Tetraalkyl Nickel

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Unexpected Formation of a Molecular Tetraalkyl Nickel Complex from an Olefin/Nickel(0) System

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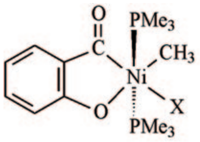
alkyl ligands · coordination chemistry ·
Group 10 elements · nickel

According to the first described method[1] nickel can be brought to its highest oxidation state +4 by fluorination under strictly anhydrous conditions. Such conditions are essential because salts with the anion $[NiF_6]^{2-}$ undergo hydrolysis and generate dioxygen. During the synthesis the oxidizing power is transferred from the reagent to the metal (low-spin d^6) that resides in the center of a regular octahedron of six fluoride ions. Within the last fifteen years several Ni^{IV} compounds have been reported that deviate from this concept in two directions: instead of the hard fluoride donors they contain soft donor atoms, and in addition to coordinatively saturated octahedral Ni^{IV} centers also coordinatively unsaturated four-coordinate species with only 14 metal-valence electrons are observed.

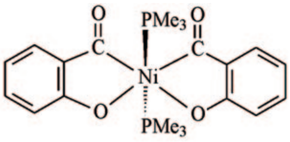
Going much further back we can trace a parallel development for the heavier homologues of nickel. As Pd and Pt adopt higher oxidation states more easily than nickel and are less prone to elimination reactions, thermally stable $[C_6F_5Pd^{IV}]$ compounds became accessible some 30 years ago.[2] Stable aryl palladium(IV) complexes without fluoride substitution could only recently be synthesized and structurally characterized.[3] All the alkyl palladium(IV) halides that have been investigated to date spontaneously decompose above 20 °C.[4] In contrast, the thermally robust and air-stable $[Me_3PtI]$[5] has been known since the beginnings of organometallic chemistry, when in many laboratories the then novel Grignard reagents were first treated with salts of transition elements. Today organoplatinum chemistry is a vast area and includes a large number of tetrameric trimethylplatinum(IV) compounds that have a common *fac*-octahedal coordination of the metal and a structure motive from a Pt_4X_4-cubane skeleton (X = F–I, OH, SR, etc.).[6] With this background in mind nobody would have expected that thermally stable alkyl nickel(IV) compounds could be generated.

For the series of structurally characterized examples of Ni^{IV} complexes with coordination numbers six and four, it is interesting to note the modification by degrees in the strength of oxidizing agents required for the synthesis. Octahedral methyl nickel compounds **1**[7] that owe their stability to a favorable balance of *trans* influences are generated by an oxidative substitution reaction with methyl halide (X = Br, I). For the formation of bis(acylphenolato)nickel **2**[8] and similarly for the homoleptic anion **5**[9] a disproportionation reaction at the Ni^{II} stage is sufficient, while the silyl nickel compound **3**[10] is generated by a thermally induced elimination of dihydrogen. In a similar modification for the synthesis of the distorted tetrahedral norbornyl nickel **4**[11] oxidation by air at −60 °C is sufficient. The most recent example, the tetraalkyl **6**,[12] appears to arise slowly but spontaneously at ambient conditions from an olefin/Ni^0 system. However, the balance of oxidation–reduction equivalents and the mode of formation are still subject to speculation.



X = Br,I

1



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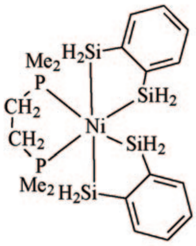

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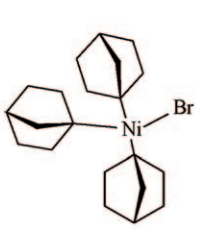
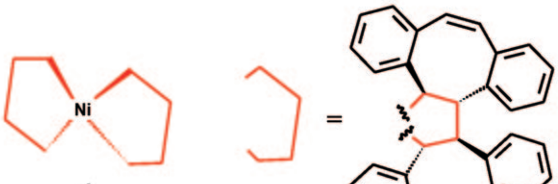


4

$[Ni(SnB_{11}H_{11})_6]^{8-}$

5



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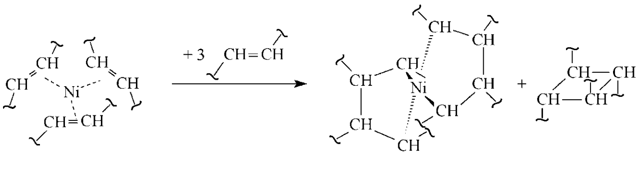
Once again, by serendipity, a new and fascinating line of research has been opened: In an investigation of nickel-induced transformations of the strained olefin (5Z, 11E)-dibenzo[a,e]cyclooctatetrene the authors of ref. [12] obtained a tris(olefin) nickel(0) complex as the primary product. In its NMR spectra and in its molecular structure they recognized a conformational relaxation that results from a triple π-olefin coordination in which only the strained *trans* double bonds are involved. Extensive steric shielding is believed to explain the good thermal stability and the low reactivity towards air and moisture of the solid Ni^0 compound. All the more surprising was a subsequent slow reaction at room temperature with another three equivalents of the olefin which, as well as the expected demetalation producing a cyclobutane derivative, afforded a nickel complex that could be isolated in 29% yield (Scheme 1). The red crystals proved resistant to air and remained stable when heated to 290 °C. In the molecular structure bond lengths and angles are only compatible with the assumption of a tetraalkyl nickel(IV) core where following C–C coupling the metal is coordinated by two 1,4-butanediyl ligands in a spirocyclic manner (highlighted in red in the pictorial representation of **6**). This conformation provides a more complete steric shielding in **6** than in the norbornyl compound **4**. In both structures the C-Ni-C angles show large deviations from an ideal tetrahedral coordination. This distortion in **6** is not sterically induced but, according to DFT calculations on the model complexes $[Ni(CH_2CH_2CH_2CH_2)_2]$ and $[Ni(CH_3)_4]$, corresponds to the ground state.[13]



6 (29%) (36%)

Scheme 1. The nickel-induced transformation of the strained diolefin (5Z, 11E)-dibenzo[a,e]cyclooctatetrene (only the *trans* double bonds are shown) into nickel complex **6** and the demetalated cyclobutane derivative.

The magnetic properties and NMR spectra of **6** indicate diamagnetism. The chemical shifts of the metal-bound ^{13}C nuclei in compounds **4** and **6** show a low-field shift when compared with corresponding Ni^{II} compounds, this low-field shift is indicative of a high formal nickel oxidation state.

Today we see a new class of Ni^{IV} compounds firmly established in which the metal is surrounded, in particular, by Group 14 elements of the Periodic Table. There is no apparent restriction to this Group, provided highly covalent metal-to-ligand bonds and a low bond polarity ensure that the synthesis can be carried out with reagents of low oxidizing power. In addition, sufficient steric shielding should be present in the ligand precursor to give access to coordinatively unsaturated compounds that can attain a remarkable thermal stability.

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