectra as the signals at δ_H = 0.15 (d, $^4J_{H,P}$ = 1.6 Hz), 0.21, 0.28 ppm, and δ_C = 1.4, 1.9 (d, $^3J_{C,P}$ = 2.6 Hz), 2.3 ppm (*pseudo*-t, $^3J_{C,P}$ = 2.5 Hz). To verify the nature of this product, pure lithium phosphinite complex **4**[10] was reacted with Me_3SiCl, thus lending further support to the proposed structure for **6**.

Ammonium phosphinite complex **5** was observed in the ^{31}P NMR spectra of reaction mixtures as a doublet at 157.9 ppm (d_{Sat}, $^1J_{P,W}$ = 309.8 Hz, $^1J_{P,F}$ = 952.9 Hz), which is very similar to the reported ^{31}P NMR data of the analogous lithium phosphinite complex **4**[10] (d_{Sat}, δ_P = 154.0, $^1J_{P,W}$ = 307.7 Hz, $^1J_{P,F}$ = 956.2 Hz, $CDCl_3$). While it was not possible to isolate labile **5** in pure form, sufficient for a full NMR characterization, we managed to obtain a few crystals of **5** suitable for an X-ray analysis.[21] Compared to the *P*-nitroxyl complex precursor **3a**, the O–N distance in **5** is significantly larger (2.6196(2) *vs*. 1.504(3) Å). This comes with a significantly shortened P–O bond (1.489(7) *vs*. 1.6256(18) Å in **3a**), while the P–F bond is elongated (1.657(6) *vs*. 1.5989(15) Å); the latter is similar to the bonding situation found for lithium phosphinite complex **4**[10] (P–O 1.501(9), P–F 1.621(7) Å). The H2–O1 distance in **5** (1.69(13) Å) suggests the presence of hydrogen bonding involving the nitrogen and the oxygen atoms.

According to DFT calculations, homolytic N–O bond cleavage (endergonic by 8.3 kcal/mol) in *P*-nitroxyl phosphane complex **3a** is significantly preferred compared over the alternative heterolytic cleavage of the N–O bond (endergonic by 19.0 kcal/mol) and the homolytic P–O bond cleavage (endergonic by 35.9 kcal/mol), thus suggesting the formation of an hitherto unknown phosphanoxyl complex **7**[22] and 2,2,6,6-tetramethylpiperidinyl (TEMP) in the first reaction step. The following hydrogen abstraction[23] and exergonic proton transfer from phosphinous acid complex **7^H** to the amine nitrogen eventually leads to meta-stable ammonium phosphinite **5**, which may dissociate back to amine and **7^H** upon warming up (Scheme 6). Final product, complex **6**, could be formed *via* two pathways. In high concentrated solutions of complex **3a**, complex **6** is formed by exergonic silyl transfer from **3a** to phosphanoxyl radical **7** (–26.4 kcal/mol). Alternatively, **6** can be formed *via* exergonic silylium transfer (–28.9 kcal/mol) from $\mathbf{7^H}$ to phosphinite complex **5**.



Scheme 6. The DFT computed free energy changes (in kcal/mol) for the thermal decomposition of *P*-nitroxyl phosphane complex **3a** in THF and in toluene (in parentheses for comparison).

Computed oxidizing abilities (defined as free energy difference with the corresponding electron-attached species, in kcal/mol) in THF for different species are decreasing in the following order: **7** (120.0) > TEMPO$^+$ (115.5) > CPh$_3^+$ (103.6) > **2a** (95.6) > TEMP (61.9) > TEMPO (53.1) > [**3a**]$^{\bullet-}$ (51.5). From these data we conclude that phosphanoxyl complex **7** can also act as a strong one-electron oxidizing agent. Oxoammonium tetrafluoroborate [TEMPO]BF$_4$ is a stronger oxidant compared to the corresponding tritylium salt, and TEMPO is not able to act as one-electron oxidant towards lithium phosphanido complexes.[cf.10] Instead, in the latter case of **1a** direct formation of corresponding *P*-nitroxyl phosphane radical anion [**3a**]$^{\bullet-}$ over a low free energy barrier of 9.2 kcal/mol is possible, followed by N–O cleavage leading to an exergonic formation (by –51 kcal/mol) of anion **7**$^-$ that may combine with lithium cation to form final complex **4**.

Conclusions

It was demonstrated that transient phosphanyl complexes can be efficiently trapped by TEMPO. Furthermore, a new and facile access to *P*-nitroxyl complexes **3a**,**b** is described using an oxoammonium tetrafluoroborate derivative as oxidative SET reagent for phosphanido complexes. Apparently, *P*-TEMPO substituted phosphanes can act as suitable precursors for novel phosphanoxyl complexes and related species; their chemistry is now under active investigation.

Notes and references

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22 The Mulliken spin density populations for **7** are 0.105 for P, 0.287 for O, and 0.411 for W; for the detailed information, see ref. 10.

23 H-Abstraction free energies (kcal/mol) in THF from some related species are computed as follows: TEMP^H (89.1) > THF (88.0) > $\mathbf{7^H}$ (86.5) > toluene (85.5) > $\mathbf{2a^H}$ (80.3) > TEMPO^H (63.1).