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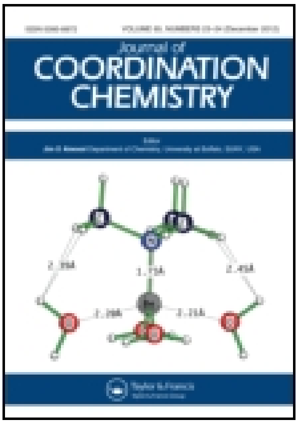

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Synthesis, structure, chemistry, and applications of tetravalent nickel complexes

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REVIEW

Synthesis, structure, chemistry, and applications of tetravalent nickel complexes¶

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This review provides an overview of the synthetic pathways, structures, and reactivity of various nickel(IV) complexes. The complexes are classified according to the various ligand types including sulfur, oxygen, nitrogen, and phosphorus donors. The main emphasis is on different ligand systems which stabilize Ni in higher oxidation state in the solid state and solution. The structural aspects of the complexes are briefly discussed. The possible applications of these nickel(IV) complexes are reviewed and future prospects are also highlighted.

Keywords: Tetravalent nickel complexes; Synthesis; Ligands; Structural aspects; Applications

1. Introduction

Understanding of chemical structure and bonding for compounds containing transition metals with unstable oxidation states is one of the most exciting and intellectually rewarding areas in inorganic chemistry. Multiple variables can be explored in designing ligands making the subject complicated, but fascinating. The choice of ligand is critical in obtaining stable metal complexes in high oxidation states, and minor variations in the ligand structure can lead to the formation of compounds with increased stability. Fluoro- and oxo-ligands are usually preferred for stabilization of the highest oxidation states, both in main-group and transition-metal chemistry. This is mainly due to large interelectronic repulsions among non-bonding electrons around the small electronegative atoms. It is also known that the highest attainable oxidation states of the elements are most likely to be stabilized as anions. In fact, many neutral complexes in the highest oxidation states have been synthesized by the use of an anionic precursor in

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the same oxidation state because they are more easily accessible [1]. One such class of compounds contain the Ni(IV) species.

Nickel in oxidation states +3 and +4 was considered comparatively rare, however during the last four decades, the number of hypervalent nickel complexes has expanded significantly [2]. In general, these oxidation states are highly reactive and can bring about oxidation of a number of organic and inorganic substrates. A detailed account of the chemistry of nickel oxidation states has been presented earlier [3]. Since then (1991, 1994), however, no review articles appeared which report exclusively on the synthesis and reactivity of nickel(IV) complexes. Kinetic studies involving various nickel(IV) species, on the other hand, have been very well-reviewed [4].

Nickel-catalyzed reactions proceed through cycles involving the nickel in various oxidation states. The catalytic applications of nickel complexes have been explored extensively [5]. It is widely believed that Ni complexes can be valuable precursors for supported bimetallic catalysts, because they contain intimately associated combinations of the metal components, their stoichiometries can be accurately controlled and may also provide better control of the size of the metal particles formed from them on supports [6]. In fact, recent studies have shown that stable nickel(IV) complexes can be prepared with surprising ease. Cluster complexes of Ni used to generate nanoparticle catalysts on mesoporous supports are unusually active hydrogenation catalysts [7].

Extensive research has been carried out on the role of nickel in various biological applications. The structural elucidation of [NiFe] hydrogenase revealed a heterodinuclear active site, with cysteine thiolates bridging a nickel ion with an iron center. The field of heterodinuclear complexes modeling [NiFe] hydrogenase has been growing actively. In contrast, bioorganonickel chemistry of olefin, cyclopentadienyl, and arene metal complexes has not yet been explored. Nickel–carbon bonds are strongly suspected of participating in various biological processes [8].

To the best of our knowledge, this is the first exclusive direct review on synthesis and chemistry of nickel(IV) complexes. Polydentate ligands with high electron density are the source of high-valent nickel complexes, while ligands having an aromatic character are preferably oxidized. This article is limited to the consideration of mononuclear complexes and will not deal with polynuclear or cluster complexes containing nickel.

2. Synthesis of nickel(IV) complexes

Tetravalent octahedral and diamagnetic compounds of nickel are expected to be stable by analogy with palladium and platinum oxidation states. The failure to obtain such complexes was generally predicted by the fact that the higher valence states become progressively less stable as the atomic number of the metal decreases, for example, while Os(VIII) complexes are quite stable Fe(VIII) complexes are unknown. Nevertheless, the number of nickel(IV) complexes now known has increased as this valence state can be stabilized fairly easily with suitable coordinating systems. In general, a higher valence state may be stabilized either by the use of a highly electronegative group with high electron affinity and hence oxidizing power, for example, fluorine, or by bonding the metal with a suitable coordinating agent which changes the oxidation–reduction potential by forming strong covalent bonds with the ligand.

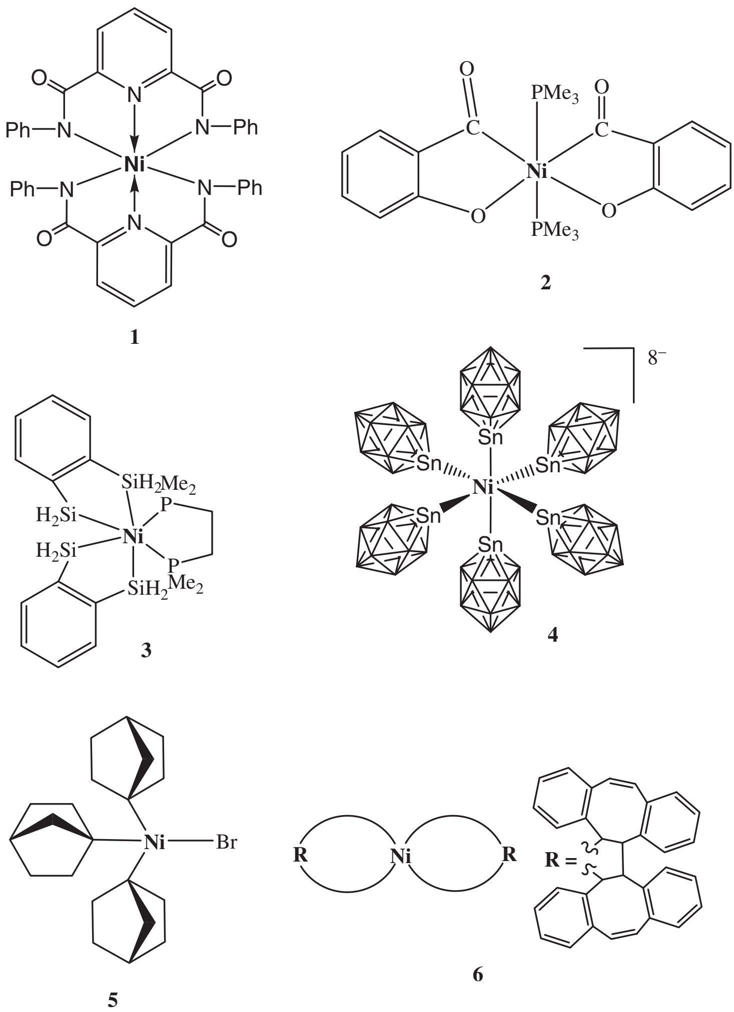
Within the past few decades, several Ni(IV) compounds have been reported with soft donors in place of the hard fluoride donors. Both coordinatively saturated octahedral Ni(IV) centers and coordinatively unsaturated four-coordinate species with only 14 metal-valence electrons have also been observed. 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 nickel compounds of type **1** [9] owe their stability to a favorable balance of *trans* influences and are generated by an oxidative substitution reaction with methyl halide ($X = Br, I$). For the formation of bis(acylphenolato)nickel (**2**) [10] and similarly for the homoleptic anion **4** [11] a disproportionation reaction at the Ni(II) stage is sufficient, while both for the neutral silyl nickel compound (**3**) [12]. In a similar manner, the distorted tetrahedral norbornyl nickel (**5**) [13] is synthesized by air oxidation at −60°C. The most recent example is the slow but spontaneous formation of tetraalkyl nickel (**6**) [14] at ambient conditions from an olefin/Ni(0) system (scheme 1). However, the balance of oxidation–reduction equivalent and the mode of formation for this complex are still subject to speculation. The most stable Ni(IV) species include σ-complexes [15, 16] having NiN_6, NiO_6, NiF_6, $NiAs_4X_2$, NiP_4X_2, NiS_6, and $NiSe_6$ coordination spheres.

There has been a lot of discussion about whether the neutral complexes really contain Ni(IV) or they are complexes of Ni(II) with partially oxidized ligands having spins that were antiferromagnetically coupled. The main feature of these non-innocent metal complexes is that both ligand and metal frontier orbitals are potentially redox-active and close to each other in energy. In most of the cases, the difficulty is not just that the ligands are redox active, but that there is strong mixing between ligand and metal orbitals such that the assignment of oxidation states to individual metal and ligand components is difficult. Typical non-innocent ligands are the dithio-α-diketones, *o*-quinones, tetrathiooxalate anion, the bidentate 1,4-diaza-1,3-dienes ($R'N{=}CR{-}CR{=}NR'$), and α,α'-bipyridine. An extensive literature on the transition metal complexes of non-innocent ligands has been reported [17].

2.1. *Nickel oxides or nickel fluorides*

A variety of nickel(IV)–oxygen species including the linear dioxide O–Ni–O, the di-peroxo complex $Ni(O_2)_2$, and possibly the peroxo-oxo complex $Ni(O_2)O$ have been identified by matrix-isolation IR spectroscopy as products of the reaction between Ni atoms and O_2 [18]. However, description as a neutral O_2 molecule bound side-on to a Lewis-acidic NiO_2 molecule may be more likely favoring the existence of another Ni(IV) species. According to the first method described earlier [19], nickel can be brought to its highest oxidation state +4 by fluorination under strictly anhydrous conditions. Such conditions are essential because salts of the $[NiF_6]^{2-}$ anion readily undergo hydrolysis and generate dioxygen. During synthesis the oxidizing power is transferred from the reagent to the metal (low-spin d^6) at the center of a regular octahedron of six fluorides.

Nickel(IV) forms diamagnetic fluoride complexes of the type A_2MF_6, containing the octahedral MF_6^{2-} unit in which nickel has the low-spin d^6 electronic configuration. Spectroscopic data have been obtained for these classical six-coordinate solids but little is known about the chemistry of these unusual species in solution [20]. The solution chemistry of Ni(IV) fluoride complexes in anhydrous hydrogen fluoride medium has



Scheme 1. Some selected examples of nickel(IV) complexes.

been investigated by ^{19}F NMR spectroscopy [21]. Some other classical examples of nickel(IV) with oxo and fluoro ligands include $Ni_xPt_3O_4$ [22], K_2NiF_6 or NiF_4 [23], $BaNiO_3$ [24], $[NiNb_{12}O_{18}]^{12-}$ [25], and $MNiI0_6 \cdot H_2O$ [26–28]. The K_2NiF_6 complex has applications in nanotechnology and is a strong oxidizing agent in several reactions.

Lithium nickelate has been considered as a stable and promising cathode material for the lithium batteries due to its low cost and high energy density, the materials $LiNi_{1-x}M_xO_2$ ($M{=}Cu^{2+}$, Al^{3+}, and Ti^{4+}) have been prepared for evaluation as cathode materials [29].

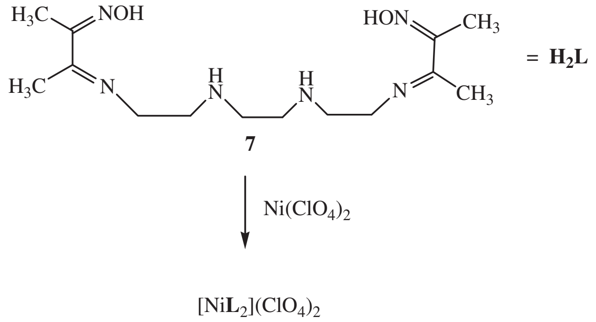
Heteropoly compounds such as $Na_{12}NiNb_{12}O_{38}$ [30] and $Ba_3NiMo_9O_{32} \cdot 12H_2O$ [31] have been shown to contain Ni(IV) with an O_6 inner coordination sphere environment. The heteropolyvanadates with transition metals of the type $Ln_2H[MV_{13}O_{38}] \cdot nH_2O$ (where Ln=La, Ce, Pr, Nd, Sm, Eu; M=Ni, Mn) have also been synthesized [32]. In addition, a 1 : 13 heteropolyvanadate containing nickel(IV), $K_7[Ni(IV)V_{13}O_{38}] \cdot 16H_2O$

has been reported [33]. 2-D lanthanide heteropolyvanadates of nickel(IV) containing hydrated lanthanide cations, $Ln_6(H_2O)_{25}(MV_{12}O_{38})(HMV_{13}O_{38}) \cdot nH_2O$ (where Ln=La, M=Ni, and $n = 28$ or Ln=Pr, M=Ni, and $n = 33$) are also known [34]. Apart from this, there are other nickel(IV) complexes of iodic acid [35], molybdic acid [36a], and telluric acid [36b] reported in the literature.

2.2. *Nitrogen-donor complexes*

The preparation and properties of nickel(IV) complexes of 2,6-diacetylpyridine dioxime have been reported [36]. These complexes are reported as having the central nickel coordinated *via* the six nitrogens of the ligands [37].

Oxidation of $Ni(H_2L)$ (where H_2L=3,14-dimethyl-4,7,10,13-tetraaza-3,13-hexadecadiene-2,15-dionedioxime, **7**) with $HClO_4$ yields a cationic nickel(IV) complex, $[NiL]^{2+}$ (**8**; equation (1)). Although the geometry of both complexes is similar, shorter Ni–N (amine) and Ni–N (imine) bonds in the Ni(IV) complex are observed which has been attributed to the increase in the formal oxidation state of Ni from +2 to +4 [38].

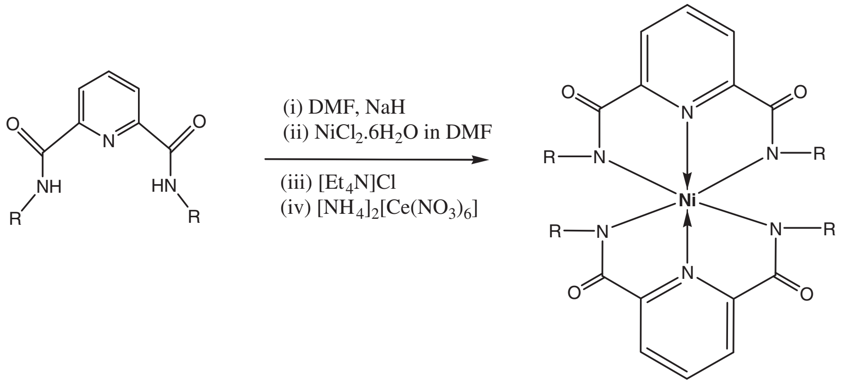


7

(1)

8

Other mixed-valence nickel complexes such as $[Ni(II)(pn)_2][Ni(IV)Cl_2(pn)_2]Cl_4$ (pn = 1,2-propanediamine) and $[Ni(II)([14]aneN_4)][Ni(IV)Br_2([14]aneN_4](ClO_4)_4$ ($[14]aneN_4$ = 1,4,8,11-tetraazacyclotetradecane) have also been prepared and characterized by X-ray photoelectron spectroscopy [39]. A series of Ni(II)–Ni(IV) mixed-valence compounds of the type $[NiL][NiBr_2L]X_4$ (L = 13-, 14-, and 15-membered tetraazacycloalkanes, 1,2-diaminocyclohexane; X=ClO_4 or BF_4) have been prepared with a bridging bromide. A structural study of these complexes was carried out by EXAFS spectroscopy, which shows significant elongation of the Ni(IV)–Br bond owing to the charge-transfer interaction between Ni(II) and Ni(IV). This results in high electrical conductivities of the Ni(II)–Ni(IV) compounds as compared with those of the Pd and Pt analogs [40]. In a similar way, other complexes such as $[Ni(IV)(en)_2Cl_2][Ni(II)(en)_2]Cl_4$ and $[Ni(IV)[H_2NCH(CH_3)CH_2NH_2Cl_2]Cl_4$ [41] and $[NiCl_2][o\text{-}CH(MMe_2)_2]_2[ClO_4]_n$ (where M=P, $n = 1$, 2; M=As, $n = 2$) [42] have been prepared. The *trans*-$[NiCl_2(en)_2]Cl$ complex disproportionates to give a mixed-valence complex $[Ni(II)(en)_2][Ni(IV)Cl_2(en)_2]Cl_4$ on exposure to moisture [43, 44]. A diamagnetic nickel(IV) complex, $Ni(IV)L_2$ (**1**) with a tridentate bis-amide 2,6-bis[N-(phenyl)carbamoyl]pyridine (H_2L) in its deprotonated form has been reported together with other Ni complexes having different oxidation states (equation (2)) [9]. Mixed-valence linear-chain materials are currently an area of intensive study, with considerable technological interest due to their anisotropic optical and electrical conduction properties.

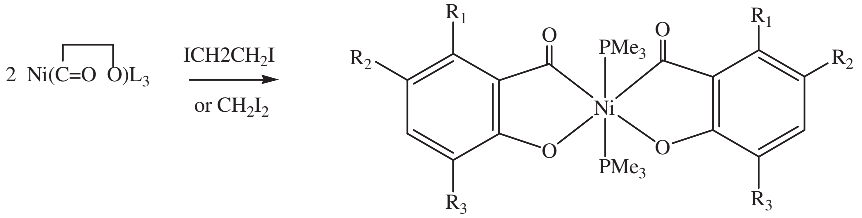


(2)

1, R = Ph or Me

2.3. *Phosphine and arsine ligand complexes*

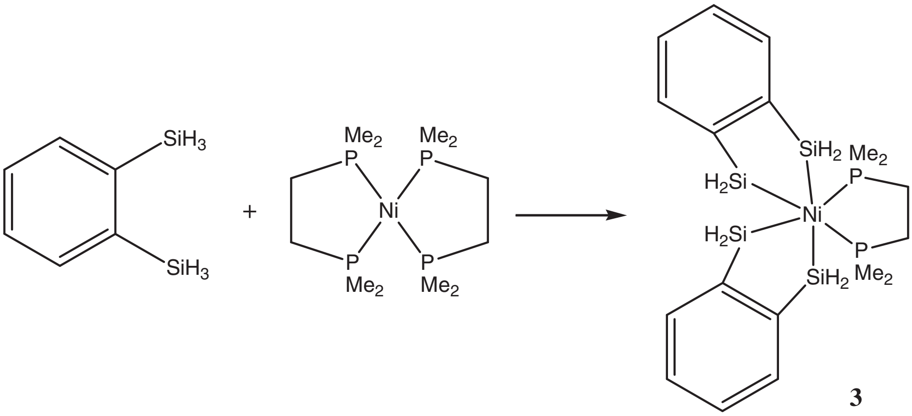
When $(PPh_3)_3Ni$ reacts with organotin halides (R_3SnCl; R=Ph, Me) in toluene, the product formed through a double oxidative addition reaction is $Ni(PPh_3)_2(SnMe_3)_2Cl_2$ containing a *trans*, *trans*, *trans* ligand arrangement [45]. Pseudooctahedral cationic Ni(IV) complexes $[NiL_2X_2]^{2+}$ and $[Ni(L_3)_2Cl_2]^{2+}$ [where X=Cl, Br; L=o-$C_6H_4(PMe_2)_2$, o-$C_6F_4(PMe_2)_2$; o-$C_6H_4(PMe_2)$ $(AsMe_2)$; o-$C_6H_4(AsMe_2)_2$; L_3=$Me_2P(CH_2)_2PMe_2$] were prepared by HNO_3 or Cl_2/CCl_4 oxidation of NiL_2X_2 followed by treatment with $HClO_4$ or HBF_4 [46]. Oxidation of 2-acylphenolato complexes of nickel(II), Ni(C=O O)$(PMe_3)_3$ by iodine or diiodoalkanes yields low-spin d^6 complexes of the type Ni(C=O O)$_2(PMe_3)_2$ (**2**, **9–12**) as shown in equation (3). The molecular structure shows two axial trimethylphosphines and a cisoidal arrangement of two acylphenolato dianions in equatorial positions [47].



(3)

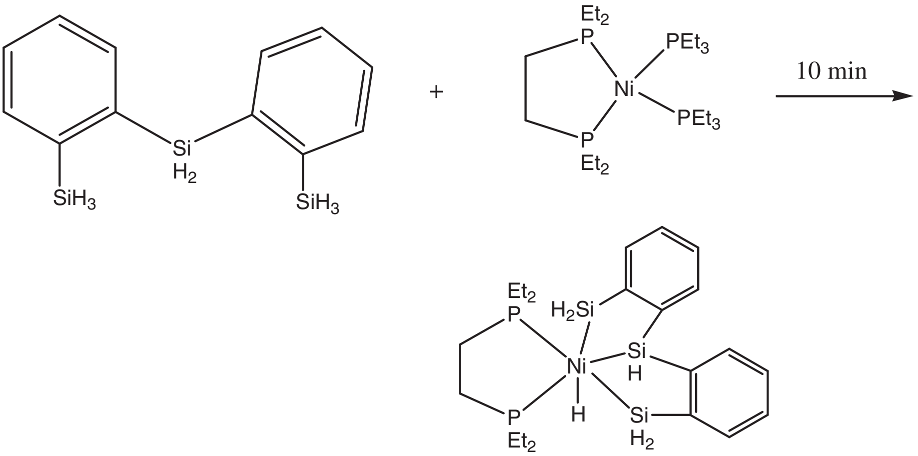
2, $R_1 = R_2 = R_3 = H$;
9, $R_1 = H$, $R_2 = R_3 = CMe_3$;
10, $R_1 = H$, $R_2 = Me$, $R_3 = CMe_3$
11, $R_1 = R_2 =$ Benzo, $R_3 = H$;
12, $R_1 = R_2 = H$, $R_3 = OMe$;

Equation (4) describes the first silylnickel(IV) complex (**3**) that has been prepared from reaction of 1,2-disilylbenzene with bis(1,2-bis(dimethylphosphinoethane)nickel(0) [$(dmpe)_2Ni$] through the bis(silyl)nickel(III) intermediate [48].



3 (4)

The first example of a hydridonickel(IV) complex (**13**) has been reported in solution at −80°C. The reaction of $(2\text{-}SiH_3C_6H_4)_2SiH_2$ with $Ni(depe)(PEt_3)_2$ was carried out to afford a new crystalline silylnickel complex, bis(silyl)η^2-(Si-H)nickel(IV) (**13**) as shown in equation (5). This complex shows fluxional behavior at room temperature; exchange of five hydrogens (two SiH_2 and one H bound to Ni) was observed, while at −80°C the exchange of hydrogens appeared frozen and the molecule adopts a tris(silyl)(hydrido)-nickel(IV) structure [49].

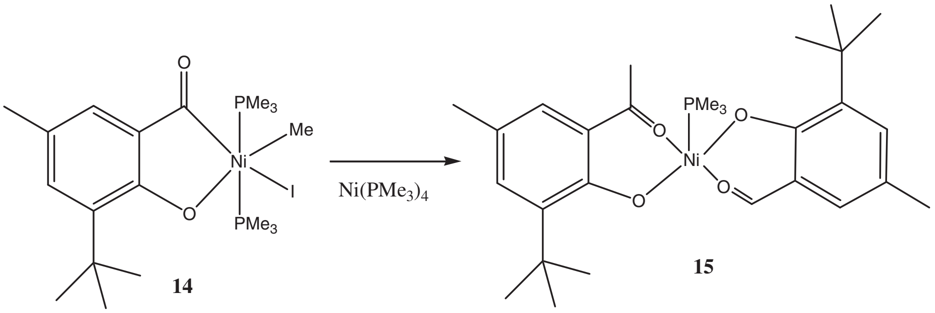


(5)

13

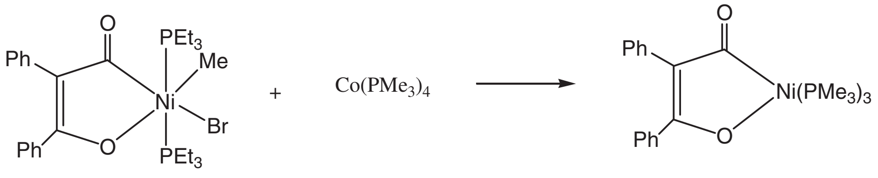
The octahedral methyl(acylphenolato)nickel(IV) halide complex (**14**) undergoes a reductive C,C-coupling reaction in the presence of $Ni(PMe_3)_4$ as a catalyst according to equation (6). In a subsequent ligand dismutation reaction, two of the resulting

2-acetylphenolate ions become coordinated as bidentate ligands to the same nickel center to form **15** [50].



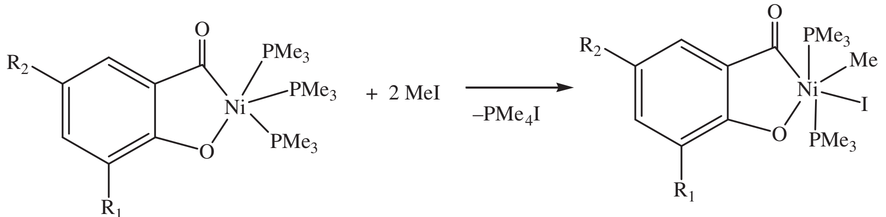
14 **15** (6)

Similarly the octahedral acyl-(methyl)nickel(IV) complex (**16**) reacts with $\mathrm{Co(PMe_3)_4}$ to afford the square-planar **17** through a reductive C,C-coupling reaction according to equation (7). It is difficult to predict the stoichiometries and direction of transmetallation reactions involving dianionic chelate systems. The only general trend that can be discerned is that $\mathrm{Co(d^8)}$ complexes are thermodynamically more stable than $\mathrm{Ni(d^6)}$ complexes with a similar set of ligands [51].



16 (7)

Equation (8) summarizes the oxidative addition of iodomethane to 18-electron nickel(II) complexes of the type $\mathrm{Ni(\overline{C{=}O\ O})(PMe_3)_3}$ coordinated to 2-oxobenzoyl-C,O chelating ligands $(\overline{\mathrm{C{=}O\ O}})$. This reaction affords the thermally labile Ni(IV) compound *trans-mer*-$\mathrm{Ni(Me)I(\overline{C{=}O\ O})(PMe_3)_2}$ (**14**) which further reacts with iodine in a ligand dismutation reaction to form stable *trans*-$\mathrm{Ni(\overline{C{=}O\ O})_2(PMe_3)_2}$ [9].

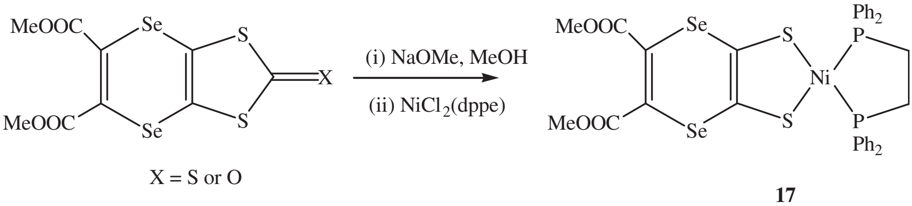


$\mathrm{R_1 = R_2 = CH_3, C(CH_3)_3}$ or H **14** (8)

2.4. *Sulfur, selenium, and tellurium donor ligands*

Some formally Ni(IV) compounds, particularly ones of sulfur ligands such as 1,2-dithiolates, contain the oxidized form of the ligand and are properly considered as Ni(II) species, for example, $\mathrm{[Ni(IV)S(S_2CPh_2)_2]_2}$–pseudooxidation state [52].

Theoretical structures of 1,2-diselones, 1,2-diselenate, and their sulfur analogs suggest that the cyclic 1,2-diselenate structure is significantly more stable than the acyclic 1,2-diselone structure of the corresponding nickel(IV) complex **17** [53] as given in equation (9).



17 (9)

The synthesis and soft X-ray-induced photochemical reduction of tris(*N*,*N*-diethyldithiocarbamato)nickel(IV) and tris(*N*,*N*-di-*n*-butyldithiocarbamato)-nickel(IV) cationic complexes to the respective nickel(II) complexes have been studied [54]. Tris(*N,N*-diethyldithiocarbamato-S,S^1)nickel(IV)1,1,2,3,3-pentacyanopropanide has been prepared and the molecular structure determined by single-crystal X-ray analysis [55]. The anionic nickel(IV) cubanes, such as $[Ni_4Se_4(Se_3)_5(Se_4)]^{4-}$ and $[Ni_4Te_4(Te_2)_2(Te_3)_4]^{4-}$, were prepared from the reaction of $Ni(S_2COEt)_2$ with Li_2Se and Se or Li_2Te and Te, respectively. The $[Ni_4Se_4(Se_3)_5(Se_4)]^{4-}$ possesses a Ni_4Se_4 cubane core with five Se_{32}^{-} chains and one Se_{42}^{-} chain bridging the Ni's on the cubane faces. In contrast to $[Ni_4Se_4(Se_3)_5(Se_4)]^{4-}$, $[Ni_4Te_4(Te_2)_2(Te_3)_4]^{4-}$ contain a Ni_4Te_4 cubane core with two Te_{22}^{-} chains bridging Ni on opposite faces of the cubane core and four Te_{32}^{-} chains bridging Ni(IV) on the remaining cubane faces [56].

A complex, bis(2,3-dimercapto-6,7-dihydro-5H-1,4-dithiepin)nickel(IV) has been structurally characterized, which has a non-planar central NiS_4 entity [57]. The oxidation of $Ni(H_2Me_2S)(C1O_4)_2$-H_2O by cold concentrated nitric acid produced a deep-violet crystalline Ni(IV) complex, $Ni(Me_xS)(ClO_4)_2$, where H_2R_xS=RC (=NOH)C(Me)=N$(CH_2)_2$ S(CH_2)S$(CH_2)_2$ N=C(Me)C(=NOH)R (R=Me, Ph; $x=2$, 3) [58].

Usually chelates with selenium donors are more difficult to prepare than the analogos sulfur compounds. The preparation of the Ni(IV) tris chelate of isomaleonitrilediselenolate which was isolated as the tetraphenylarsonium salt was reported. When hydrated $NiCl_2$ reacts with $[Se_2C{=}C(CN)_2]^{2-}$ in methanol in the presence of tetraalkylammonium bromide, a nickel chelate with an unsaturated 1,1-diselenolate ligand $[(C_6H_5)_4As]_2[Ni(Se_2C{=}C(CN)_2)_3]$ is formed. This complex reacts with iodine in acetonitrile to yield a dark green product, identified as $[(C_6H_5)_4As]_2$ $[Ni(Se_2C{=}C(CN)_2]_2$ [59].

An Ni(IV)$(Bu_2Dtc)_3$Br (tris(*N*,*N*-di-*n*-butyldithiocarbamato)nickel(IV)bromide) has been prepared and structurally characterized by X-ray crystallography. This complex reacts with acetonitrile or related solvents under photochemical or thermal conditions to yield thiuram disulfite and a nickel(II) species [60, 61]. Similarly, tris(*N*,*N*-di-*n*-butyldiselenocarbamato)nickel(IV) bromide has been reported with six seleniums coordinated to a central nickel in an octahedral arrangement [62].

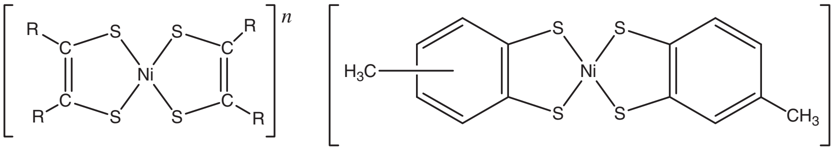
A tris(*N,N*-di-*n*-butyldithiocarbamato)nickel(IV) bromide complex has been prepared by bromine oxidation of bis(*N*,*N*-di-*n*-butyldithiocarbamato)nickel(II), in CCl_4. The nickel in Ni(IV)$(Bu_2dtc)_3$Br is surrounded symmetrically by three formally uninegative dithiocarbamate ligands and the cation clearly is electron deficient relative to normal oxidation states for the elements involved. The presence of disulfide in a solution of Ni(IV)(Bu_2dtc)$_3$Br inhibited the photochemical and thermal bleaching [61]. Similar Ni(IV) complexes with different ligand substituents (R=Et, Ph) have been prepared [60].

The existence of planar metal complexes of the type **18** and **19** in which one of the significant features is the stability of the electronically unusual systems with $n = 0, -1$ has been established (scheme 2). Although the $n = -2$ complexes can be successfully formulated in the usual fashion as containing dianionic ligands and divalent metal ions, the $n = -1$, 0 complexes show chemical and physical properties inconsistent with classical Ni(III) ($n = -1$) and Ni(IV) ($n = 0$) formulations [63, 64].

Some mixed-valence chain compounds similar to those of Pt^{II}–Pt^{IV} units linked as Ni^{II}–X–Ni^{IV} by hydrogen bonds have been reported [40, 65].

2.5. *Carborane cage ligands*

Hawthorne *et al.* [66] have reported the oxidation of $[Ni(III)(C_2B_9H_{11})]^{2-}$ to a diamagnetic Ni(IV)$(C_2B_9H_{11})_2$ (**20**) in the presence of aqueous $FeCl_3$. The molecular structure of **20** has the shape of two icosahedra, each composed of nine borons and two carbons, and a commonly shared vertex (Ni) (scheme 3). The carbons in opposite cages



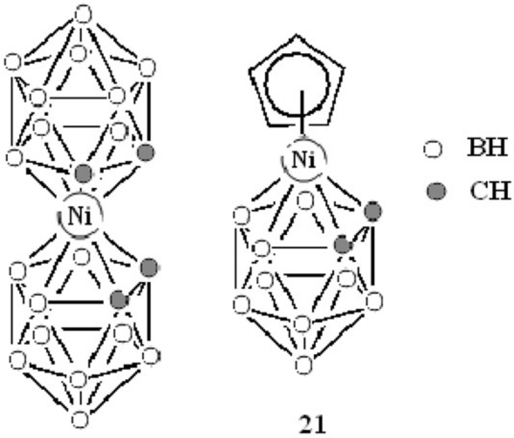
$n = 0, -1, -2$
$R = CN, C_6H_5, CF_3$

18

$n = 0, -1, -2$

19

Scheme 2. Examples of planar nickel complexes.



21

20

Scheme 3. Nickel(IV) complexes with carborane cage ligands.

are as close to each other as is possible in the staggered configuration [67]. The reaction of bis(*o*-dicarbollyl)nickel(IV) with PPh_3 in ethanol yielded a metallacarborane complex, 3,3-$(PPh_3)_2$-3,1,2, Ni-$C_2B_9H_{11}$ [68].

The Ni(IV)-monocarborane anionic species $[Ni(IV)(B_{10}H_{10}CH)_2]^{2-}$ and some of its substituted derivatives were the first examples of nickel-carbollides reported [69–72]. The neutral η-cyclopentadienylnickeI(IV) complexes of the carbollide ligand [73] as well as the neutral bimetallic monocarbon complexes of $CB_7H_8^{5-}$ containing a formal $(\eta\text{-}C_5H_5Ni)^{3+}$ unit [74] are also reported. A novel nickel(IV) complex of $(\eta\text{-}1\text{-}CB_8H_9)^{3-}$, η-cyclopentadienyl-η-nonahydro-1-carba-*nido*-nonaboratonickel(IV) (**21**) constituting the first *closo*-metallacarborane in which a metal is unambiguously bound to a B_4 face has been reported [75–77] (scheme 3).

Nickel-disubstituted dicarbollide complexes have been prepared by Hawthorne and co-workers [78] by complexation of $[7,(8)\text{-R-}7,8\text{-}C_2B_9H_{10}]^{2-}$, $[3\text{-R-}7,8\text{-}C_2B_9H_{10}]^{2-}$, $[5,(6)\text{-R-}7,8\text{-}C_2B_9H_{10}]^{2-}$, and $[5,6\text{-}R_2\text{-}7,8\text{-}C_2B_9H_{10}]^{2-}$ with $Ni(acac)_3$. These nickel dicarbollides exhibit cisoid conformation with Ni(IV). The transition between Ni(IV) and Ni(III) oxidation states may be effected by Fe(III) oxidation and $NaBH_4$ reduction, respectively [78].

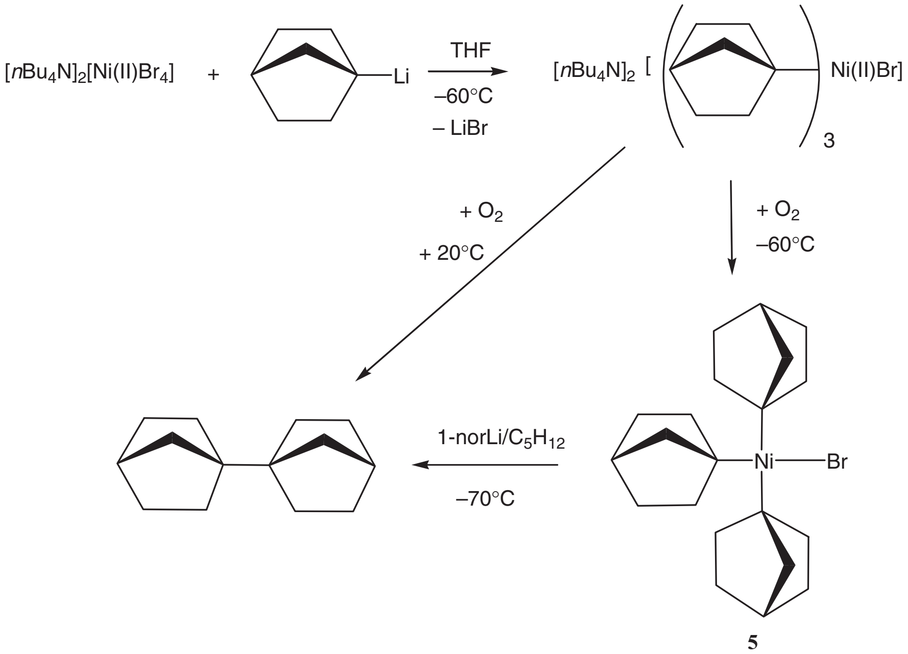
The synthesis of homoleptic octahedral group 10 metal complexes (M=Ni, Pd, Pt) of the type $[M(SnB_{11}H_{11})_6]^{8-}$ (**4**, M=Ni) has been reported. The strong σ-donor properties of the $[SnB_{11}H_{11}]^{2-}$ have been discussed [79].

2.6. *Hydrocarbon ligands*

Organonickel compounds in the formal oxidation state +4 have been obtained by the oxidation of decamethylnickelocene [80] and in a trinickelacarborane complex [81]. The first examples of octahedral diorganonickel(IV) compounds containing σ-bonded methyl and acylphenolato ligands were reported only recently [9]. The occurrence of tetracoordinate organonickel(IV) intermediates has been proposed in some cases [82, 83], but there are no previous reports of the isolation of a tetrahedral nickel(IV) compound containing σ-bonded organic ligands. Examples of stable, high oxidation state homoleptic transition-metal alkyl complexes are rare [84].

The reaction of $[^nBu_4N]_2[Ni(II)Br_4]$ with three equivalents of 1-norbornyllithium in THF at −60°C gave a blue-green solution of the anionic complex, $[nBu_4N]_2[norbornyl)_3Ni(II)Br]$ (scheme 4). This anionic complex was oxidized at −60°C by bubbling air through the THF solution to obtain a red-brown crystalline nickel(IV) complex **5**. This diamagnetic pseudotetrahedral triorganonickel(IV) compound is reported to be stable in air for several days. On heating in solution, dinorbornane was formed as a result of an elimination reaction. The high stability of the complex can be attributed to the strong σ-bond-donating capability of the 1-norbornyl group, which provides the necessary electron density for stabilizing the formal +4 oxidation state. In addition, the electron-donating ability of the bromo ligand (through a resonance effect) can also contribute to the stabilization of the coordinatively and electronically unsaturated complex **5** [85, 86].

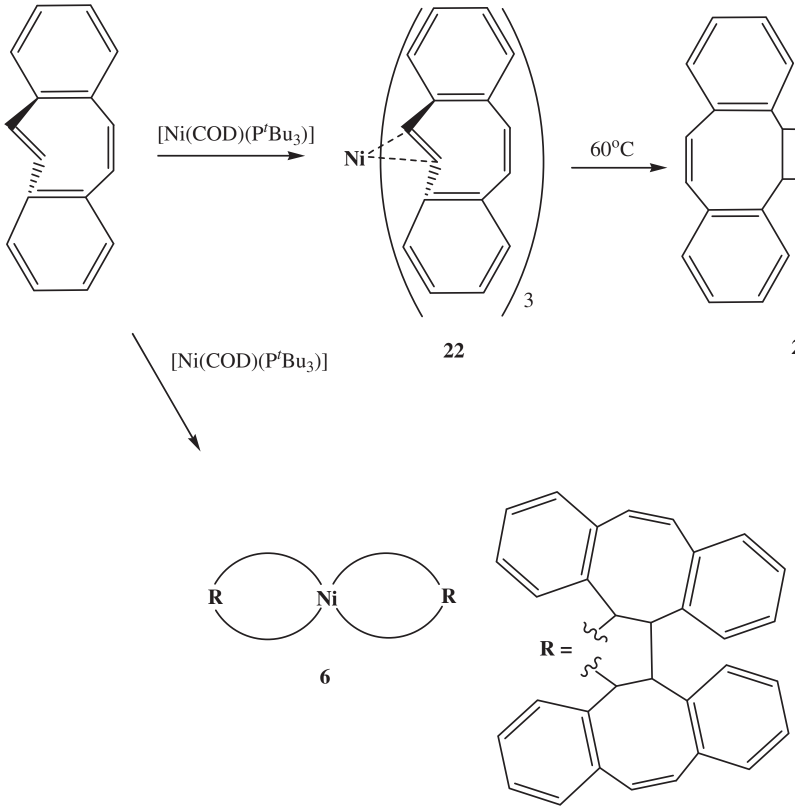
Complexes of this type can also form when a Ni(0) complex reacts with a strained alkene to form a stable tris(alkene) complex, which upon heating can eliminate the corresponding *trans*, *trans*, *trans*-cyclobutane. In the presence of higher proportion of alkene, the Ni(0) precursor forms a stable tetraalkylnickel(IV) complex. It has been



Scheme 4. Synthetic route to triorganonickel(IV) complex.

shown that the ligand-coupling reactions are driven by relief of ring strain in the alkene [87–89]. When a strained alkene reacts with Ni(COD)(P^tBu_3) in cyclohexane, a nickel alkene complex tris((5Z,11E)-dibenzo-[a,e]cyclooctatetraene)nickel(0) (**22**) is formed. This nickel complex **22** with three very bulky alkene ligands is relatively stable at ambient temperature, however on heating at 60°C in benzene a reductively eliminated cyclobutane (**23**) is obtained. It is interesting to note that the reaction of alkene precursor with two-fold excess of Ni(COD)(P^tBu_3) yielded a tetraalkyl complex of nickel(IV) (**6**). This nickelaspirocyclononane (**6**) formed with concomitant release of strain from the ligand is stable and the reverse transformation is greatly disfavored (scheme 5). It is also remarkable that the C–C bond-forming step occurs twice to give a metallaspirocycle. Complex **6** contains two metallacyclopentane units and, especially in view of the very high nominal oxidation state of the nickel center, appears to be a candidate for reductive elimination [89].

In an investigation of nickel-induced transformations of the strained olefin (5Z, 11E)-dibenzo[a,e]cyclooctatetraene, Nuckolls *et al.* [90] obtained a tris(olefin) nickel(0) complex as the primary product. 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 the pictorial representation of **6**). This conformation provides 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 according to DFT calculations on the model complexes $Ni(CH_2CH_2CH_2CH_2)_2$ and $Ni(CH_3)_4$, but corresponds to the ground state [91].



Scheme 5. Preparation of stable tetraalkylnickel(IV) complex.

3. *Structural aspects*

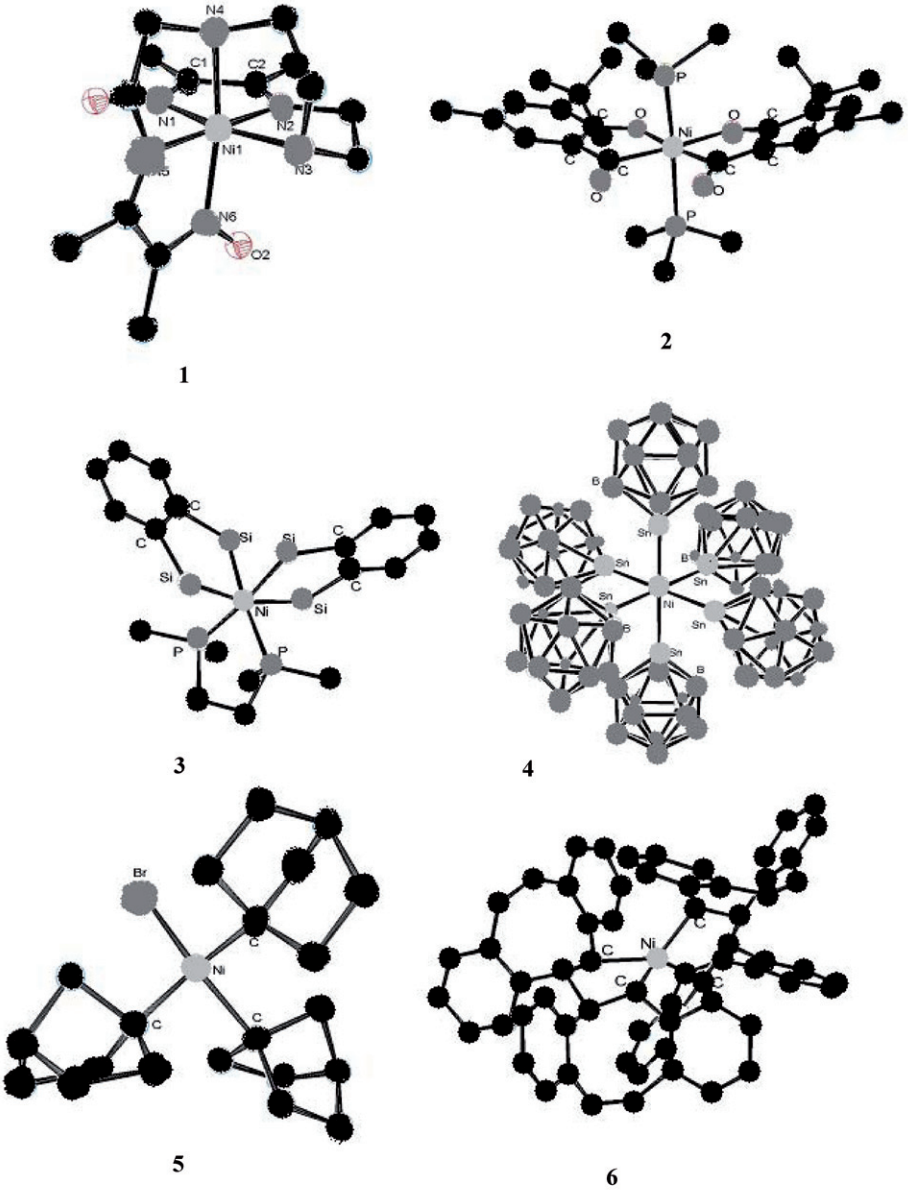
A variety of structural arrangements is possible for Ni(IV) complexes and coordination numbers of four, five, and six are known for tetravalent nickel complexes of the type under review; some examples are given in scheme 6.

3.1. *Four-coordinate complexes*

Single-crystal X-ray structural analysis of a diamagnetic pseudotetrahedral triorganonickel(IV) compound (**5**) shows the four-coordinate Ni with the tetrahedral geometry stretched in the direction of the bromide, so that the C–Ni–C angles are all significantly smaller than normal tetrahedral angle, while the Br–Ni–C angles are correspondingly larger [13]. The structural analysis of a stable nickelaspirocyclononane (**6**) reveals two metallacyclopentane units in a distorted tetrahedral geometry [14].

3.2. *Five-coordinate complexes*

The X-ray structure of bis(silyl)[η^2-(Si–H)]nickel at 113 K was reported by Saigo and co-workers [49]. At this low temperature the complex adopts a distorted



Scheme 6. The ORTEP figures are drawn from Cambridge Structural Database at 50% probability with hydrogen omitted for clarity. Only the ligand atoms bonded directly to Ni are labeled.

trigonal-bipyramidal structure with the Si–H bond coordinated in an η^2-fashion. Interestingly, in solution at slightly higher temperature conversion to the tetravalent tris(silyl)(hydrido)nickel(IV) complex (**13**) is observed with a consequent change in molecular geometry from distorted trigonal bipyramidal to distorted octahedral. This suggests that tris(silyl)nickel complexes of this type are very sensitive to the nature of the surrounding environment [49].

3.3. *Six-coordinate complexes*

The single-crystal X-ray analysis of tris(*N,N*-di-*n*-butyldithiocarbamato)nickel(IV) bromide was one of the first Ni(IV) complexes determined in 1973 by the research group of J.P. Fackler. The octahedral NiS_6 core described by the three dithiocarbamate ligands and nickel center is twisted by 45.4° from a trigonal prismatic arrangement with the distortion from planarity of the $S_2CN(C)_2$ group ascribed to crystal-packing strain [61].

Octahedral arrangement of the tetrakis(silyl)nickel(IV) complex (**3**) was confirmed by X-ray structure analysis. The axial Ni–Si bonds are longer than the equatorial Ni–Si bonds in this complex due to the stronger *trans* influence of silicon than that of phosphorus [48].

The molecular structure of **8** formed by Ni(IV) with the hexadentate amine–imine–oxime ligand is distorted octahedral, with the hexadentate ligand bonded to nickel through its nitrogens. The Ni–N bond lengths in this complex are significantly shorter than those measured in similar Ni(II) complexes. These shortened bond lengths are attributed to the higher oxidation state of nickel [39].

In the octahedral methyl(acylphenolato)nickel(IV) halide complex (**14**) the two trans trimethylphosphine ligands show significant deviation from linearity with a bond angle of 174°, while the metal chelate ring retains its planarity [10a].

The bis(2,6-diacetylpyridine dioximato)nickel(IV) complex (**1**) displays the archetypal six-coordinate geometry with the nickel surrounded by an octahedral ligand field. However, there is a very noticeable closing of the chelate angles from the expected value of 120°. Due to the small size of Ni(IV) severe distortion occurs on complexation of the tridentate ligand in order to accommodate the nickel ion. This results in the chelating oxime groups pulled toward nickel and hence the reduced bite angle of the ligand. The Ni in the two molecular structures mentioned above have a similar distorted-octahedral coordination environment in which the hexadentate ligand is bonded to Ni through nitrogens [38].

The first known example of a structurally determined complex containing a Ni(IV) octahedrally coordinated to six seleniums is tris(*N,N*-di-n-butyldiselenocarbamato) nickel(IV) bromide, reported by Beurskens and Cras [62] in 1971. This complex is isostructural to the tris(*N,N*-di-*n*-butyldithiocarbamato)nickel(IV) bromide.

4. Stability, reactivity, and dynamic behavior

Stabilization of nickel in its higher (>2) oxidation state [92–94] was a challenge to inorganic chemists during the 1970s and 1980s. The ligands used to fulfill the electronic requirements of Ni(III) or Ni(IV) states were primarily oximes [95–99] or deprotonated amides [100–102]. The other cationic complexes such as $[Ni(S_2CNR_2)_3]^+$ (R=Et, Bu) react with CNR_1 ($R_1={}^t$Bu or *p*-ClC_6H_4), $PMePh_2$ or dppe giving $[NiL_2(S_2CNR_2)]^+$ (L=Lewis base) or $[Ni(dppe)(S_2CNR_2)]^+$ [103]. Reaction of tris(dithiocarbamato) nickel(IV) cations, $[Ni(S_2CNR_2)_3]^+$ (R=Et, Bu) with Lewis bases yielded $[NiL_2(S_2CNR_2)]^+$, where L=CNR_1(Me_2CH, Me_3C, *p*-C_6H_4Cl), $PMePh_2$, L_2=dppe. These complexes also react with Ph_3P to yield PPh_3S and $Ni(S_2CNR_2)_2$ [104].

Acid decomposition studies of a dianionic nickel(IV) complex, $[\mathrm{Ni(dmg)_3}]^{2-}$ in the presence of various nucleophiles have been carried out. However, no reaction of the nucleophile with the nickel(IV) complex was observed under the same experimental conditions [105]. It has been reported that titanium(II) solutions (prepared by dissolving titanium metal in triflic acid and HF) can reduce Ni(IV) complex in the presence of catalytic Ti(IV) species. It is proposed that the initially formed cation pairs undergo geminate follow up reactions to give the observed stable products [106]. The simultaneous formation and decomposition of a Ni(IV)–N_3 adduct in aqueous medium has been observed. The spectrophotometric data have been ascribed to a ligand-to-metal charge-transfer mechanism (LMCT), where Ni(II) is oxidized to a brown solution of Ni(IV)–N_3. Further, the Ni(IV)–N_3 is reduced back to Ni(II) and N_3 is oxidized to molecular N_2 [107].

A number of studies pertaining to the formation of nickel(IV) species in solution have been reported [108]. These include the attempted stabilization of nickel(IV) as its periodato and molybdato complexes [109]. Feigl [110] was the first to describe the formation and nature of a nickel(IV)–dmg complex, formed by the treatment of nickel(II)–dmg with iodine in sodium hydroxide solution. Other workers have attempted to isolate nickel(IV)–dmg, but without success [111]. There are conflicting reports as to the valency of nickel when nickel(II)–dmg is treated with an oxidant: some [110, 112] reporting +4 state and others +3 state. Both Feigl [110] and Okac and Simek [112] postulated a dimer of nickel(IV)–dmg.

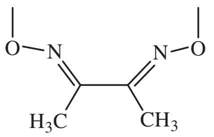
A base-controlled equilibrium has been demonstrated between the monomeric **24** and dimeric **25** nickel(IV)–dmg complexes in solution [113]. These studies revealed that in an ammonia solution, Ni(IV)–dmg in the presence of $\mathrm{Fe(CN)_6^{3-}}$ is a monomer, while the same mixture in sodium hydroxide solution is found to be a dimeric species as shown in equation (10).

$$\mathrm{NiD_3^{2-}} \underset{\mathrm{NH_4OH}}{\overset{\mathrm{NaOH}}{\rightleftharpoons}} \mathrm{Ni_2D_6^{4-}} \qquad (10)$$

24, Monomer

25, Dimer

D =



The kinetic and mechanistic features associated with electron-transfer reactions of various nickel(IV) complexes have been reviewed extensively and categorized with respect to the type of nickel complexes [114]. In addition, investigations on orientation effects in electron-transfer reactions of bis(oxime-imine)nickel(IV) have also been carried out. These ion pairs serve as models for the electron-transfer precursor assemblies in self-exchange reaction and cross-reactions [115]. Ni(IV) oxidation of various reducing agents has been reported including a variety of sulfur compounds, such as thioglycolic acid, thiourea, and N-substituted derivatives, thiosulfate, 2-aminoethanethiol, sulfur(IV) [116], nitrite [117], azide [118], hydroxylamine, hydrazine [119], various metal cations (Fe(II), Sn(II), U(IV)) [120], ascorbic acid [121], aliphatic aldehydes, amines, and alcohols [122–124], tris(1,10-phenanthroline)cobalt(II), hydroquinone [125], EDTA complexes of Co(II) [126], 1,2-dihydroxybenzene and 1,4-dihydroxybenzene [127], luminol [128], and sodium pyruvate [129].

5. Electrochemistry

Electrochemical studies of high-valent nickel complexes involving kinetics and mechanism of electron-transfer reactions provide important information in the evaluation of various self-exchange rate parameters of the oxidizing and reducing species [3, 4]. There has been some debate concerning whether the reduction of Ni(IV) to Ni(II) complexes invariably proceeds through a 1e− transfer (i.e., formation of Ni(III) intermediate) or if there are circumstances favoring a direct 2e− transfer for this conversion. The electrochemically irreversible oxidation of six chelate N_2S_2-type nickel(II) complexes is reported to yield bis(2-amidothiophenolato)nickel(IV) [130]. The stable $[Ni(IV)(dmg)_3]^{2-}$ showed one-electron reduction at pH 12.4, forming the trivalent nickel complex and a two-electron reduction in $1.5\,mol\,L^{-1}$ sodium hydroxide solution [99, 121]. Persulfate oxidation of $[Ni(II)(dapd)_2]^{2-}$ in alkaline solutions yielded violet needles of stable and neutral $[Ni(IV)(dapd)_2]$ [37, 38].

Substitution of divalent nickel ions by other metal species leads to the formation of the unusual oxidation state nickel(IV) during electrochemical oxidation of the matrix nickel hydroxide (equation (11)) [131].

$$2\,Ni(OH)_2 + Cd(OH)_2 \longrightarrow NiOOH + Cd + 2\,H_2O \qquad (11)$$

Electrochemical oxidation of nickel(II) precursor, $[Ni(\eta4\text{-}P_3P')X]^+$ (X = Cl, Br, I), to the analogos nickel(III) and nickel(IV) species is known [132]. In addition, $Ni(IV)L_2(ClO_4)_2$ has been prepared by electrochemical oxidation of $Ni(III)(HL)_2L(ClO_4)_2$ and $Ni(II)(HL)_2(ClO_4)_2$ in alkaline medium (where HL=RC(:NOH)C(R_1): $NCH_2CH(CH_3)NH_2$, R = Me, R_1 = Me, Et, Ph; R = Et, Ph, R_1 = Me) [133]. Studies with cationic $Ni(IV)N_6$ complex, NiL^{2+} of the hexadentate dioxime ligand have also been carried out [134]. Electrochemical studies of $(C_5H_5)_2Ni$ and bis(dicarbollyl) nickel(IV) have shown the formation of formal d^6 Ni(IV), $(C_5H_5)_2Ni^{2+}$, and $(dicarbollyl)_2Ni(IV)$ through the corresponding Ni(III) intermediates. These strong oxidizing Ni(IV) species ($E\,½ = +0.55$ V *vs.* SCE) rapidly decompose in solution [135].

Nickel(II)dithiocarbamate bearing two ferrocenyl groups has been oxidized to nickel(IV) dithiocarbamate bearing three ferrocenyl groups [136]. The electrochemical oxidations of Ni(bpy) (bpy=2,2′-bipyridine) to the corresponding Ni(IV) species in liquid sulfur dioxide were studied by cyclic voltammetry [137].

Cyclic voltammetric studies of the five-coordinate nickel complexes $[Ni\text{-}(mtas)_2]^{2+}$ (mtas=bis(2-(dimethylarsino)phenyl)methylarsine), $[Ni(ptas)_2]^{2+}$ (ptas=bis(2-(dimethylarsino)-phenyl)phenylarsine), $[Ni(L_2)(mtas)^{12+}$ (L_2=1,2-bis(dimethylarsino)benzene (diars), 1,8-bis(dimethylarsino)naphthalene (dman), 1,2-bis(dimethylarsino)tetrafluorobenzene (F_4-diars)), and $[Ni(L_2)(ptas)]^{2+}$ (L_2=diars, dman) show the formation of Ni(IV) within the accessible potential range. These homoleptic hexacoordinate Ni(IV) species were stable with respect to disproportionation. For the heteroleptic complexes, a molecule of solvent or an electrolyte anion coordinates to the Ni(IV) center and the kinetic stability is reduced [138]. Chemical and electrochemical oxidation of

$[Ni(II)Me_2LH_2]^{2+}$ to highly colored diamagnetic $[Ni(IV)Me_2L]^{2+}$ was reported [139]. The reported redox potentials in water for the couples Ni4+/3+ and Ni3+/2+ have been reported as +0.66 and +0.275 V *versus* SCE, respectively.

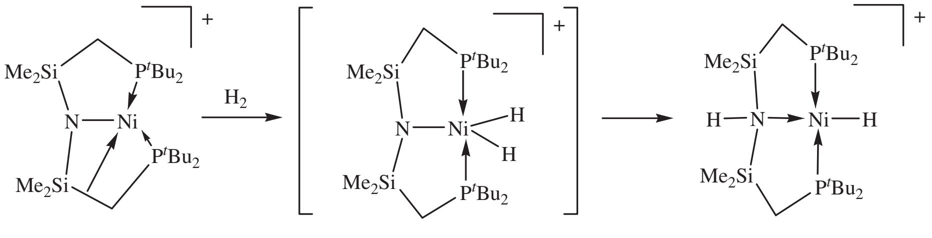
6. Significance and applications

Homogeneous catalysis as the major industrial driver of fundamental organometallic research has been enjoying great benefit from organotransition metal species that promote bond formation between hydrocarbon fragments [140]. Most of the commercially important processes that serve to produce large-volume organic feedstock chemicals such as linear α-olefins (Shell Higher Olefins Process), linear aldehydes (hydroformylation), acetaldehyde (Wacker-Hoechst), acetic acid (Monsanto), adiponitrile (DuPont hydrocyanation of butadiene) operate at low-valent metal centers, which also includes nickel in various oxidation states as active species. It is not surprising that by far most organometallic research during the past few decades has been directed toward an understanding and improvement of these catalytic reactions as well as toward the related stoichiometric chemistry. As a matter of consequence, the chemical relationship and interconvertability between high and low oxidation states within a given class of compounds play an important role in the chemistry of organotransition metal complexes [141].

Catalytic autoxidation of atmospheric sulfur(IV) in alkaline medium by Ni_2O_3 has been investigated [142]. Caulton and co-workers [143] reported a reaction of $[(PNP)Ni]BAr_4^F$ with 1 atm of H_2 in CH_2Cl_2 at 25°C yielding (below equation) a BAr_4^F salt (Ar^F=3,5-$(CF_3)_2C_6H_3$) of the cation $(PN(H)P)NiH^+$. It has been proposed that the reaction occurs through the formation of a tetravalent nickel intermediate $[(PNP)NiH_2]^+$ (**26**) and the subsequent proton transfer to the nitrogen attached to the metal as indicated in scheme 7 [143].

The catalyst system containing a mixture of Ni catalyst and NaOCl provides virtually complete oxidation of the reduced sulfur species to non-odorous species. This process is useful for the treatment of condensates, permitting their reuse within industrial applications [144].

The role of tetravalent nickel species as active intermediates in oxygen-transfer reactions catalyzed by square-planar nickel(II) complexes of bis(*N,N′*-disubstituted



26, a Ni(IV)dihydride intermediate

Scheme 7. Proposed mechanism of [(PNP)Ni] [BAr4F]-Hydrogen reaction.

oxamides) and related ligands in an aerobic epoxidation of olefins has been shown [145]. Electrochemical devices have been developed based on hydrotalcite [Ni/Al–Cl] electrodes for the amperometric determination of oxidizing species. Studies on the oxidation of Ni(II) to tetravalent nickel have been carried out [146]. Novel electrically conducting charge-transfer complexes have been prepared from the reaction of (*closo*-(3)-1,2-$C_2B_9H_{11})_2$Ni(IV) and tetraselenotetracene (TSeT) with tetrathiotetracene (TTT) [147].

The cationic Ni(IV)N_6 complex, NiL^{2+}, of the hexadentate dioxime ligand $(MeC(=NOH)C(Me)=NCH_2CH_2NHCH_2-)_2$ has been incorporated by ion-exchange methods into poly(*p*-styrenesulfonate) (P-SS) films attached to a basal pyrolytic graphite electrode surface over the pH range 1–9. Studies on the electroprotic behavior of this binding Ni(IV) complex have been carried out and these properties can be used to develop polyelectrolyte-coated electrodes for surface binding of electroactive complex ions [134].

Similarly, a variety of nickel(II) complexes derived from different tetraaza macrocycles, Schiff base, porphyrins, and phosphine ligands have been examined for catalytic epoxidation of olefins. The catalytic activity is tentatively ascribed to an active oxo-nickel(IV) intermediate [148].

The high valence of metals like Ni(IV) and Co(III) in the active component of hydrodesulfurization (HDS) catalysts is important in heterogeneous catalysis as the electronic structure of the transition metal is a key factor that determines catalytic activity [149].

Organometallic chemistry of later transition metals in high oxidation states has been of considerable interest because of its relevance to certain catalytic reactions [150–153]. The synthesis of high-valent nickel complexes [154–156] has also attracted the attention of bioinorganic chemists as possible model complexes [155, 156], particularly for the Ni sites in [NiFe]-hydrogenases [157]. Industrial applications of these complexes are evidenced by the report of pure tetravalent nickel in cobalt-substituted nickel oxyhydroxide, $Ni_{0.70}Co_{0.30}O_2K_{0.30}(H_2O)_{0.42}$ as a secondary battery electrode [158].

The majority of reported nickel(IV) complexes contain the metal ion surrounded by an octahedral field of electronegative elements: oxygen, sulfur, nitrogen, phosphorus, carborane, and fluorine, for example, heteropolyniobate and heteropolymolybdenate complexes of the type M_2NiF_6 (M=Na, K, Rb, Cs).

7. Concluding remarks

This review highlights the synthesis and reactivity of nickel(IV) complexes with various donor ligand systems containing mainly O, S, N, P, B as well as C. It not only illustrates a rich chemistry, but also a number of important features. A variety of interesting nickel(IV) complexes has been synthesized and this has greatly contributed to increased understanding of nickel coordination chemistry. The stability of tetraalkyl nickel(IV) complexes can lead to more such stable species by designing appropriate ligand systems. It is hoped that this article will stimulate further research on the variable oxidation states of nickel chemistry since this metal not only plays a significant role in catalysis and biochemistry but opens new frontiers in chemistry.

Abbreviations

dmpe	1,2-bis(dimethylphosphino)ethane
depe	1,2-bis(diethylphosphino)ethane
dppe	1,2-bis(diphenylphosphino)ethane
dmg	dimethylglyoxime
en	ethylenediamine
pn	1,2-propanediamine
[14]aneN_4	1,4,8,11-tetraazacyclotetradecane
acac	acetylacetonate
mtas	bis(2-(dimethylarsino)phenyl)methylarsine
ptas	bis(2-(dimethylarsino)phenyl)phenylarsine
diars	1,2-bis(dimethylarsino)benzene
dman	1,8-bis(dimethylarsino)naphthalene
F_4-diars	1,2-bis(dimethylarsino)tetrafluorobenzene
EXAFS	extended X-ray absorption fine structure

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