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DOI
10.1002/anie.201901470
10.1002/ange.201901470

Publication date
2019

Document Version
Final published version

Published in
Angewandte Chemie, International Edition

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Citation for published version (APA):

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Download date: 06 Nov 2021
Interconversion of Phosphinyl Radical and Phosphinidene Complexes by Proton Coupled Electron Transfer

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This paper is dedicated to Professor Thomas Fässler on the occasion of his 60th birthday

Abstract: The isolable complex [Os(PHMe₅*)H(PNP)] (PHMe₅* = 2,4,6-[Bu₃]₂C₆H₃; PNP = N(CHCHP[Bu₃]₂)) exhibits high phosphinyl radical character. This compound offers access to the phosphinidene complex [Os(PMe₅*)H(PNP)] by P–H proton coupled electron transfer (PCET). The P–H bond dissociation energy (BDE) was determined by isothermal titration calorimetry and supporting DFT computations. The phosphinidene product exhibits electrophilic reactivity as demonstrated by intramolecular C–H activation.

Electronically unsaturated phosphorous compounds, such as phosphinyl radicals (PRs), are key transient species in P–C bond forming reactions, like olefin phosphination. Structural and spectroscopic characterization of free and coordinated phosphinyl radicals facilitated the examination of (electronic) structure/reactivity relationships. Free phosphinides (PR) could only very recently be sufficiently stabilized. While a variety of transition metals form isolable phosphinidene complexes (M = PR) with promising stoichiometric reactivity, such as P–C bond formation, catalytic phosphinidene transfer protocols remain rare, compared to, for example, nitrene transfer which has emerged as a powerful method for C–N bond formation.

The scarcity of catalytic PR-transfer might in part be attributed to a lack of suitable oxidizing PR-transfer reagents, such as analogs of iminoiodane (ArI=NR) or azide (RN₃).

We previously utilized the four-coordinate complex [OsCl₂(PNP)] (3, PNP = N(CHCHP[Bu₃]₂)). Complex 3 readily reacts with PHMe₅* in Et₂O to the dark blue P–H oxidative addition product [OsCl(PHMe₅*)(H(PNP))] (4) (Scheme 3). Complex 4 decomposes over the course of a few hours in solution at room temperature but could be fully characterized including single crystal X-ray diffraction. NMR spectra are in agreement with C¹ symmetry at −30°C. All signals (¹H, ¹³C, ³¹P) are broadened supporting hindered rotation around the Os–P bond. The phosphine P-
atom exhibits trigonal-planar coordination in the solid state, indicating P to Os π donation.[16]

Reduction of 4 with cobaltocene affords the radical product [OsH(PHMes*)(PNP)] (5) in 80% isolated yield (Scheme 3). The magnetic moment in solution (μeff = 1.51 μB) derived by Evan’s method is in agreement with an S = 1/2 system with unquenched orbital momentum. Complex 5 can also be directly synthesized from 3 by one pot P–H oxidative addition and subsequent reduction. Characteristic bands for the PHMes* and hydride ligands were detected in the IR spectrum (vPHMes* = 2345 cm⁻¹; νOsH = 2180 cm⁻¹). In the solid state, complex 5 features distorted square pyramidal coordination geometry with the hydride ligand in the apical position (Figure 1). Upon reduction from 4 to 5 the Os–P bond to the PHMes* ligand is slightly elongated by Δd = 0.04 Å.

The EPR spectrum of 5 in frozen toluene exhibits a rhombic signal that is in agreement with an S = 1/2 low-spin configuration (Figure 1). The g-anisotropy is considerably smaller than that of typical osmium(III) complexes, in line with reduced spin-orbit interaction due to ligand redox non-innocence.[15a,17] Accordingly, large and slightly rhombic hyperfine interaction (HFI) with one 31P nucleus is observed in all principal directions of the g-tensor (Figure 1), supporting considerable spin delocalization to the PHMes* ligand. The free phosphinyl radical PPh3 exhibits axial 31P-HFI with an isotropic coupling constant (Aiso(31P) = 260 MHz) close to that of 5 (Aiso(31P) = 201 MHz).[18] The higher isotropic HFI, yet reduced dipolar coupling, found for the transient phosphinyl radical complex [W(PPPh3)(CO)3] (Aiso(31P) = 499 MHz) was attributed to pπ–dπ spin delocalization (ρπ ≈ 75%) and concomitant polarization of the P lone-pair.[44] For 5, the higher g-anisotropy and smaller isotropic and anisotropic contributions of the 31P-HFI tensor are consistent with increased P–M spin delocalization. Comparing the isotropic and anisotropic (T1 = 144 MHz, T2 = −96 MHz, T2* = 239 MHz) contributions to the 31P-HFI with atomic parameters allows for a rough estimate of phosphorus spin densities (ρπ ≈ 2%; ρπ ≈ 42%) when treating the HFI as approximately axial (T1 = (T1 + T2*))/2.[18]

DFT calculations fully support this interpretation. Both the molecular structure and the EPR parameters (Figure 1) were excellently reproduced computationally. The SOMO of 5 represents an antisymmetric (π*) combination of the metal dπ, orbital and a phosphorus p-orbital. Reduced π-bonding is expressed by the Os–PHMes* Mayer bond index (1.46). In consequence, the computed spin density (Figure 1) is almost equally distributed between the P (ρπ = 47%) and Os atoms (ρOs = 50%).

Complex 5 represents an unprecedented, isolable phosphinide complex with large phosphinyl redox non-innocent character (OsV–PR). We therefore examined PCET reactivity of the radical ligand, specifically as an entry to phosphinidene chemistry. Two experimental methods are widely used to estimate E-H BD(F)Es, that is, a) bracketing based on hydrogen transfer reactions with reference H-donor/acceptor reagents and b) quantification by the “square-

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**Scheme 3.** Synthetic access to phosphanide and phosphinidene complexes 4–6 and 9 (R = C(CF3)2).

**Figure 1.** Top: Molecular structure of 5 in the solid state from single-crystal X-ray diffraction (thermal ellipsoids set at 50% probability); solvent molecules, anions, and hydrogen atoms, except the P–H and Os–H hydrogen atoms, are omitted for clarity. Selected bond lengths [Å] and angles [°]: 5 Os1–H111 1.69(6), Os1–N1 2.069(4), Os1–P1 3.2723(12), Os1–P2 2.3537(13), Os1–P3 2.2301(13), P3–H112 1.33(5), P1–Os1–P2 160.20(4); N1–Os1–P3 172.17(11). Bottom: X-band EPR spectrum of 5 (9.4366 GHz) in toluene at 148 K (black) and simulation (red) with the following parameters (DFT computed values in brackets): g∥ = 1.952 (1.951), g∥ = 2.033 (2.024), g∥ = 2.214 (2.230); A∥(31P) = +57 MHz (+58 MHz), A∥(31P) = +105 MHz (+95 MHz), A∥(31P) = +440 MHz (+441 MHz); Euler angles: α = −73 (−74.3), β = +137 (+142.7), γ = −7.5 (−7.3); A∥(31Os) = −240 (−277) MHz. Insert: Computed spin density plot.
Scheme 4: Reactivity of phosphinidene complex 6.

Parent 5 offers two potential sites for H-atom transfer (HAT). The generation of 6 indicates higher Os–H over P–H bond strength if the reaction proceeds under thermodynamic control. BDE quantification was attempted by stepwise oxidation and deprotonation. The cyclic voltammogram of 5 reveals quasi-reversible reduction at $E_{pa} = -2.06$ V and reversible oxidation at $E_{pc} = -0.88$ V (vs. FeCp$_2$). Chemical oxidation with Ag[Al(OC(CF$_3$)$_3$)$_2$] at $-35^\circ$C immediately gives the deep blue osmium(IV) phosphide complex 9 (Scheme 5). Complex 9 readily decomposes at room temperature but could be characterized at low temperatures including crystallography. Deprotonation of in situ prepared 9 with KOtBu at $-80^\circ$C gives phosphinide 6 almost quantitatively. However, the low thermal stability of 9 hampered reliable $p_K$ determination.

The P–H bond strength of 5 was therefore derived by isothermal titration calorimetry (ITC). Titration of 5 with Mes$^+$ in benzene or THF afforded the reaction enthalpies for HAT ($\Delta H^{\text{ITC}} = -16.5$ kcal mol$^{-1}$, $\Delta H^{\text{ITC}} = -17$ kcal mol$^{-1}$) and consequently the BDE$_{\text{P–H}}$ of 5 ($\text{BDE}_{\text{P–H}} = 65.1 \pm 1$ kcal mol$^{-1}$, BDE$^{\text{THF}}_{\text{P–H}} = 67.1 \pm 1$ kcal mol$^{-1}$). DFT analysis of 5 supports the experimental P–H BDE (calibrated BDE$_{\text{P–H}}$ = 67.5 kcal mol$^{-1}$; non-calibrated value: 64.0 kcal mol$^{-1}$) that is, considerably lower than the Os–H bond (calibrated BDE$_{\text{Os–H}}$ = 74.2 kcal mol$^{-1}$; non-calibrated: 70.1 kcal mol$^{-1}$), indicating that phosphinidene 6 is the thermodynamic PCET product. The calorimetric and electrochemical data also allows for calculating the $p_K$ of 9 ($p_K^{\text{THF}} = 16$) from a thermochemical square-scheme (Scheme 5).

Scheme 5: Thermochemical square-scheme of 5, 6 and 9.

In conclusion, we presented the first spectroscopically and crystallographically characterized phosphide complex with large phosphinyl radical character. The rhombic $^3$P-HFI tensor and the DFT model are in line with even spin delocalization over the Os–P core. Versatile access to an electrophilic phosphinidene complex that undergoes intramolecular C–H activation was demonstrated by P–H PCET. Thermochemical analysis by means of ITC was utilized due to thermal instability of 9. The data indicates that concerted or stepwise ET/PT are both viable routes from phosphide to phosphinidene complexes.

Acknowledgements

This work was funded by the European Research Council (ERC Grant Agreement 646747), the Fond der Chemischen Industrie (FCI Doktoranden Stipendium for J.A.), the Deutsche Forschungsgemeinschaft (DFG, GRK2455) and The Netherlands Organisation for Scientific Research (NWO TOP-Grant 716.015.001) for financial support. Furthermore, the authors thank Dr. A. C. Stückl and R. Schöne for EPR and NMR measurements, respectively.

Conflict of interest

The authors declare no conflict of interest.

Keywords: osmium · phosphanyl radical · phosphinidene · pincer · proton coupled electron transfer
How to cite: Angew. Chem. Int. Ed. 2019, 58, 6338–6341
Angew. Chem. 2019, 131, 6401–6407


[11] The BDE(NH) was calculated using a Hesse cycle: BDE(NH) = Δf°(N) + 2Δf°(H) - BDE(NH) - Δf°(N).