Oxidation of a phosphasalen nickel(II) complex,
What Phosphorus changes

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Salen derivatives constitute a very successful class of ligands that have found numerous applications, in particular in (bio)-inorganic chemistry and catalysis. The presence of the 2 phenoxides and imine functions is reminiscent of the coordination environment generated by two histidines and two tyrosine residues, encountered in several enzymes. Thus, 15 years ago, the persistent phenoxy radical obtained by one-electron oxidation of a [(salen)CuII] complex was established as a biomimetic functional model of galactose oxidase.[1] Since then, one-electron oxidized salen metal complexes of first-row transition metals have received considerable attention allowing either the isolation of high valent metal complexes (metal centred oxidation) or metal-ligand radical species (ligand centred oxidation) were characterized.

Since we have recently developed the phosphorous analogue of salen ligands, incorporating two iminophosphoranes (P=N) in place of imines that we have termed phosphasalen,[2] we were interested in studying the oxidation of their complexes and started with a [NiII(Psalen)] complex.

Combining different techniques, we demonstrated that in presence of a phosphasalen ligand, the one-electron oxidation is centred on the metal leading to a high valent nickel(III) complex. This constitutes a rare example of tetracoordinated NiIII complexes and to the best of our knowledge, the only one featuring a phenoxy ligand.[3] This observation markedly differs from precedents in the salen chemistry where NiIII complexes were only observed at low temperature, or in presence of additional ligands or coordinating anions.

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References:
PNP-Pincer Type Phosphaalkene Complexes of Ir(I): A Remarkable Enhancement of Reactivity by a P=C Bond

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Phosphaalkenes with a P=C double bond have an extremely low-lying $\pi^*$ orbital and act as strong $\pi$-acceptors toward transition metals.\[1\] Herein, we demonstrate that this particular ligand property remarkably enhances the reactivity of PNP-pincer complexes of Ir(I).\[2\] A representative example includes facile cleavage of the N–H bond of ammonia by K[Ir(Cl)(PPEP*)] (3) (Scheme 1).

Heating a toluene solution of [Ir(Cl)(BPEP)] (1) at 70 °C resulted in selective formation of the unsymmetrical PNP-pincer complex [Ir(Cl)(PPEP)] (2) via intramolecular C–H addition of a tBu group to the P=C bond. Treatment of 2 with tBuOK in Et$_2$O caused deprotonation at the benzylic position to form 3 with a dearomatized PNP-pincer type phosphaalkene ligand (PPEP*), which was isolated as [K(18-crown-6)][Ir(Cl)(PPEP*)] (3a) and identified by X-ray diffraction analysis.

Complex 3 instantly reacted with NH$_3$ (1 atm) at room temperature via metal–ligand cooperation, to afford parent amido complex 4 in quantitative yield. Similarly, PhNH$_2$ and $n$-C$_9$H$_{13}$NH$_2$ were converted to 5 and 6, respectively. The reactivity of 3 was much higher than that reported for PNP-pincer complex analogues without the phosphaalkene unit.\[3\]

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References:
Synthesis, Structures and Reactions of Nickel Complexes with a PN-Chelate Phosphaalkene Ligand

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Phosphaalkenes with a P= C double bond are an interesting class of supporting ligands, often providing unique structures and reactivities arising from effective π-back-bonding with transition metals.\(^1\) Thus, their nickel complexes would be also attractive particularly in connection with catalysis; however, only three papers have documented the isolation of nickel phosphaalkene complexes with CO and π-allyl ligands.\(^2\)

Herein, we describe novel nickel complexes \(2-4\) with a PN-chelate phosphaalkene ligand, 2-(1-phenyl-2-phosphaethenyl)pyridine (PEP), which are prepared from \([\text{Ni(\text{Br})}](\mu-\text{Br})(\text{pep})]_2\) (1) and \(\text{R}_2\text{Mg(thf)}_2\) (\(\text{R} = \text{Ph}, \text{Me}, \text{Me}_2\text{SiCH}_3\)) (Scheme 1). Complex 1 has a dimeric structure in the solid state, but is in equilibrium with its monomeric form in solution as evidenced by magnetic susceptibility measurement. Treatment of 1 with \(\text{R}_2\text{Mg(thf)}_2\) in \(\text{Et}_2\text{O}\) leads to three types of complexes depending on the \(\text{R}\) groups and reaction conditions. Complex 2 is a dimer of Ni(I) bromide, whereas 3a and 3a are dialkyl complexes with a significantly distorted square planer configuration around Ni(II). On the other hand, 4 is an aryl bromide complex formed by aryl–alkyl exchange between Ni and P atoms. In the presentation, we will discuss their unique structures and formation processes.

Scheme 1

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**References:**


Facile Synthesis of Phospha-amidines and Phospha-amidinates using Nitrilium Ions as Imine Synthon

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Nitrilium ions A are reactive intermediates in a number of classic organic reactions, such as the Beckmann rearrangement, the Ritter and the Ugi reaction.[1] The isolation of the first stable nitrilium salts was already reported by both Klages and Meerwein in 1955, but the development and application of these imine synthons has remained rather limited, likely for practical reasons.

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\begin{array}{ccc}
\text{A} & \text{B} & \text{C} & \text{D} \\
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We were keen on developing a scalable and efficient synthesis of a range of nitrilium ions and explore their use in the preparation of 1,3-P,N-ligands. The archetypical P,N-ligand 2-pyridyldiphenyl-phosphane (B) has found widespread application in coordination chemistry and catalysis in spite of its structurally limited N-donor site. Iminophosphanes (i.e., phospha-amidines C), on the other hand, offer an easily tunable imine fragment that allows for facile steering of the steric and electronic properties of the ligand, but they are difficult to access. Moreover, convenient synthetic access to the phosphorus analogues of the highly versatile and much used amidinate ligands, i.e., the anionic phospha-amidinates D, is neither available other than by using silyl-phosphanides and nitriles. In this lecture, we report the synthesis of nitrilium triflates and their reactivity toward primary and secondary phosphanes, which allows the facile synthesis of phospha-amidinates C, phospha-amidinates D, as well as bis-iminophosphanes.[2]

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References: