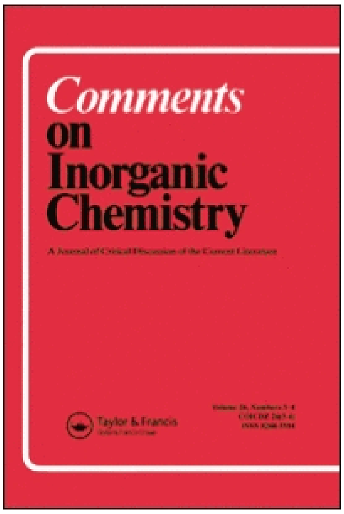

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The Redox Behavior of Transition Metal Complexes with Soft Ligands

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The Redox Behavior of Transition Metal Complexes with Soft Ligands

Recent electrochemical investigations of binary mesityl compounds of the early transition metals and of a series of nickel(0) complexes illustrate the influence of the nature and oxidation state of the central atom and of the ligands on the redox behavior. On the basis of macrocyclic nickel(II) complexes, the effects of ring size and unsaturation of the ligand on the redox potential and on the site of electron addition [one-electron reduction of nickel(II) or of the ligand] are demonstrated. The electrochemical data may be used for an explanation or even for a prediction of the course of chemical reactions. A remarkable process is the nucleophilic substitution of unsaturated organic substrates (maleic acid anhydride, quinones) within the coordination sphere of nickel(0) which yields a radical anion.

INTRODUCTION

Many redox couples of the types

$$\mathrm{Fe^{II}L_6 \rightleftharpoons Fe^{III}L_6 + e^-} \quad \text{or} \quad \mathrm{Co^{II}L_6 \rightleftharpoons Co^{III}L_6 + e^-}$$

have been studied by electrochemical methods and an important influence of the ligands on the standard electrode potential has been demonstrated (Table I). For the cobalt(II) couples the replacement of aquo by cyano ligands causes a decrease of E_0 by 2.67 V. On the other hand, water, ammonia and 2,2'-bipyridine (bpy)[1] are hard ligands, and cobalt and iron of oxidation states II and III are hard central atoms. Therefore most of the complexes mentioned in Table I are thermodynamically or at least kinetically stable in air and in aqueous solution.

During the last few years many complexes with soft central atoms and soft ligands have been prepared. According to Pearson's model they are fairly stable at room temperature, but are sensitive to air and humidity. The electrochemical investigation of such complexes requires more effort than the study of the above-mentioned cobalt compounds. But the results are of considerable importance for an understanding of reactivity since

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TABLE I
Standard electrode potentials E_0 of some oxidation-reduction couples (volts)

$[Fe(CN)_6]^{4-} \rightleftharpoons [Fe(CN)_6]^{3-} + e^-$	+0.36
$Fe^{2+}_{aq} + 6F^- \rightleftharpoons [FeF_6]^{3-} + e^-$	+0.40
$Fe^{2+}_{aq} + 2PO_4^{3-} \rightleftharpoons [Fe(PO_4)_2]^{3-} + e^-$	+0.61
$Fe^{2+}_{aq} \rightleftharpoons Fe^{3+}_{aq} + e^-$	+0.77
$[Fe(bpy)_3]^{2+} \rightleftharpoons [Fe(bpy)_3]^{3+} + e^-$	+1.10
$[Co(CN)_6]^{4-} \rightleftharpoons [Co(CN)_6]^{3-} + e^-$	−0.83
$[Co(NH_3)_6]^{2+} \rightleftharpoons [Co(NH_3)_6]^{3+} + e^-$	+0.1
$Co^{2+}_{aq} \rightleftharpoons Co^{3+}_{aq} + e^-$	+1.84

many reactions of the complexes of soft central atoms and soft ligands involve electron transfer.

Soft ligands (alkyl and aryl anions, olefins, phosphines, carbon monoxide, dithiolenes,[3] carbon disulfide,[4] mercaptide and iodide ions) are easily polarizable and their donor atoms are of medium electronegativity.[2] The rigid tetramesityl compounds of early transition metals are discussed first in order to demonstrate the influence of the central atom on the electrochemical behavior. Then the zerovalent complexes of the nickel triad are presented to show the role of the ligands. Some macrocyclic complexes form the subject of the third part. In this case the donor atoms are the hard oxygen and nitrogen, but because of the delocalized π-electron systems of most macrocyclic ligands and the resulting polarizibility, these systems bear some relation to simple soft ligands.

For all three classes of transition metal compounds the use of electrochemical data for explanation and even prediction of the course of chemical reactions is illustrated.

BINARY MESITYL COMPOUNDS OF TRANSITION METALS

Because of the medium electronegativity of carbon, σ-hydrocarbyls are strong n-donors. Therefore, in transition metal compounds they stabilize high oxidation states [$W(CH_3)_6$, Ref. 5] and favor low coordination numbers in electron-rich complexes[6] ($[Li(Me_4en)_2][MeNi(C_2H_4)_2]$).[7] Most transition metal σ-hydrocarbyls are sensitive to oxidants, acids and high temperature. Stabilization is possible by bulky ligands that completely shield the central atom. In this way an additional interaction between the already σ-bonded hydrocarbyl groups and the central atom, a requirement for α- or β-hydride elimination, is inhibited. Based on this conception, during the last few years it has been possible to prepare stable transition metal σ-hydrocarbyls with norbornyl, neopentyl, trimethylsilylmethyl, and adamantyl ligands.[8-10] Seidel and coworkers[11] have opened the field of transition metal

TABLE II
Half-wave potentials of binary transition metal mesityls[14,15]

	$E_{1/2}$(V)	Change of d-orbital occupation
$Ti(Mes)_4^- \rightleftharpoons Ti(Mes)_4 + e^-$	−1.24 (rev.)[a]	$3d^1 \longrightarrow 3d^0$
$V(Mes)_4^- \rightleftharpoons V(Mes)_4 + e^-$	−0.53 (rev.)[a]	$3d^2 \longrightarrow 3d^1$
$Cr(Mes)_4^{2} \rightleftharpoons Cr(Mes)_4^- + e^-$	−2.13 (irrev.)[a]	$3d^4 \longrightarrow 3d^3$
$Cr(Mes)_4^- \rightleftharpoons Cr(Mes)_4 + e^-$	−0.81 (rev.)[a]	$3d^3 \longrightarrow 3d^2$
$Mo(Mes)_4^{2} \rightleftharpoons Mo(Mes)_4^- + e^-$	−2.51 (irrev.)[b]	$4d^4 \longrightarrow 4d^3$
$Mo(Mes)_4^- \rightleftharpoons Mo(Mes)_4 + e$	−1.47 (rev.)[b]	$4d^3 \longrightarrow 4d^2$
$Mo(Mes)_4 \rightleftharpoons Mo(Mes)_4^+ + e^-$	+0.47 (rev.)[b]	$4d^2 \longrightarrow 4d^1$

[a] Room temperature in thf, Hg-dropping electrode, SCE as a reference; [complex] = 1.10^{-3} M, $[NH_4(PF_6)] = 1.10^{-1}$ M. Mes = mesityl is an abbreviation for the 2,4,6-trimethylphenyl group.
[b] Room temperature in dmf, Hg-dropping electrode, SCE as a reference; [complex] = 1.10^{-3} M, $[NEt_4ClO_4] = 1.10^{-1}$ M.

mesityls. Of special interest are the distorted tetrahedral tetramesityl compounds. The four mesityl ligands are closely "locked" together and form a rigid cage which is only slightly influenced by the central atom. Thus the bond angles $V(Mes)_4$ and $[V(Mes)_4]^-$ are equal, but the mean V–C distance of the anion is somewhat longer (2.14 Å compared to 2.08 Å).[12,13] (Mes = mesityl is an abbreviation for the 2,4,6-trimethylphenyl group). For the tetramesityls we thus find a behavior which is unusual for high-valent vanadium, chromium, and molybdenum compounds: the oxidation state may change without any change of the coordination sphere. Therefore these compounds are suitable for electrochemical studies.

Table II shows†:

(a) The half-wave potentials are reversible with the exception of the couples Mo(II)/Mo(III) and Cr(II)/Cr(III). This may be caused by the kinetic instability of $[Mo(Mes)_4]^{2-}$ or $[Cr(Mes)_4]^{2-}$

$$[M^{II}(Mes)_4]^{2-} \rightleftharpoons [M^{II}(Mes)_3]^- + Mes^- \qquad M = Cr,Mo \qquad (1)$$

and is a result of the preference of low coordination numbers in σ-hydrocarbyl complexes of low-valent central atoms.[6] [Recently $LiCr(Mes)_3$-(dioxane)(Et_2O) was described.[16]]

(b) The half-wave potentials increase with increasing oxidation state of the central metal atom.

(c) The relative values of the half-wave potentials illustrate the influence of d-electron configuration. The configurations $3d^0$ [Ti(IV)] and nd^2[V(III),

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† As the half-wave potentials of the molybdenum compounds have been measured in dimethylformamide, they cannot be directly compared with those of the titanium, vanadium, and chromium compounds.

Cr(IV),Mo(IV)] are the favored ones. This is in accord with the simple crystal-field model prediction of a special stabilization for tetrahedral complexes with a vacant or half-filled *e* level.

(d) The driving force for electron transfer originates not only in the different ligand-field stabilization of oxidant and reductant. Thus, the step $[V(Mes)_4]^- \rightarrow V(Mes)_4$ is rendered more difficult when compared to $[Ti(Mes)_4]^- \rightarrow Ti(Mes)_4$ and $[Cr(Mes)_4]^- \rightarrow Cr(Mes)_4$, but is not excluded. Probably the increase in the V–C bond length which is connected with the oxidation {see the V–C distances in $[V(Mes)_4]^-$ and $V(Mes)_4$} is of critical importance.

(e) The redox series $[Mo(Mes)_4]^{2-} \rightarrow [Mo(Mes)_4]^+$ is, to our knowledge, the most extended one with binary σ-organometallic compounds.

It follows from the half-wave potentials that the reactions

$$2\,[Li(thf)_4][M(Mes)_4] + \tfrac{1}{2}\,O_2 \rightarrow M(Mes)_4 + Li_2O + 8\,thf, \qquad (2)$$

$$M = Ti, V, Cr, Mo,$$

$$Mo(Mes)_4 + \tfrac{3}{2}\,I_2 \rightarrow [Mo(Mes)_4]I_3 \qquad (3)$$

can occur. On the other hand, it is quite understandable why all experiments to prepare salts of the anion $[V(Mes)_4]^{2-}$ have been unsuccessful: up to a potential of −2.8 V no reduction of $[V(Mes)_4]^-$ occurs.

The following comparison illustrates the influence of the coordination number on the course of redox reactions in the field of organometallic complexes. $Li_4VPh_6(Et_2O)_4$ was prepared from vanadium trichloride and lithium phenyl[17]:

$$VCl_3(thf)_3 + 7\,LiPh \xrightarrow[Et_2O]{thf} Li_4VPh_6(Et_2O)_4 + 3\,LiCl + \tfrac{1}{2}\,Ph\text{–}Ph$$

The six phenyl ligands occupy octahedral sites stabilizing vanadium(II) as a $3d^3$ species. Six mesityl groups, because of their bulkiness, cannot fit around vanadium(II). It is the result of the steric requirements and of the different ligand-field stabilization of tetrahedral and octahedral $3d^3$ species that anionic mesityl complexes of vanadium(II) do not exist.

ELECTRON-RICH NICKEL TRIAD COMPLEXES

By choice of the ligands the redox potential of nickel(0) complexes can be varied by more than 1 V (Table III). The lowest values are found for complexes with n-donor ligands (PEt_3, bpy), the highest ones for complexes with π-acids (cod). The partial substitution of triphenylphosphine by the π-acid ethene causes an increase of ~0.5 V. PPh_3 is a weaker n-donor than

TABLE III

Redox potentials $\mathrm{Ni^0 \rightleftharpoons Ni^I + e^-}$ in tetrahydrofuran[a]

$\mathrm{Ni(PEt_3)_4}$	−0.74 V	CV	Ref. 18
(bpy)Ni(cod)	−0.55 V	P	Ref. 19
$\mathrm{(bpy)Ni(PPh_3)_2}$[b]	−0.5 V	P	Ref. 19
$\mathrm{Ni(PPh_3)_4}$[c]	−0.41 V	CV	Ref. 18
	−0.33 V	P	Ref. 19
$\mathrm{(Cy_3P)_2Ni(C_2H_4)}$	−0.20 V	P	Ref. 19
$\mathrm{(Ph_3P)_2Ni(C_2H_4)}$	+0.16 V	P	Ref. 19
$\mathrm{Ni(cod)_2}$	+0.30 V	P	Ref. 19
$\mathrm{(bpy)Ni^{II}(Mes)_2}$[d]	+0.31 V	P	Ref. 19

[a] P = polarography (room temperature, Hg-dropping electrode, SCE as a reference; [complex] = 1.10^{-3} M, $[\mathrm{NH_4(PF_6)}] = 1.10^{-1}$ M). CV = cyclic voltammetry (room temperature, SCE as a reference: [complex] = 1.10^{-3} M, $[\mathrm{NR_4ClO_4}] = 1.10^{-1}$ M). cod = 1,4-cyclooctadiene; Cy = cyclohexyl.

[b] In dilute solution dissociates to $\mathrm{(bpy)Ni(PPh_3)}$ or $\mathrm{Ni(PPh_3)_3}$.

[c] $\mathrm{Ni(PPh_3)_4}$ is completely dissociated to $\mathrm{Ni(PPh_3)_3}$ and $\mathrm{PPh_3}$.

[d] $\mathrm{Ni^{II} \rightleftharpoons Ni^{III} + e^-}$.

$\mathrm{PEt_3}$,[20] and therefore $\mathrm{Ni(PPh_3)_4}$ has a more positive redox potential than $\mathrm{Ni(PEt_3)_4}$. Interestingly, the half-wave potentials of $\mathrm{Ni(cod)_2}$ and $\mathrm{(bpy)Ni(Mes)_2}$ are equal. This is the reason for the similar reactivities of nickel(0)- and $\mathrm{(bpy)Ni^{II}R_2}$-type complexes.[21]

The influence of the different redox potentials becomes quite evident in the oxidative addition of aryl halides. In the case of $\mathrm{Ni(PEt_3)_4}$, the oxidative addition is independent of the substrate and the following mechanism has been demonstrated:

$$\mathrm{Ni(PEt_3)_4 \rightleftharpoons Ni(PEt_3)_3 + PEt_3}, \qquad (4)$$

$$\mathrm{Ni(PEt_3)_3 + ArX} \longrightarrow \underset{\mathbf{A}}{[\mathrm{Ni^I(PEt_3)_3ArX^{\bullet-}}]}, \qquad (5)$$

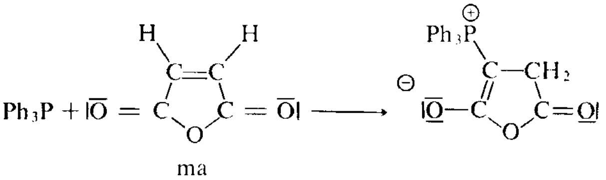
$$[\mathrm{Ni^I(PEt_3)_3ArX^{\bullet-}}] \left\{ \begin{array}{ll} \longrightarrow \mathrm{(PEt_3)_2Ni^{II}(Ar)X + PEt_3} & (6) \\ \longrightarrow \mathrm{Ni(PEt_3)_3^+ + X^- + Ar^\bullet} \ldots & (7) \end{array} \right.$$

The rate-limiting step is the outer-sphere electron transfer process (5) which yields the tight ion pair **A**. Competition between (6) and (7) determines the partitioning of the products. Cage collapse of the ion pair (6) is preferred for aryl chlorides, while fragmentation of the $\mathrm{ArX^{\bullet-}}$ moiety (7) followed by diffusion of aryl radicals out of the solvent cage occurs with aryl iodides.

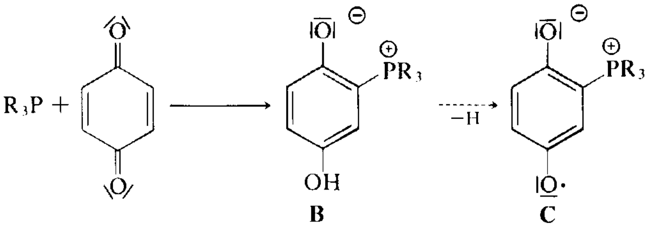
In the case of the weaker reductant $\mathrm{Ni(PPh_3)_4}$ the oxidative addition is significantly slower. The mechanism depends on the substrate.[18,22] Aryl halides with electron-withdrawing substituents ($\sigma > 0.2$) react according to the electron-transfer mechanism (4)–(7). A three-center process is proposed for substrates with electron-releasing substituents ($\sigma < 0.2$).

The influence of the redox potentials of nickel(0) complexes on the reactivity is further illustrated by the following more qualitative results: benzonitrile adds to $Ni(PEt_3)_3$ but not to $Ni(PPh_3)_3$,[23] $Ni(PEt_3)_3$ is more active for oxidative additions than $(Et_3P)_2Ni(cod)$,[24] and $Ni(cod)_2$ does not react with aryl halides in thf or toluene.[25]

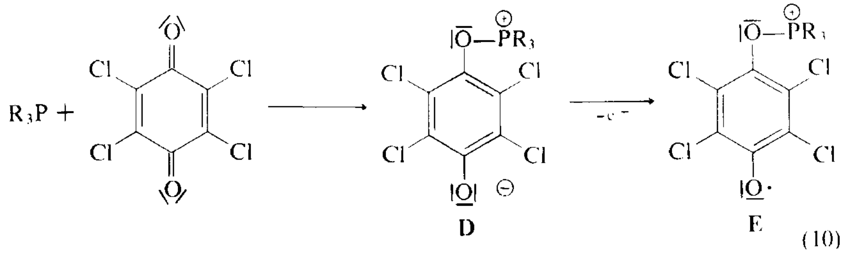
In all of the cases discussed above, the influence of the ligands was restricted to the kinetics of redox reactions [the total failing of a reaction, as for $Ni(cod)_2$, may be considered to be an extreme case]. But there are also some processes which involve the direct participation of the ligands. Nucleophilic additions of tertiary phosphines to unsaturated carbonyl complexes have long been known:



(8)[26]

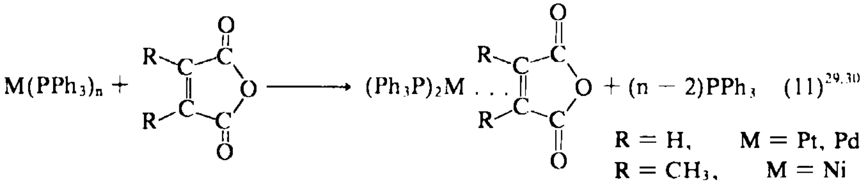


(9)[27]

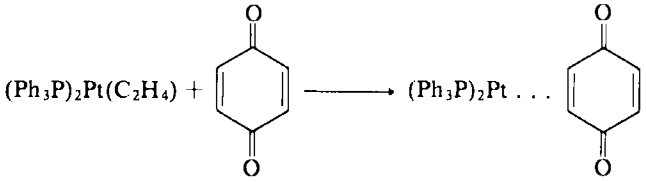


(10)[28]

These reactions fail to occur in the coordination sphere of platinum(0) or palladium(0) evidently because of the weakening of both the nucleophilicity of the phosphine and the electrophilicity of the substrate through their interaction with the central atom:

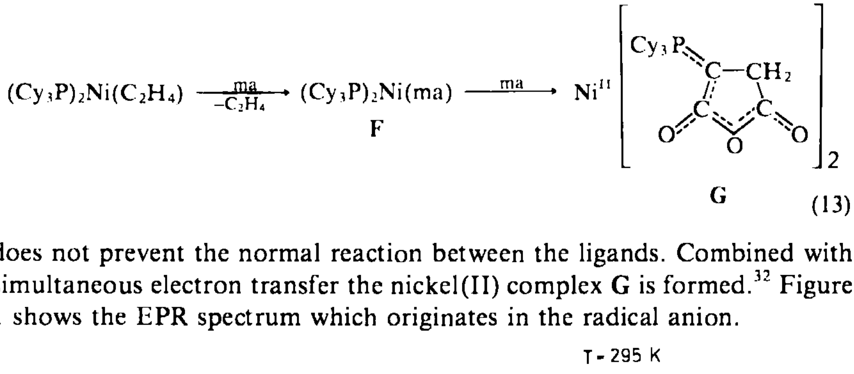


(11)[29,30]



(12)[31]

Nickel(0) as the central atom of the intermediate **F** in reaction (13)



F

G (13)

does not prevent the normal reaction between the ligands. Combined with simultaneous electron transfer the nickel(II) complex **G** is formed.[32] Figure 1 shows the EPR spectrum which originates in the radical anion.

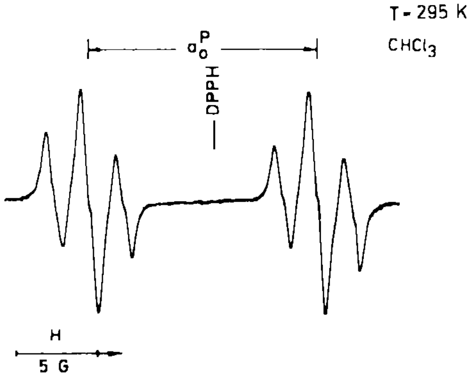
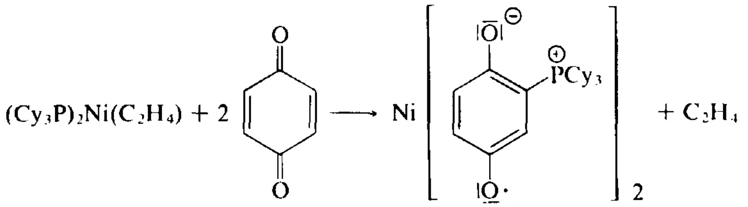


FIGURE 1 EPR spectrum of compound **G**.

The formation of G needs a proton shift. Therefore dimethylmalcic acid anhydride (Me$_2$ma) does not yield a compound which is analogous to G but rather a normal substitution product [Eq. (11)]. The isolation of (Cy$_3$P)$_2$Ni(Me$_2$ma) clearly implicates F as an intermediate of reaction (13).

H, a product comparable to G, is obtained as a dark precipitate from a solution of (Cy$_3$P)$_2$Ni(C$_2$H$_4$) and *p*-benzoquinone in benzene/thf[33]:

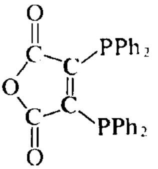


H

(14)

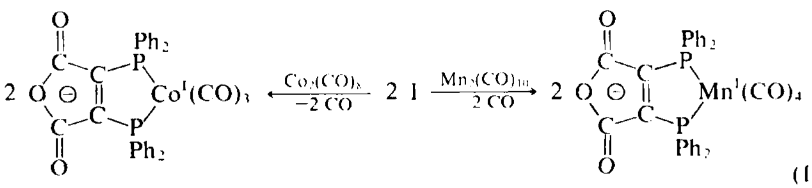
It is fairly stable in the absence of a solvent and air. The magnetic moment ($\mu_{eff} = 3.13$ B.M.) originates in a radical anion of type C[27] (identified by the solid-state EPR spectrum with $g_0 = 2.0046$). Up to now no good crystals have been obtained. Therefore we cannot state anything reliable about the bond between the radical anions and the central atom. Phosphine-containing radical anions are evidently also formed from Ni(PEt$_3$)$_4$ and chloranil.[34]

Fenske *et al.*[35] have studied the coordinative behavior of



I

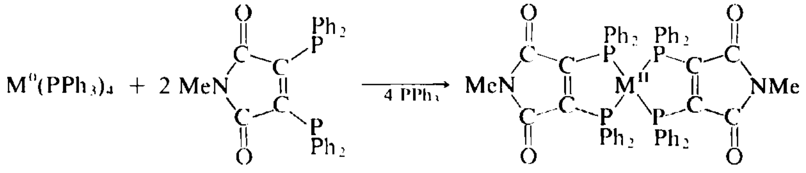
a ligand combining the functions of ma (electron acceptor) and of a bidentate phosphine (soft chelating ligand). They prepared a normal diamagnetic 1,1-complex of I with nickel(II). But there are remarkable reactions with the simple binary carbonyls of cobalt and manganese:



(15)

An electron transfer from the central atom to the LUMO of the ma function yields cobalt(I) or manganese(I) with 26 or 24 electrons, respectively. By coordination of five or six soft donor groups, these central atoms form mononuclear complexes obeying the rare gas rule.

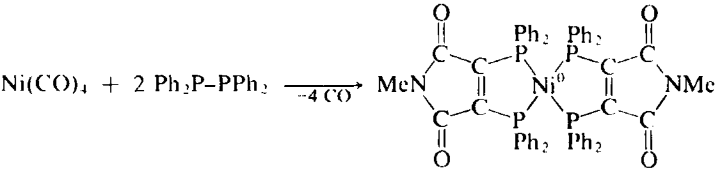
Radical anions are also constituents of the square-planar complexes **K**:[36]



M = Pd, Pt (Ph₂P–PPh₂)

K

(16)



(17)

L

At first sight it is surprising that in the corresponding nickel complex the central atom remains zerovalent. We suggest the following explanation: independent of the oxidation state, the σ-bond share is decisive for the overall bond strength between platinum or palladium and soft ligands. But the σ-bond energy is higher for complexes of the divalent central atoms. Therefore the complex formation between platinum(0) or palladium(0) and $Ph_2P\text{–}PPh_2$ is connected with an electron transfer to the low lying LUMO of the ligand and produces the isomer $M^{II}(Ph_2P\dot{-}PPh_2)_2$. π interactions are essential for the stability of nickel complexes with soft ligands. They are much stronger in nickel(0) than in nickel(II) compounds.[37] Therefore $Ni^0(Ph_2P\text{–}PPh_2)_2$ is the stable isomer (**L**).

$Ph_2P\text{–}PPh_2$ as a ligand with an electron sink completely reverses the redox behavior found for zerovalent nickel triad complexes with simple phosphine ligands.[38]

TABLE IV
Electrochemical behavior of macrocyclic complexes of nickel (CV)[39]

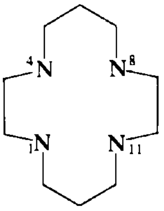
	Redox potential[a] $NiL^{+} \rightleftharpoons NiL^{2+} + e^{-}$	Type of electron exchange
$N_4(14)$	−1.70 V	$Ni^{I}L/Ni^{II}L$
$Me_6N_4(14)$	−1.57 V	$Ni^{I}L/Ni^{II}L$
$N_4(15)$	−1.5 V (irrev.)	$Ni^{I}L/Ni^{II}L$
$Me_6N_4(16)$	−1.40 V	$Ni^{I}L/Ni^{II}L$
$Me_6N_4(14)$4,11-diene	−1.57 V	$Ni^{I}L/Ni^{II}L$
$Me_6N_4(14)$1,4,8,11-tetraene	−1.35 V	$Ni^{I}L/Ni^{II}L$
$Me_6N_4(14)$1,3,7,11-tetraene	−0.76 V	$Ni^{II}L^{-}/Ni^{II}L$

[a] In acetonitrile, 0.1 M NBu_4BF_4, Ag/Ag^{+}(0.1 M) as a reference.

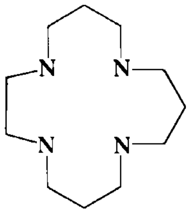
MACROCYCLIC NICKEL COMPLEXES

An essential subject of the investigations of macrocyclic complexes is the modeling of metalloenzymes (hemoglobin, corrin, cobalamin, etc.) and of their metabolic reactions. Among these complexes redox processes are of high importance. Busch *et al.*[39] studied the redox process $NiL^{+} \rightleftharpoons NiL^{2+} + e^{-}$ of nickel complexes NiL^{2+} of ligands with the framework $N_4(14)$, $N_4(15)$, and $N_4(16)$ and stated the following variables (Table IV):

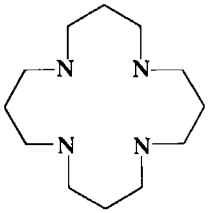
(a) In a progression to larger macrocyclic rings [$N_4(14) \rightarrow N_4(15) \rightarrow N_4(16)$] the reduction occurs with greater ease. As to the increased "hole size," the 16-membered ligand can more easily accommodate the larger nickel(I). This applies also to the methyl-substituted ligands $Me_6N_4(14)$ and $Me_6N_4(16)$.



$N_4(14)$



$N_4(15)$



$N_4(16)$

(b) Ligand unsaturation influences the magnitude of the redox potential and also the site of electron addition. Compared to the saturated $Me_6N_4(14)$ ligands with isolated double bonds, $Me_6N_4(14)$4,11-diene and $Me_6N_4(14)$1,4,8,11-tetraene afford only a slight shift of the redox potential. The added electron occupies a MO which is predominantly localized on the central atom, an EPR spectrum characteristic of axially symmetric nickel(I) complexes is observed. Ligands with conjugated double bonds [$Me_6N(14)$1,3,7,11-

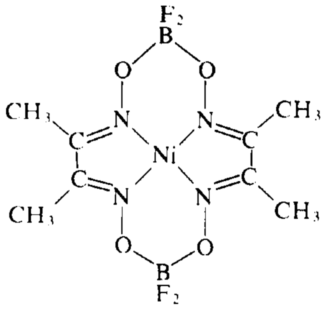
tetraene] produce more positive redox potentials. As the LUMO of the nickel(II) complex is predominantly a π^*-ligand orbital, the one-electron reduction results in a nickel(II) complex of a radical anion (identified by EPR spectroscopy).

In special cases, by the addition of carbon monoxide in an axial position, a ligand-to-metal intramolecular electron transfer can be induced within the reduced species; this is the case for the reduction product of $Ni^{II}M$ [reaction (18)][40]:

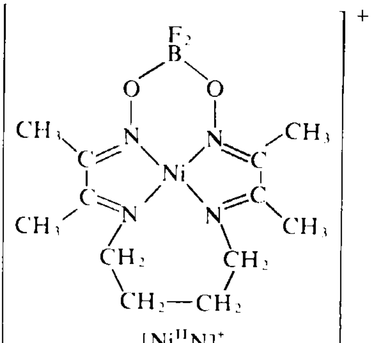
$$[Ni^{II}M^{\bar{\cdot}}]^{-} + CO \rightarrow [Ni^{I}M(CO)]^{-} \qquad (18)$$

$$[Ni^{II}N^{\bar{\cdot}}] \rightleftharpoons [Ni^{I}N] \qquad (19)$$

As there is only a small energy difference between the isomers of reduced $[Ni^{II}N]^+$, a temperature-dependent equilibrium is established [reaction (19)].[40] The structures of $Ni^{II}M$ and of $[Ni^{II}N]^+$ are shown below:



$Ni^{II}M$



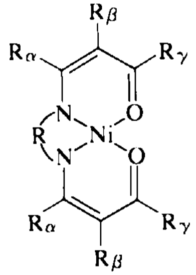
$[Ni^{II}N]^+$

At 232 K the left side of reaction (19) is favored, increasing temperature causing a shift to the right side. The g value of $N^{\bar{\cdot}}$ (2.048) is uncommonly high for a radical anion of such a type. Therefore further studies are needed.

Complexes of radical anions are distinguished by unusual reactions. They may dimerize at low temperatures[40] or in concentrated solutions[41] [the bond between the half-dimers results from a nickel(II)–nickel(II) interaction and direct ligand–ligand π bonds] and, when produced as intermediates of electrochemical reductions, they may be hydrogenated by a protic solvent like methanol[39] (C=N bonds are converted to CH–NH bonds).

Jäger and Rudolph[42] studied the redox behavior of tricyclic metal chelates with the donor set N_2O_2[NiP]. For the process [NiP] → $[NiP]^-$ they found an additive influence of the substituents R_α, R_β, and R_γ (R = Me, Ph, COMe, COOEt, CN) on the half-wave potential. The existence of a linear relation between log K of the reaction

$$[\mathrm{NiP}] + 2\ \mathrm{py} \rightleftharpoons [\mathrm{NiP(py)_2}] \qquad (20)$$



[NiP]

and the half-wave potential is of great interest.† This means that Lewis acidity and redox behavior of tricyclic nickel(II) complexes are influenced by peripheral substituents in a similar way, and mainly by electronic factors. For the complexes [CuP] a reversible one-electron reduction was observed in one case only.[43] But the few data, in accordance with the results of pyridine addition, illustrate one important feature of macrocyclic copper(II) complexes, and this is the poor penetration of the peripheral ligands. Their influence on the reactions at the central atom is much smaller than in nickel complexes.

The comparison of the complexes [NiP] and [CuP] demonstrates the individuality of the central atom in macrocyclic complexes, but also the different influences of the substituents. The specific reactivity of the metalloenzymes, such as the reversible transport of oxygen by hemoglobin and the methyl group transfer by the cobalamins, originates in the complicated interaction of these factors.

CONCLUSIONS

It was the intention of this comment to show the importance of redox processes for the chemistry of mononuclear transition metal complexes with soft ligands. The reaction theory of these compounds has benefited from the earlier experimental and theoretical work of organic chemists. However the easy change of oxidation state, as is characteristic of transition metals, favors reactions which are initiated or connected with electron transfer. Prerequisite for an interpretation of such processes are, among other things, the knowledge of redox potentials and the unambiguous identifica-

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† If the added electron resides mainly on the ligand (formation of [$\mathrm{Ni^{II}P^{-}}$]), this relation is not obeyed.

tion of paramagnetic metal complexes of different lifetimes. We may therefore expect that electrochemical methods such as cyclic voltammetry and polarography, and EPR spectroscopy will attain still greater importance. In the field of transition metal complexes EPR spectroscopy may finally compete with NMR spectroscopy.

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