Nickel(IV) Chemistry

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Organonickel(IV) Chemistry: A New Catalyst?**

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C–X couplings · Group 10 metals ·
high oxidation states · nickel · scorpionate ligands

*Dedicated to Professor Uwe Rosenthal
on the occasion of his 65th birthday*

Over the past few decades, there have been scattered reports on the synthesis and properties of organonickel(IV) compounds. The scanty development and interest in Ni^{IV} chemistry must be viewed in the context of the higher-oxidation-state chemistry of its heavier homologues palladium and platinum. The first examples of Pt^{IV} compounds with the general formula $[\{Me_3Pt(\mu\text{-}X)\}_4]$ were described by Pope and Peachey already at the beginning of the last century and have also opened the field of Group 8–10 alkyl chemistry.[1] A systematic study of Pt^{II} and Pt^{IV} compounds and their interconversions was intensely pursued in particular by Puddephatt and his group.[2a] More recently, Goldberg et al.[2b] have established the relevance of five-coordinate Pt^{IV} complexes as key intermediates in the $Pt^{IV} \rightarrow Pt^{II}$ reduction step. The high stability of organoplatinum(IV) compounds explains why catalytic reactions involving $Pt^{II} \leftrightarrow Pt^{IV}$ redox cycles are rare, with the most prominent example probably being the Shilov alkane activation.[2c]

In contrast, the involvement of Pd^{IV} intermediates or transition states has been postulated for countless Pd^{II}-catalyzed reactions, but the first alkyl Pd^{IV} complex was only isolated by Canty et al. in 1986. Since then, this group, among others, has isolated a few dozen alkyl Pd^{IV} complexes and established the "rules" that determine whether such complexes are stabilized or triggered to react.[3] Experience has shown that planar Schiff base like N(sp^2) ligands, such as 2,2-bipyridine (bipy), are more suitable than phosphines for stabilizing Pd^{IV} species, and that related *fac*-tripodal ligands, such as the anionic Trofimenko ligand $(pz)_3BH^-$ (Tp; pz = 1-pyrazolyl) and its neutral alternatives $(pz)_3CH$ and $(py)_3CH$ (py = 2-pyridyl), are in turn superior to bipy. Cyclic ligands such as 1,4,7-trithiacyclononane exert an even greater stabilization effect. These tripodal ligands are also known as "inorganic Cp ligands" (to which they are isolobal) and "scorpionate ligands", the latter referring to the fact that these ligands can tightly grab a metal with two of their donor sites, like the pincers of a scorpion, and (reversibly) sting it with the third (the tail). Reactions of such Pd^{IV} complexes[3c] are often initiated by the dissociation of a monoanionic ligand, such as a halide or triflate (OTf^-).

What is the situation for Ni^{IV}? Higher-oxidation-state nickel chemistry is marked by an exceedingly large number of inorganic Ni^{III} complexes, but relatively few examples of Ni^{IV} compounds. Aside from some inorganic Ni^{IV} complexes, which mainly contain polydentate nitrogen ligands (amides and deprotonated oximes),[4] the decamethylnickelocene(IV) dication[5] (**A**) was identified early on (in 1982; Figure 1).

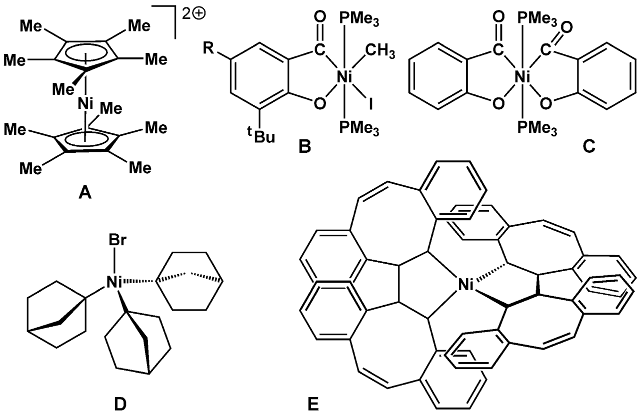

Figure 1. Previously isolated organonickel(IV) complexes.

Klein et al. succeeded in synthesizing the first octahedral di(σ-organyl)nickel(IV) complexes **B** and **C**.[6] These 18-electron d^6 complexes have subsequently been complemented by the tetrahedral 14-electron complexes tris(1-norbornyl)-nickel(IV) bromide[7] (decomp. 130 °C; **D**) and nickelaspirocyclononane **E** (decomp. 290 °C).[8a] In the formal tetraalkyl Ni^{IV} complex,[8b] two nickelacyclopentane rings share a common Ni^{IV} center. The enormous stability of **D** and **E** can be attributed to kinetic stabilization by blocking available decomposition pathways.

There are a vast number of C–C and C–X coupling reactions that are catalyzed by nickel. These transformations mainly involve $Ni^0 \leftrightarrow Ni^{II}$ oxidation-state changes, although there is also increasing evidence for the participation of Ni^{III}.[9] However, no reliable evidence for the generation of Ni^{IV} species as part of a catalytic cycle has been provided thus far. Cross-coupling reactions, for example, which are possible candidates for the involvement of Ni^{IV} intermediates by oxidative addition, are actually thought to be initiated by single-electron transfer (SET) from the starting Ni^{II} compound to the electrophile, which provides entry into

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a $Ni^{I}\leftrightarrow Ni^{III}$ catalytic cycle, and the generation of Ni^{IV} species is thus avoided.

An intriguing example of modern nickel-mediated chemistry that most likely involves a higher oxidation state of the metal is the nickel-mediated oxidative late-stage fluorination of organic compounds for positron emission tomography (PET) with aqueous [^{18}F]fluoride. According to Ritter and co-workers,[10a] treatment of the Ni^{II} complex shown in Figure 2 with an iodine(III) oxidant in the presence of aqueous fluoride induces the virtually instantaneous C–F coupling of the aryl group with ^{18}F, presumably by reductive elimination from an intermediate featuring a nickel center in a higher oxidation state. Interestingly, although Ritter and co-workers had previously performed related studies involving Pd^{IV} intermediates,[10b] the authors refrained from assigning an exact oxidation state to the nickel atom in this process, leaving the question as to whether Ni^{III} or Ni^{IV} is involved unanswered.

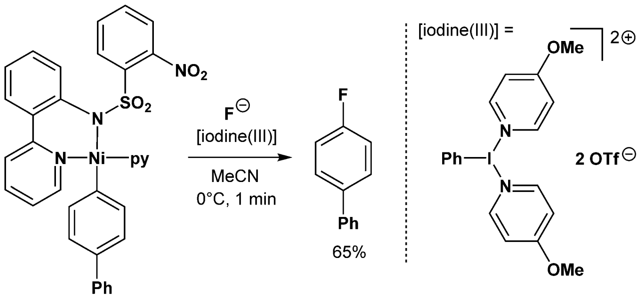

Figure 2. Nickel-mediated oxidative fluorination.

All this provides the backdrop for Camasso and Sanford's recent study into Ni^{IV} complexes.[11a] In continuation of their studies on Pd^{IV} chemistry, the authors reacted the metallacyclic bipy-containing Ni^{II} complex **1** with various oxidants. Using the CF_3^+ oxidant *S*-(trifluoromethyl)dibenzothiophenium triflate (TDTT), they generated Ni^{IV} species **2**, which is stable enough to be characterized in solution. Starting from the complexes **3** and **5** with the scorpionate ligands $(py)_3CH$ and $(pz)_3BH^-$, respectively, they successfully isolated the octahedral Ni^{IV} complexes **4** and **6** (Figure 3), thereby adding isolable non-phosphorus-based complexes to the set of complexes **B** and **C** (see above). In view of Canty's systematic work on tripod Pd^{IV} compounds and Klein's cue by creating the octahedral phosphine Ni^{IV} complexes, it is somewhat surprising that it took a generation until tripod Ni^{IV} compounds were investigated. The new Schiff base Ni^{IV} complexes resemble their Pd^{IV} congeners in many aspects; for example, they undergo a thermally induced reductive elimination of benzocyclobutane. When complex **6** is treated with a variety of ammonium salts $[NMe_4]X$ (X = OAc, OPh, SPh, $N(Me)(SO_2Me)$) at ambient or slightly elevated temperature, it undergoes stoichiometric $C(sp^3)$–X bond-forming reactions to exclusively afford the Ni^{II} compounds **7** in quantitative yield. These reactions are best described as an exogenous S_N2-type attack of the nucleophile at the Ni^{IV}-bound $C(sp^3)$ carbon atom of the metallacycle, which triggers a $Ni^{IV}\rightarrow Ni^{II}$ reduction. When $[NMe_4]N_3$ is used, a pendant azide species is formed, which releases 3,3′-dimethylindoline after nitrene generation by loss of N_2, cyclization, and protonation by water.

The results of the Ritter and Sanford groups indicate that rapid stoichiometric and selective C–X couplings may emerge as a possible domain of higher-oxidation-state nickel chemistry. However, it remains to be seen whether the reactivity of

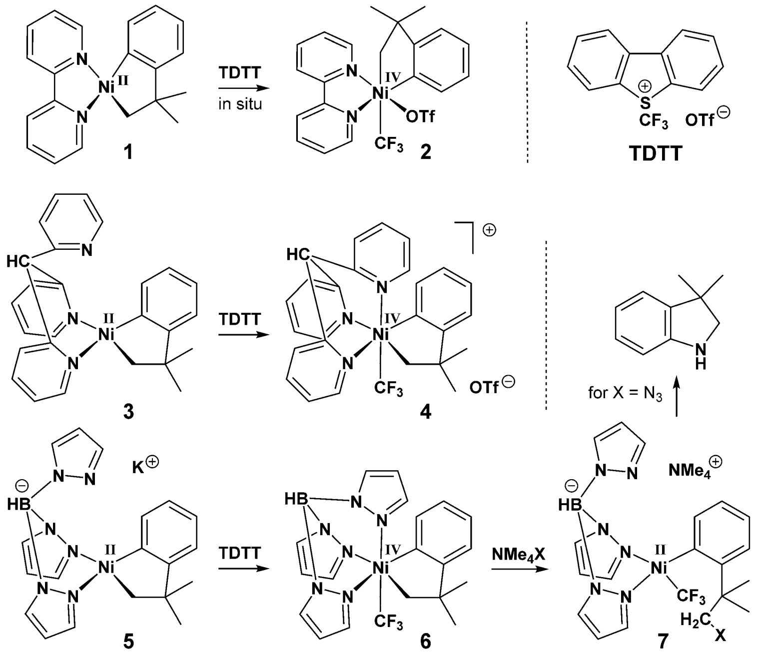

Figure 3. Synthesis and reactivity of the novel nickel(IV) complexes.

organonickel(II) complexes can be successfully tuned with tripodal scorpionate ligands in such a way that by employing an organic substrate and a suitable oxidant, clear-cut $\mathrm{Ni^{II}} \leftrightarrow \mathrm{Ni^{IV}}$ catalytic reactions that avoid $\mathrm{Ni^{III}}$ intermediates are possible.[11b] Clearly, a systematic study of scorpionate organonickel(II) and -nickel(IV) chemistry, as initiated by the Sanford group, seems more than overdue.

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