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# Chelating cyclic aminomethylphosphines and their transition metal complexes as a promising basis of bioinspired mimetic catalysts

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**The synthetic and coordination chemistry of cyclic aminomethylphosphines with two phosphorus centers in the ring is summarized with a focus on the applications of their metal complexes as electrocatalysts, which mimic natural hydrogenases.**

The first representatives of cyclic aminomethylphosphines with two donor phosphorus centers in the ring, namely 1,5-diaza-3,7-diphosphacyclooctanes, have been described in 1980,[1,2] and these heterocyclic diphosphines have attracted a steady but not very wide attention for a long time mainly as available P,P-chelating ligands possessing relative conformational rigidity.[3–11] However, in 2006, the bis-ligand nickel(II) complexes of 1,5-diaza-3,7-diphosphacyclooctanes were found highly efficient electrocatalysts for both hydrogen evolution and hydrogen oxidation.[12] These complexes containing pendant amines incorporated into diphosphine ligands appeared to be synthetic molecular catalysts that mimic the structure and/or function of hydrogenase enzymes.[13,14] The increased use of alternative and renewable energy sources requires means for energy storing, and the promising possibility is the efficient interconversion of electrical energy into the energy of chemical bonds; thus, new generations of inexpensive and efficient electrocatalysts are necessary. The discovery of such electrocatalysts among the complexes of 1,5-diaza-3,7-diphosphacyclooctanes with abundant inexpensive metals[14,15] inspired a renaissance in the chemistry of these heterocycles and relative cyclic nitrogen-containing diphosphines. Much of the focus of these investigations has been on an examination of factors responsible for the structures and catalytic activities of their transition metal complexes in hydrogen oxidation and production and in interactions with other small molecules.

Here, we survey the synthetic and coordination chemistry of cyclic aminomethylphosphine ligands with two phosphorus atoms in the ring, which are promising for the design of a new generation of bioinspired catalysts.

**Synthesis and main structural characteristics of cyclic aminomethylphosphines with two phosphorus centers in the ring.** The Mannich-type condensation between primary or secondary phosphines (diphosphines), formaldehyde and amines is a powerful tool of the synthesis of various aminomethylphosphines. 1,5-Diaza-3,7-diphosphacyclooctanes are available nitrogen-con-

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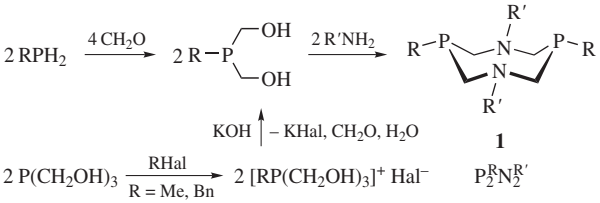
taining diphosphines because these heterocycles are obtained on the basis of simple primary phosphines. Their preparation is usually performed as a convenient one-pot process. The first step is the addition of formaldehyde (from solid paraformaldehyde or from formaldehyde solution) to a primary phosphine with the formation of 'bis(hydroxymethyl)organylphosphine', which is used without additional purification. An alternative and rare route is the alkylation of tris(hydroxymethyl)phosphine followed by the decomposition of the phosphonium salt with a strong base (Scheme 1). This method was employed for the synthesis of bis(hydroxymethyl)methylphosphine in order to avoid the use of highly pyrophoric methylphosphine.[16,17] Note that, in the case of bulky substituents on the phosphorus atom, these bis(hydroxymethyl)organylphosphines are complex mixtures of monosubstituted secondary phosphines $ArPH(CH_2O)_nH$ (major components) and tertiary phosphines $ArP(CH_2OH)(CH_2O)_{n-1}H$ (Ar = Mes, Tipp) (minor components).[18] Nevertheless, at the second step, they also smoothly react with primary amines in a stoichiometric ratio of 1:1 to give desired 1,5-diaza-3,7-diphosphacyclooctanes **1** ($P_2^RN_2^{R'}$) in reasonable or good yields (Scheme 1, refs. 1, 2, 6, 8–12, 16, 17, 19–35). The condensation step is usually carried out in ethanol at elevated temperatures (65–80 °C).




R = Me, Bu, Bu$^t$, Ph, Bn, $(CH_2)_2$Ph (PE), L-menthyl (Ment), ferrocenyl (Fc), ferrocenylmethyl ($FcCH_2$), 2,4,6-tri(isopropyl)phenyl (Tipp), cyclohexyl (Cy), mesityl (Mes), CH(Et)Bu$^t$, 2-pyridyl (2-Pyr), 2-$HOC_6H_4$, 2-EtO-5-$AllC_6H_3CH_2$, 2-R′O-5-R″-C6H3 (R′ = H, CH2OMe; R″ = H, Me)

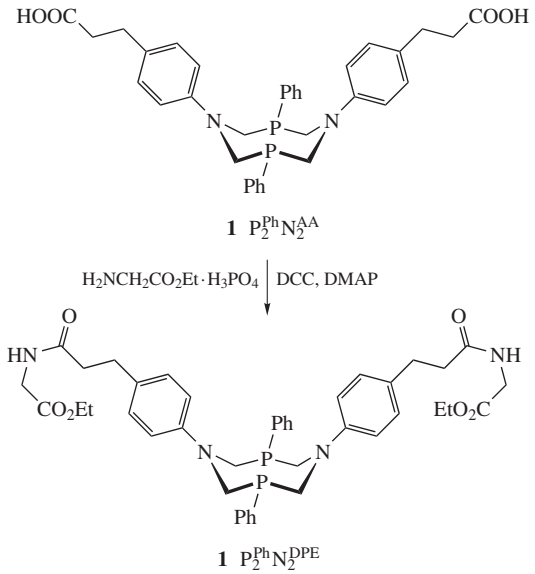
R′ = Me, Ph, Bn, Bu$^t$, *p*-Tol, 2-Pyr, 4-$BrC_6H_4$, 3-$HO_2CC_6H_4$, 4-$HO_2CC_6H_4$, 3,5-$(HO_2C)_2C_6H_3$, 4-$NaSO_3C_6H_4$, 4-$MeOC_6H_4$, 4-$[(EtO)_2P(O)CH_2]C_6H_4$, 4-$F_3CC_6H_4$, $CH_2CH_2OMe$, (*R*)-CH(Me)Ph, (*S*)-CH(Me)Ph, benzothiazol-5-yl, 2-mercaptobenzimidazol-5-yl, isoxazol-3-yl, 4-$HO_2C(CH_2)_2C_6H_4$ (AA), 4-$EtO_2C(CH_2)_2C_6H_4$ (AAE), (pyren-3-yl)methyl

**Scheme 1**

This method allows one to wide vary the exocyclic substituents on both nitrogen and phosphorus atoms and to tune both the stereoelectronic and macroscopic properties of cyclic diphosphines **1**. For example, the heterocycles with hydrophilic oxy, carboxy and sulfoaryl substituents are water-soluble[11,34] and one with ferrocenyl groups on the phosphorus atoms is redox active.[10] Another very strong advantage of this condensation is its excellent and favorable stereoselectivity. Only the *cis* isomers of cyclic diphosphines **1** with *syn*-disposition of phosphorus lone electron pairs have been isolated.

Most of 1,5-diaza-3,7-diphosphacyclooctanes **1** are air-stable in a solid state, and they do not undergo decomposition in solutions (even in water, DMF and DMSO) excluding strongly acidic conditions. The relative chemical stability of their framework allowed one to perform the peripheral modification of $P_2^{Ph}N_2^{AA}$ and to incorporate peptide fragments into its exocyclic substituents under the standard conditions of peptide synthesis (Scheme 2).[25]

According to X-ray analysis data in the solid state, test 1,5-diaza-3,7-diphosphacyclooctanes **1** have similar chair–chair conformations and *syn*-positions of axial phosphorus lone pairs to each other. The pseudoaxial substituents on nitrogen atoms are also oriented approximately in the same direction relative to the PNPN plane. The main difference in the structures of the eight-membered cores is the type of coordination of endocyclic nitrogen atoms (trigonal planar for *N*-aryl[6,11] and trigonal pyramidal for *N*-benzyl substituted heterocycles[9,36]). According to NMR spectral data [including variable-temperature 1D and 2D NMR experiments for $P_2^{Ment}N_2^{Tol}$ (ref. 37) and $P_2^{Bu^t}N_2^{R}$ (ref. 30)] the same chair–chair conformations are predominant in solutions though for $P_2^{Bu^t}N_2^{Bn}$ the presence of a minor chair–boat conformer was observed at –50 °C.[30] Thus, 1,5-diaza-3,7-diphosphacyclooctanes are well-predisposed for metal chelation.

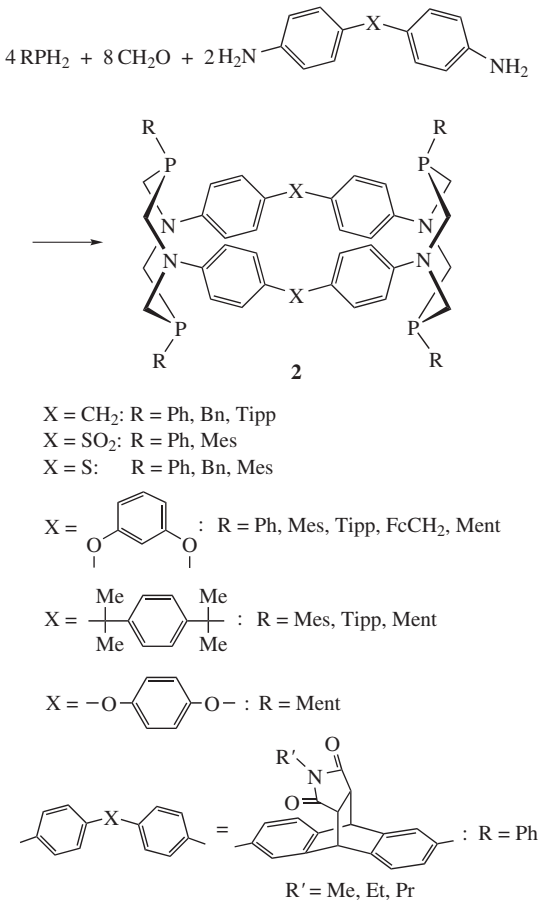



**Scheme 2**

The Mannich-type condensation of primary phosphines with formaldehyde and primary aromatic diamines with spatially divided amine groups in DMF or toluene at 100–110 °C proceeded as thermodynamically-driven covalent self-assembly and allowed one to obtain several types of cage P,N-containing cyclophanes **2** with two 1,5-diaza-3,7-diphosphacyclooctane fragments incorporated into the macrocyclic frameworks of various sizes and structures (Scheme 3).[38–46] The spacers of the starting diamines were formed by two[38–40,44] or three[41–45] phenylene fragments linked by one-atom bridges, or these were 9,10-dihydro-9,10-ethanoanthracene-2,6-diyl moieties.[44,46] According to X-ray analysis data for all types of cyclophanes[38–44,46] and DNMR data for 38-membered macrocycles,[47] the diazadiphosphacyclooctane fragments have chair–chair conformations with *syn*-phosphorus lone pairs directed inward the macrocyclic cavities.

Other types of nitrogen-containing cyclic diphosphines have been synthesized based on less available secondary diphosphines. The addition of formaldehyde to 1,3-bis(arylphosphino)propanes followed by the condensation of the resulting P-containing diols with 5-aminoisophthalic acid in ethanol led to the stereoselective formation of *meso*-1-aza-3,7-diphosphacyclooctanes **3** (Scheme 4) in spite of the fact that the starting diphosphines were the mixtures of *meso* and *rac* diastereoisomers. According to NMR spectra and X-ray analysis data for **3b**, these heterocycles have chair–chair conformations with axial *syn*-oriented phosphorus lone electron pairs and the pseudoaxial aryl group on the nitrogen atom.[48] The structures of ligands **3** are also favorable for metal chelation. Surprisingly, analogous condensations with more basic amines lead to 1,9-diaza-3,7,11,15-tetraphosphacyclohexadecanes instead of eight-membered heterocycles.[44,49,50]

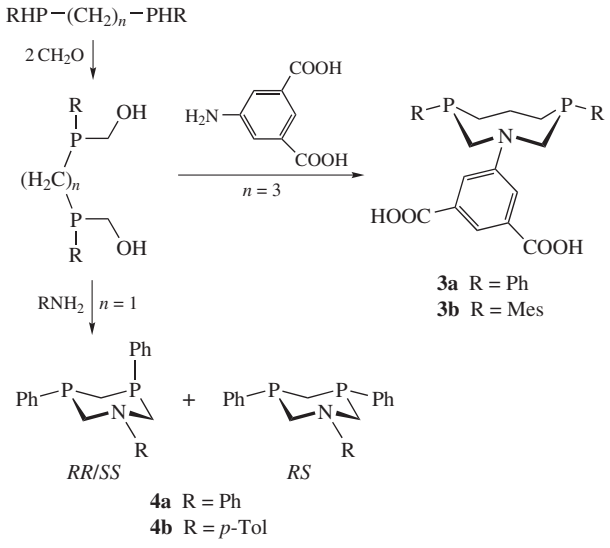
The formation of aminomethylphosphines of smaller ring sizes is not stereoselective. The condensation of the mixture of *meso*- and *rac*-bis[(hydroxymethyl)phenylphosphino]methane prepared from bis(phenylphosphino)methane and formaldehyde with primary arylamines in ethanol afforded 1-aza-3,5-diphospha-



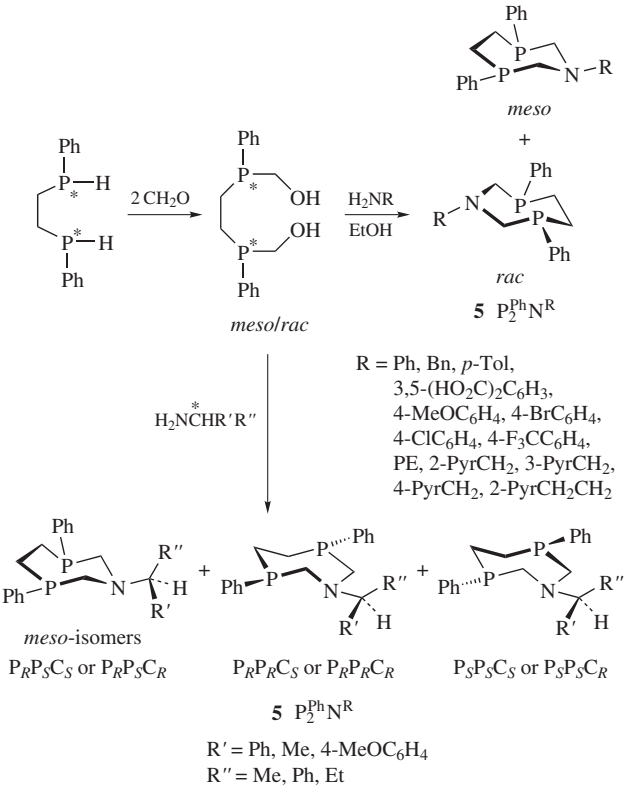

**Scheme 3**

cyclohexanes **4** as approximately 1:1 mixtures of *RS* and *RR*/*SS* isomers (Scheme 4). Only less soluble *RS* isomers were isolated in pure forms by fractional crystallization.[51]

The condensations of the mixture of *rac*/*meso*-1,2-bis[(hydroxymethyl)phenylphosphino]ethane with primary amines in ethanol or acetonitrile also lead to the stereoisomeric mixtures of seven-membered 1-aza-3,6-diphosphacycloheptanes **5** ($P_2^{Ph}N^R$) (Scheme 5, refs. 52–55). The stereochemical results of the condensation depend on the nature of amines. The reactions with arylamines give $P_2^{Ph}N^R$ as approximately 1:1 mixtures of *meso* and *rac* isomers,[52,55] and only the isomers of $P_2^{Ph}N^{C_6H_3(COOH)_2}$ have been separated.[52] The condensations with benzyl-, pyridinylalkyl- and phenethyl-




**Scheme 4**



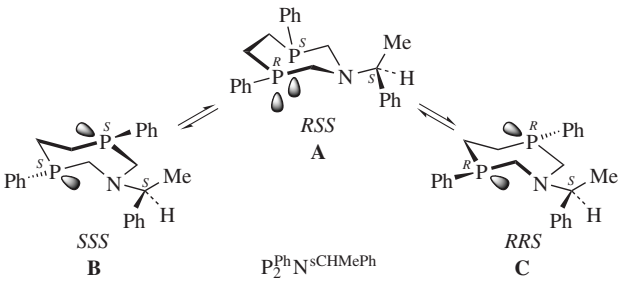

**Scheme 5**

amines lead to the predominant formation of *rac*-isomers, *rac*-$P_2^{Ph}N^{Bn}$ and *rac*-$P_2^{Ph}N^{PE}$ being formed in practically pure forms.[52,53] With the use of optically active benzylamines, the *meso* isomers $P_RP_SC_{S(R)}$ and two different isomers with identical configurations at phosphorus, namely $P_SP_SC_{S(R)}$ and $P_RP_RC_{S(R)}$, are formed. The presence of three stereoisomers is caused by additional C-chiral substituents on the nitrogen atoms. In contrast to the previous cases, the prevalence of *meso* isomers is observed (80–90% for $P_2^{Ph}N^{sCHMePh}$, $P_2^{Ph}N^{rCHMePh}$ and $P_2^{Ph}N^{rCHMeC_6H_4OMe}$; 60% for $P_2^{Ph}N^{rCHEtPh}$). These *meso* isomers are kinetically controlled products, which were isolated in pure forms except the last one.[54]

The structures of both *rac* and *meso* isomers of 1-aza-3,6-diphospacycloheptanes were studied by X-ray analysis. The seven-membered rings of *rac* isomers have typical twist–chair conformations, the phenyl groups at the phosphorus atom are in pseudo-equatorial positions, and the pseudo-axial electron lone pairs of phosphorus are pointing towards opposite sides of the ring. Nitrogen atoms are in a planar (for *N*-aryl heterocycles[52]) or pyramidal [for *RRS*-$P_2^{Ph}N^{sCHMePh}$ (ref. 54)] environment and the exocyclic substituents on the nitrogen atom are pseudoaxial.

The structures of *meso*-$P_2^{Ph}N^{sCHMePh}$ and $P_2^{Ph}N^{rCHMeC_6H_4OMe}$ are more interesting. The seven-membered rings exhibit unusual chair conformations with almost planar P–C–C–P fragments and P–C bonds in eclipsed positions. Both phenyl substituents on the phosphorus atoms are pseudo-equatorial, and the electron lone pairs of the phosphorus atoms are in axial positions. The P···P distances are very short (3.118–3.120 Å)[54] in comparison with those of *rac* isomers (3.599–3.985 Å).[52,54] The nitrogen atoms are in pyramidal environments with exocyclic substituents in the axial positions. Thus, the *meso* isomers of 1-aza-3,6-diphosphacycloheptanes have favourable structures for metal chelation.[54]

In solutions, the graduate selective stereoconversion of pure *meso*-$P_2^{Ph}N^{sCHMePh}$, $P_2^{Ph}N^{rCHMePh}$ and $P_2^{Ph}N^{rCHMeC_6H_4OMe}$ into mixtures containing corresponding *RRS*, *SSR* and *SSR* stereoisomers as the predominant products was observed (Scheme 6). The ratio between stereoisomers in an equilibrium mixture of $P_2^{Ph}N^{sCHMePh}$




**Scheme 6**

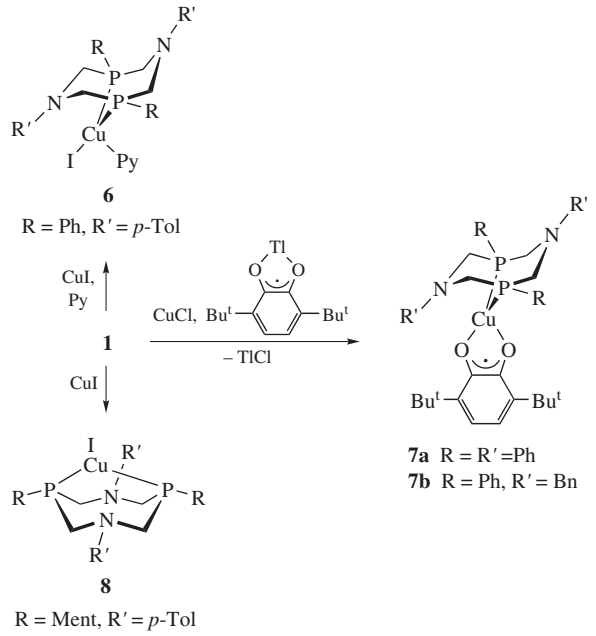
(*RSS*:*RRS*:*SSS* in a 24:48:28 ratio) is in accordance with their relative energies which were calculated with the B3LYP/6-31G* basis. The results of the kinetic studies of the stereoconversion of $P_2^{Ph}N^{sCHMePh}$ are indicative of a bimolecular interconversion mechanism, which is supposedly the reason for the relatively low activation energies of inversion at phosphorus.[54]

The stereoconversion of 1-aza-3,6-diphosphacycloheptanes is very important direct evidence of the lability of P–C–N fragments in aminomethylphosphines. This lability should be taken into account in studies of the coordination chemistry of these ligands and the design of their metal complexes.

Thus, at present, several types of chelating cyclic diphosphines with pendant amines incorporated into the ring are synthetically available, and they can be used as a basis for the design of transition metal complexes.

**Transition metal complexes of cyclic aminomethylphosphines with two phosphorus atoms in the ring.** The coordination chemistry of the oldest and most numerous family of cyclic N-containing diphosphines, namely, 1,5-diaza-3,7-diphosphacyclooctanes **1** ($P_2^RN_2^{R'}$), is studied better than that of other cyclic aminomethylphosphines. These ligands with two phosphine donor centers easily form stable complexes with soft transition metals of different groups.

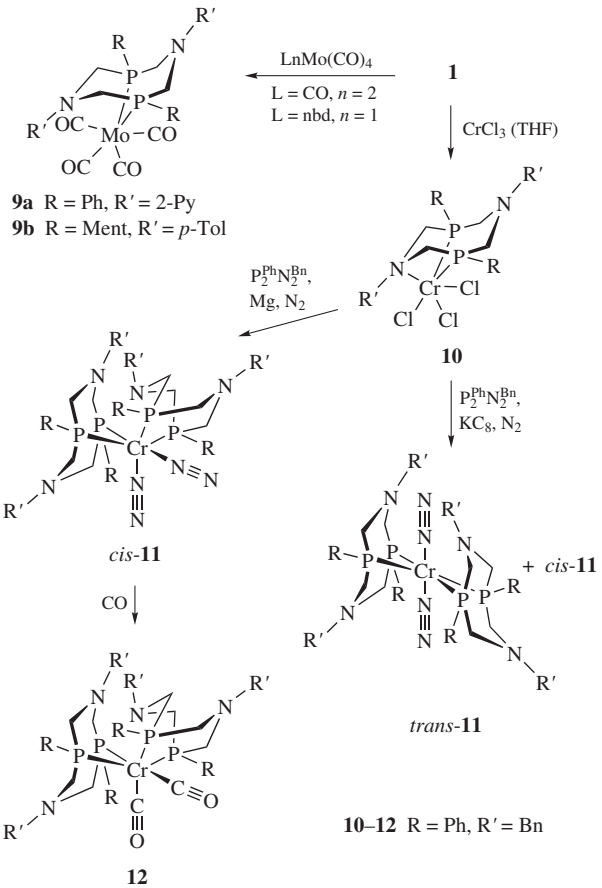
The Group I metal complex $[P_2^{Ph}N_2^{Tol}]Cu(Py)I$ **6** occasionally became the first complex of diazadiphosphacyclooctane, which was studied by X-ray analysis. Compound **6** is a monoligand P,P-chelate with pyridine as a co-ligand (Scheme 7).[4] The treatment of $P_2^{Ph}N_2^{R'}$ with copper(I) chloride and thallium 3,6-di(*tert*-butyl)benzosemiquinolate led to paramagnetic benzosemiquinone copper(I) complexes **7** (Scheme 7) of a similar P,P-chelate structure.[7] X-ray analysis of **6** and **7a**,**b** confirmed the distorted tetrahedral environment of copper ions and showed the important peculiarities of the metal complexes of this type of ligands: the narrowed bite P–Cu–P angles (86.8–90.2°) due to the relative rigidity of the cyclic ligands in comparison with acyclic diphosphines and the location of at least one endocyclic nitrogen atom (pendant amine) in the close proximity of a metal ion (Cu···N distances are 3.29–3.42 Å) due to chair–boat (for **6** and **7a**) or chair–chair (for **7b**) conformations of the eight-membered ligands. Lone pairs of nitrogen atoms were directed outward, so that Cu···N contacts were non-bonding.[4,7]




**Scheme 7**

The interaction of copper(I) iodide with the bulky ligand $P_2^{Ment}N_2^{Tol}$ led to P,P-chelate **8** with a trigonal-planar copper ion. According to variable-temperature 1D and 2D NMR data, the ligand in **8** had a stable chair–chair conformation.[37]

The complexes of diazadiphosphacyclooctanes with Group VI and VII metals were not widely studied. The interaction of $P_2^{Ph}N_2^{2\text{-}Py}$ and $P_2^{Ment}N_2^{Tol}$ with $(nbd)Mo(CO)_4$ or $Mo(CO)_6$, respectively, afforded monoligand *cis*-P,P-chelate complexes **9a**,**b** (Scheme 8). According to X-ray analysis data for **9a**[6] and variable-temperature NMR data for **9b**,[37] the ligands had chair–boat conformations. In the solutions of **9b**, a fast exchange between two chair–boat conformations takes place.[37]

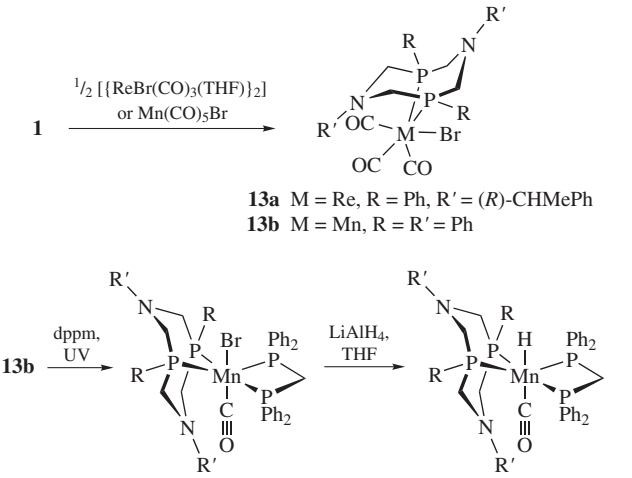



**Scheme 8**

The reaction of $CrCl_3(THF)_3$ and $P_2^{Ph}N_2^{Bn}$ in THF gave paramagnetic complex **10** (Scheme 8), where the cyclic ligand unexpectedly exhibited a $\kappa^3$-facial coordination mode with one endocyclic nitrogen and two phosphorus atoms bound to a distorted octahedral chromium ion. It is the only example of this binding mode for diazadiphosphacyclooctane ligands. The reduction of **10** with Mg or potassium graphite under $N_2$ in the presence of the starting ligand led to the *cis*-isomer or a *cis*/*trans* isomeric mixture of bis-ligand complex **11** with two terminally coordinated dinitrogen ligands, respectively. The exposure of *cis*-**11** to CO (1 atm)

generated dicarbonyl complex **12** (Scheme 8). The structures of *cis*-**11** and **12** are very similar: both heterocyclic ligands are in chair–boat conformations and the nitrogen atoms of chair parts are pointed away from the $N_2$ or CO ligands decreasing electrostatic interactions between them. The N≡N triple bonds are slightly longer in comparison with free $N_2$ (1.133 *vs.* 1.0975 Å) reflecting the slight activation of $N_2$ upon coordination to chromium.[56]

The reaction of $P_2^{Ph}N_2^{rCHMePh}$ with $\{ReBr(CO)_3(THF)\}_2$ in DMF yielded monoligand P,P-chelate complex **13a** with a *fac*-$ReBr(CO)_3$ fragment (Scheme 9).[9] The interaction of $P_2^{Ph}N_2^{Ph}$ with $Mn(CO)_5Br$ afforded analogous complex **13b**. The photolysis of **13b** in the presence of dppm gave mixed-ligand complex **14b** which was reduced to hydride complex **15b**. According to X-ray analysis data, the cyclic ligand of **15b** had a chair–boat conformation with the nitrogen atom of the boat part directed toward the carbonyl ligand. The distance N···$C_{CO}$ was 3.17 Å indicating a weak interaction between them.[57]



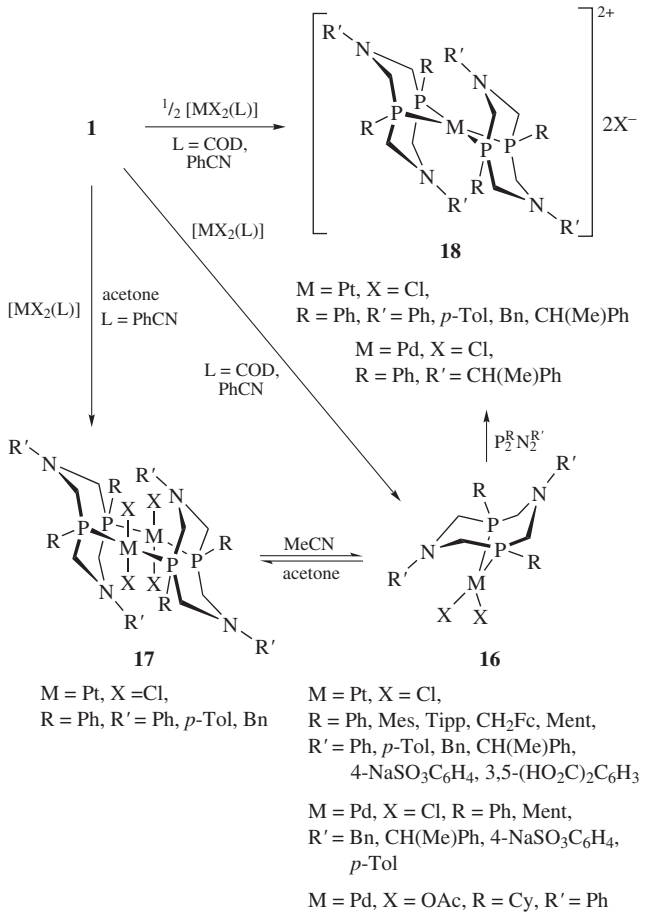

**13a** M = Re, R = Ph, R′ = (*R*)-CHMePh
**13b** M = Mn, R = R′ = Ph

**Scheme 9**

Any catalytic activity data of copper and Group VI and VII metal complexes of 1,5-diaza-3,7-diphosphacyclooctanes were not still reported.

Complexes of 1,5-diaza-3,7-diphosphacyclooctanes with Group VIII transition metals are well-studied. The interaction of these ligands with $MCl_2(COD)$ or $MCl_2(PhCN)_2$ (M = Pt, Pd) in a stoichiometric ratio of 1:1 in different solvents (from dichloromethane to DMF and water) gave a wide variety of monoligand neutral *cis*-P,P-chelate complexes **16** with terminal M–Cl bonds (Scheme 10).[5,6,8,9,11,29] These complexes are smoothly formed even on the basis of ligands with bulky mesityl,[11] triisopropylphenyl,[11] ferrocenylmethyl[8] and menthyl[29] substituents on phosphorus atoms. Analogous complex **16** of palladium acetate with $P_2^{Cy}N_2^{Ph}$ was obtained in water.[58] Ligands with phenyl groups on phosphorus atoms can form two other types of platinum(II) and palladium(II) complexes. The interaction of $P_2^{Ph}N_2^{R'}$ (R′ = Ph, *p*-Tol, Bn) with 1 equiv. of $PtCl_2(PhCN)_2$ in acetone led to binuclear complexes **17** (Scheme 10) with two bridging ligands and *trans*-configurations of platinum ions. These complexes were isolated due to their low solubility in acetone, but they were unstable in acetonitrile solutions and converted into usual chelate complexes **16**.[5] In the cases of a metal : ligand ratio of 1:2, unbulky ligands readily form cationic bis-ligand complexes **18**.[5,9,11] Note that the formation of complexes **16** and **18** sometimes proceeded simultaneously, and it complicated their separation.[9]

The structures of platinum complexes **16** (R = R′ = Ph;[5] R = Ph, Mes; R′ = $C_6H_3(COOH)_2$;[11] R = Ment, R′ = *p*-Tol[29]) were studied by X-ray crystallography, and they were found very similar. The platinum ions are in slightly distorted *cis*-square-planar




**18**
M = Pt, X = Cl,
R = Ph, R′ = Ph, *p*-Tol, Bn, CH(Me)Ph
M = Pd, X = Cl,
R = Ph, R′ = CH(Me)Ph

**17**
M = Pt, X =Cl,
R = Ph, R′ = Ph, *p*-Tol, Bn

**16**
M = Pt, X = Cl,
R = Ph, Mes, Tipp, $CH_2Fc$, Ment,
R′ = Ph, *p*-Tol, Bn, CH(Me)Ph,
4-$NaSO_3C_6H_4$, 3,5-$(HO_2C)_2C_6H_3$
M = Pd, X = Cl, R = Ph, Ment,
R′ = Bn, CH(Me)Ph, 4-$NaSO_3C_6H_4$,
*p*-Tol
M = Pd, X = OAc, R = Cy, R′ = Ph

**Scheme 10**

environments with relatively small P–Pt–P angles (84–85°); the ligands in all complexes have chair–boat conformations, so that one of the nitrogen atoms is located in the close proximity of a metal center (distances N···Pt are about 3.2 Å). The configurations of nitrogen atoms vary from trigonal-pyramidal to almost planar. Analogous palladium complex **16** (R = Ph, R′ = Bn, X = Cl) also showed a narrowed bite P–Pd–P angle of 82.5°, but its ligand had a strongly distorted chair–chair conformation with both nitrogen atoms flattened towards four ring-carbon plane.[6] Unlike these complexes, the platinum ion of cationic complex **18** (R = Ph, R′ = *p*-Tol) was in a strongly tetrahedrally-distorted square-planar environment (the dihedral angle between two P–Pt–P planes was 24.3°). The bite P–Pt–P angles were even smaller (80.6°) than in monoligand complexes **16**. Both ligands had chair–boat conformations.[5]

The conformational dynamics of **16** (R = Ment, R′ = *p*-Tol, M = Pd, Pt) in solutions was studied by DNMR methods because the chiral substituents on phosphorus atoms eliminate degeneration thus allowing the conformational analyses of these structures. Both complexes exhibit an equilibrium of two chair–boat conformations. The interconversion barriers between these two conformations are quite high ($\Delta G^{\neq}$ = 10.25 kcal mol$^{-1}$) and about two times higher than that for corresponding Mo complex **9b**.[37]

In spite of numerosity of the described platinum and palladium complexes of 1,5-diaza-3,7-diphosphacyclooctanes, the reported data of their catalytic properties are scarce and fragmentary. Palladium dichloride complexes **16** (R = Ph; R′ = *p*-Tol, Bn; M = Pd, X = Cl) showed moderate activity and relatively high selectivity (82–88%) in catalysis of the liquid-phase hydrogenation of hept-1-yne to hept-1-ene, but their catalytic activities were less than that of palladium dichloride complexes of monodentate 1,3-diaza-5-phosphacyclohexanes.[59] Analogous platinum complexes were inactive in these hydrogenation reactions.[59] Platinum

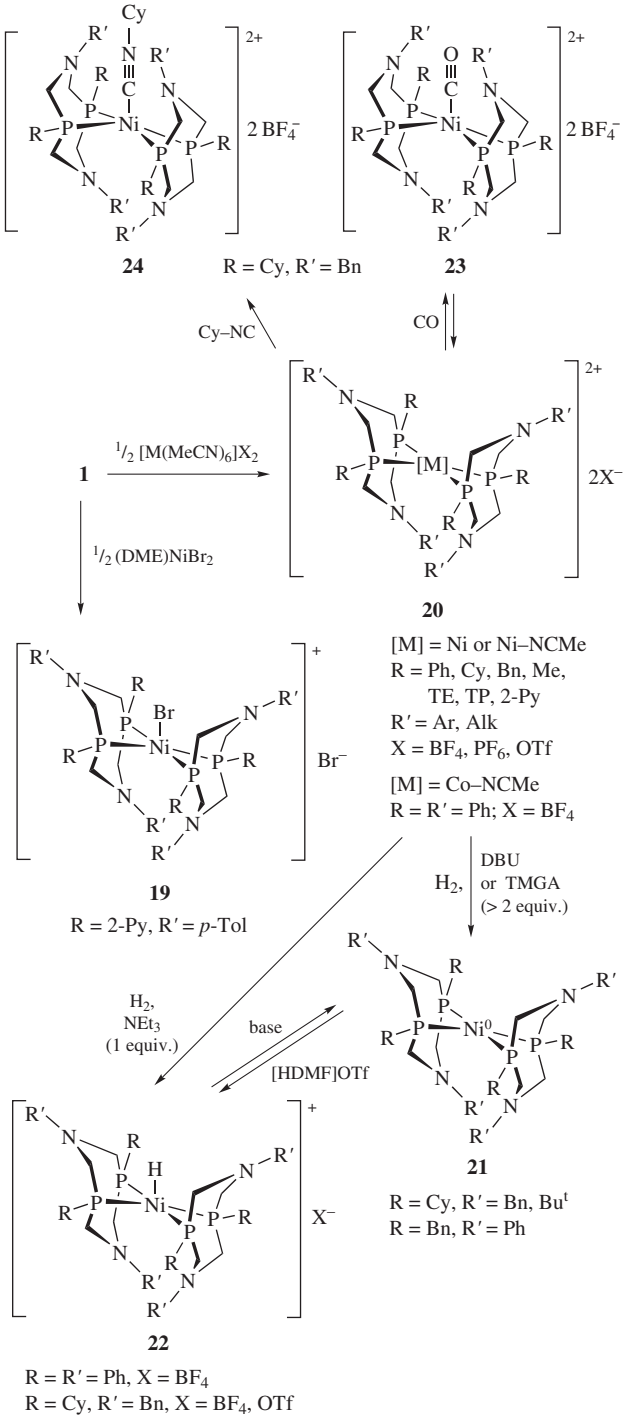
complex **16** (R = Ph, R′ = Bn, M = Pt, X = Cl) showed moderate catalytic activity in the homogeneous electrochemical reduction of 2-carbomethoxy-2-methyl-1,1-dichlorocyclopropane, whereas the catalytic activities of double mediator systems containing complexes **16** (R = Ph; R′ = Bn, *p*-Tol; M = Pt, Pd; X = Cl) and anthracene as an electron carrier were also lower than that of the metal complexes of ligands with 1,3-diaza-5-phosphacyclohexane fragments.[60] Palladium-based systems containing water-soluble and chiral ligands $P_2^RN_2^{R'}$ [R = Ph, Mes, Tipp; R′ = CHMePh, $C_6H_3(COOH)_2$, $C_6H_4SO_3Na$] and palladium(II) acetate were tested in the catalysis of the copolymerization of olefins with CO and showed moderate catalytic activities in comparison with those of similar tertiary bisphosphines.[9,11,61] Recently, palladium complex **16** (R = Cy, R′ = Ph, M = Pd, X = OAc) was found to be an effective catalyst of the Suzuki–Miyaura coupling reactions in neat water without any phase-transfer reagent.[58]

The treatment of $P_2^{Ph}N_2^{2\text{-Py}}$ with $(DME)NiBr_2$ led to five-coordinated low-spin complex **19** (Scheme 11),[33] whereas the interaction of ligands $P_2^RN_2^{R'}$ with nickel(II) salts containing uncoordinating anions {as a rule, $[Ni(NCMe)_6](BF_4)_2$} allowed one to obtain a very wide set of complexes **20** (Scheme 11), where nickel formed only four stable coordination bonds. The fifth coordination place is often occupied by a weakly bonded acetonitrile ligand. Due to their applicability to electrocatalysis,[12,14] complexes **20** are of great interest, and they have been synthesized on the basis of practically all known 1,5-diaza-3,7-diphosphacyclooctanes with unbulky substituents on phosphorus atoms including cyclohexyl ones.[12,16,17,21–23,25–27,31–33] These complexes were successfully prepared even from ligands $P_2^{Ph}N_2^{Me}$ (ref. 23) and $P_2^{Cy}N_2^{CH_2CH_2OMe}$ (ref. 22) which could not be isolated in pure forms. Paramagnetic cobalt(II) complex **20** (R = R′ = Ph, [M] = Co–NCMe, X = $BF_4$) was prepared analogously starting from $[Co(NCMe)_6](BF_4)_2$.[62]

The structures of complexes **20** have been determined by X-ray analysis. The most typical ones may be shown for **20** (R = R′ = Ph, [M] = Ni–NCMe, X = $BF_4$)[12] and **20** (R = Ph, R′ = *p*-Tol, [M] = Ni, X = $BF_4$).[21] In the first complex, the nickel atom is five-coordinated. The overall structure is that of a trigonal bipyramid with two apical phosphorus atoms and two phosphorus atoms and an acetonitrile molecule in the equatorial positions. Each ligand is in a chair–boat conformation, so it forms two six-membered metallocyclic rings. One of these rings is in a chair form, and the other is in a boat form. The two nitrogen atoms (pendant amines) in the rings with boat conformations are folded toward the nickel atom, so they are in the close proximity of a nickel center (non-bonding distances N···Ni ~3.4 Å). The P–Ni–P bond angles are small (81.5–82.7°).[12] The overall structure of the second complex may be described as square plane with tetrahedral distortions resulting from a twisting of the diphosphine ligands to minimize steric interactions between their P-phenyl groups. The dihedral angle between two P–Ni–P planes is 24.16°. Both ligands are in chair–boat conformations, and the minimal distance N···Ni is 3.15–3.33 Å. The P–Ni–P bite angles are also small (82.1–83.6°).[21] Note that, in a crystal, the ligands of some complexes **20** have chair–chair conformations, so all endocyclic nitrogen atoms are close to the metal.[12,32] The NMR spectra of complexes **20** indicate their high conformational lability in solutions.

Test nickel complexes **20** reveal two distinct and reversible reduction waves assigned to the $Ni^{II/I}$ and $Ni^{I/0}$ couples. The corresponding values of $E_{1/2}$ range from –0.63 to –0.93 and from –0.89 to –1.45 V, respectively, depending on the nature of the exocyclic substituents.[12,16,21,27,32]

The reactivity was studied mainly for the nickel(II) complexes of 1,5-diaza-3,7-diphosphacyclooctanes. Complexes **20** with electron-donating substituents in solutions react with $H_2$ (1 atm, room temperature) to give N-protonated $Ni^0$ complexes.




**Scheme 11**

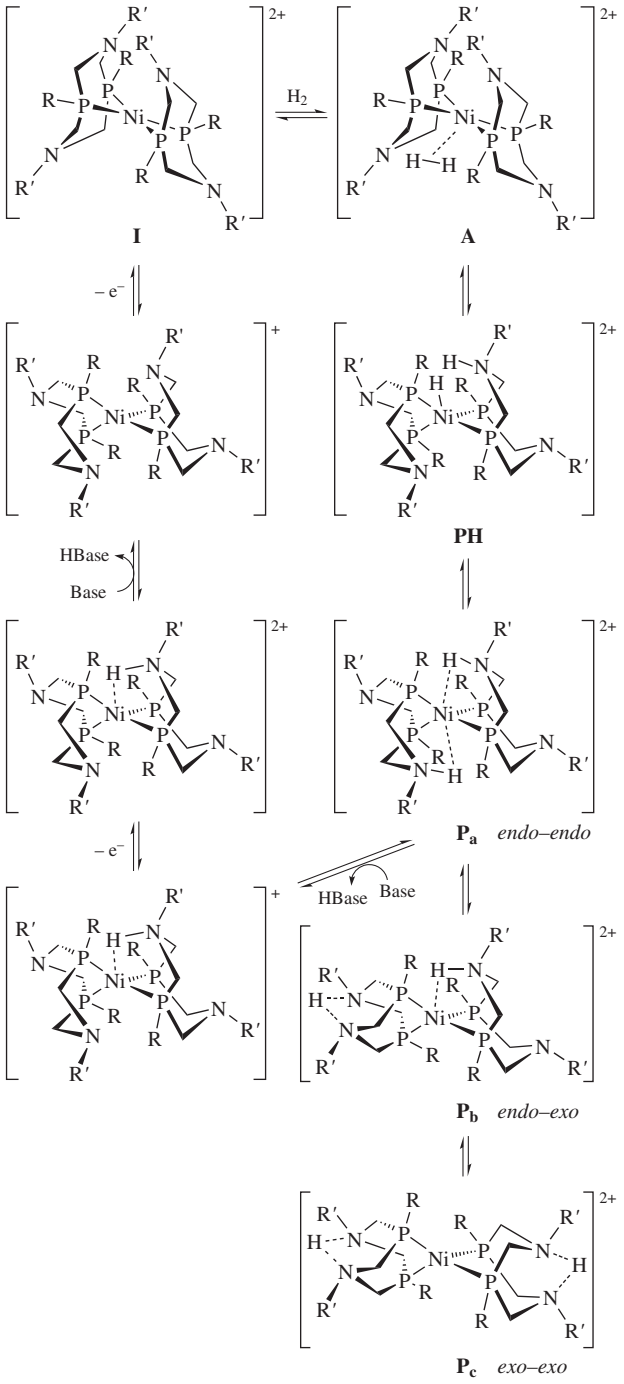
The treatment of these complexes by strong bases leads to stable $Ni^0$ complexes **21** (Scheme 11),[12,27,32] which contain $Ni^0$ atoms in a distorted tetrahedral configuration and two ligands in chair–chair conformations according to X-ray analysis data.[27] Both *P*-aryl- and *P*-alkyl-substituted **20** react with hydrogen in the presence of weaker bases (anisidine or $NEt_3$) to give hydride complexes **22** (Scheme 11).[12] The complex **20** (R = Cy, R′ = Bn, X = $BF_4$) reacts rapidly and reversibly with carbon monoxide at 25 °C to form complex **23** and with cyclohexyl isocyanide to produce similar isocyanide adduct **24**. Quantitative studies revealed that **20** binds $H_2$ more strongly than CO.[63]

Complexes **20** exhibit catalytic activities in the processes of electrocatalytical hydrogen evolution or hydrogen oxidation.[12,14,15,17] The most efficient electrocatalysts for hydrogen oxidation are *N*-benzyl- and *N*-alkyl-substituted nickel complexes

**20** (R = Cy, R′ = Bn and R = Cy, R′ = Bu$^t$), which provide the turnover frequencies of 10 and 50 $s^{-1}$, respectively.[12,14,32] The most efficient catalysts for hydrogen evolution among complexes of diazadiphosphacyclooctanes are compounds **20** with aryl substituents on nitrogen atoms, namely, R = Me, R′ = Ph and R = Ph, R′ = $C_6H_4CH_2P(O)(OEt)_2$. Under optimal conditions (the use of [(DMF)H]OTf as a source of protons and the presence of water which facilitates the catalytic proton reduction) these catalysts show the catalytic rates of 6700 and 1850 $s^{-1}$, respectively.[17,21] Note that other complexes **20** also have satisfactory electrocatalytic activities.[21,25] The important advantages for both hydrogen evolution and hydrogen oxidation with elecrocatalysts **20** are relatively low required overpotentials.[14,15] Complex **20** (R = Ph, R′ = $CH_2CH_2OMe$) is a unique reversible catalyst which electrocatalytically produces and oxidizes hydrogen close to the thermodynamic potential. This is the first example of a synthetic homogeneous electrocatalyst capable of performing this task, which is otherwise most commonly observed in hydrogenase enzymes.[22] Another specific type of electrocatalysts was designed on the basis of complexes **20** with fused pyrenyl fragments [R = Ph, Cy; R′ = (pyren-1-yl)methyl]. These complexes were grafted to multiwalled carbon nanotubes (MWCNTs) through the establishment of π–π stacking interactions between the pyrene moieties and graphene motifs, and modified MWCNTs were included into the membrane electrode assemblies which display electrocatalytic activities for $H_2$ evolution and $H_2$ oxidation and appeared to be highly robust and CO-tolerant.[26] Several isolated and prepared *in situ* complexes **20** were tested in a real fuel microcell, and they provided an increase in current densities up to 25–55%, whereas complexes with halide counterions were inactive in these processes.[64,65]

Various aspects of the electrocatalytic processes of hydrogen evolution and oxidation (the electrochemical parameters, thermodynamics and p$K_a$ of possible intermediates,[15,66–68] the influence of a proton source and water,[69] the equilibria between protonated intermediates and their proton mobilities[70,71]) have been thoroughly and systematically studied both experimentally and by quantum-chemical calculations. The combination of these studies and experimental results obtained for complexes **19** allowed us to suggest a reaction scheme for the catalytic cycle of hydrogen oxidation[14,15] (Scheme 12).

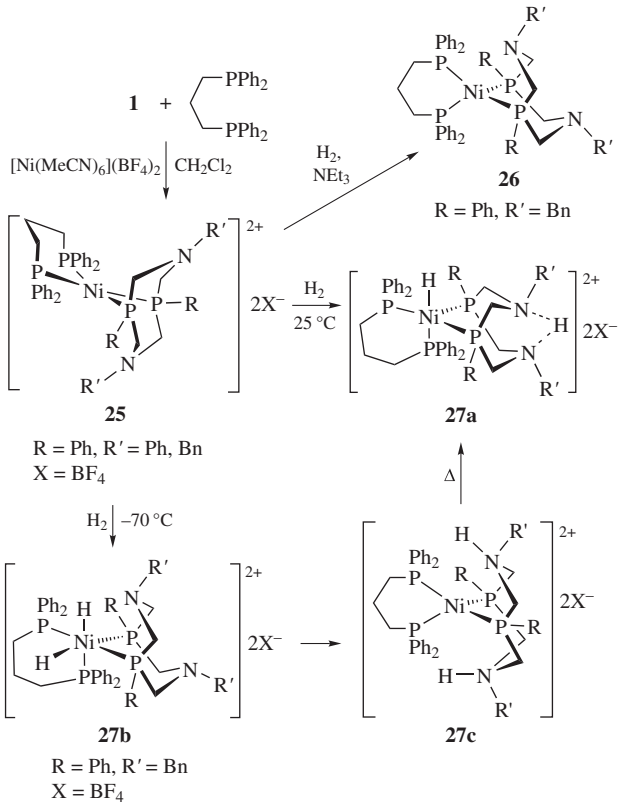
The initial $H_2$ splitting proceeds heterolytically and involves a transient dihydrogen adduct (**A**), proton-hydride intermediates (**PH**) and doubly protonated nickel species (**P**). Two proton transfers and two electron transfers (or proton-coupled electron transfers) complete the catalytic cycle for hydrogen oxidation. The evolution of hydrogen may follow the same cycle, but in the reverse order, and include two reduction/protonation steps with the initial protonation on the pendant amine (endocyclic nitrogen). The presence and the positioning of these noncoordinating amine basic sites near the metal center is a key requirement for the efficient catalysis. At the step of hydrogen splitting, the metal center and the pendant amine act as a 'frustrated' Lewis acid/base pair. During the catalytic cycle, the pendant amines serve as proton relays. Their role is related to the function of proton channels in enzymes, lowering the barrier for intramolecular proton mobility by moving the proton away from the metal, where it can be readily transferred to an external base. Thus, the catalytically active metal complexes of cyclic aminomethylphosphines, in particular, 1,5-diaza-3,7-diphosphacyclooctanes, may be regarded as biologically inspired functional models (mimetics) of hydrogenases. These complexes retain two of the critical features of enzymes: the use of abundant, inexpensive metals and the incorporation of a pendant amine as a proton relay, but they do not emulate the precise structural features of enzymes.[13–15]




**Scheme 12**

In the studies of the mechanistic aspects of hydrogen oxidation/reduction, unsymmetrical $Ni^{II}$ complex **25** (Scheme 13) with one $P_2^{Ph}N_2^{Bn}$ ligand was obtained. The treatment of **25** with hydrogen in the presence of a base furnished $Ni^0$ complex **26** (Scheme 13); however, in the absence of the base, the splitting of $H_2$ took place which formed hydride-proton complex **27a**. The reaction with $H_2$ at low temperature allowed one to observe the formation of unusual $Ni^{IV}$ dihydride complex **27b**, which is in equilibrium with $Ni^0$ complex **27c** with two protonated nitrogen atoms. The warming of the reaction mixture to room temperature led to stable complex **27a**[67] (Scheme 13).

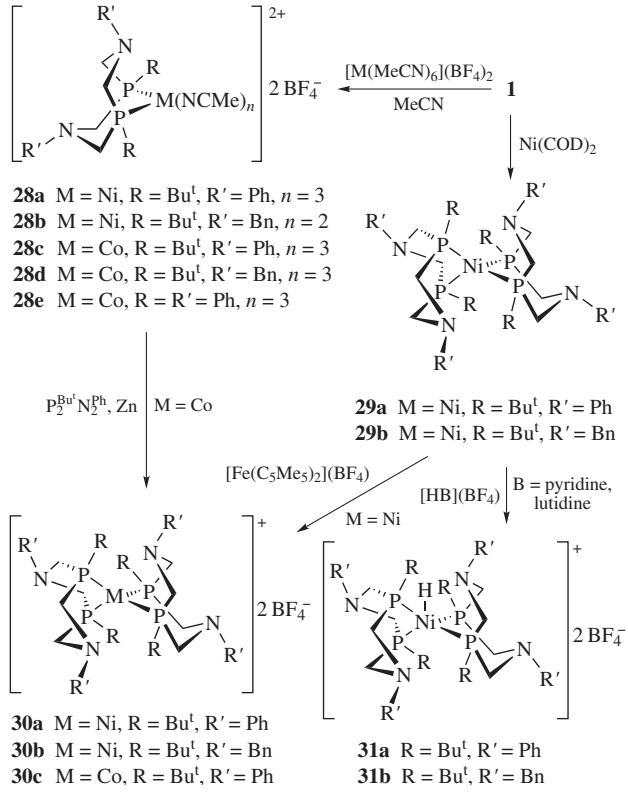
Sterically demanding $P_2^{Bu^t}N_2^{R'}$ ligands form with nickel(II) and cobalt(II) salts only monoligand complexes **28**[30] with three or two acetonitrile co-ligands in the coordination sphere of the metal (Scheme 14). Analogous complex **28e** was also obtained on the basis of the $P_2^{Ph}N_2^{Ph}$ ligand.[62] All complexes contain a P,P-chelating ligand in a typical chair–boat conformation.[30,62]




**Scheme 13**

Catalytic production of $H_2$ was observed by cyclic voltammetry for cobalt complex **28c**[30] and **28e**.[62]

The interaction of $P_2^{Bu^t}N_2^{R'}$ ligands with $Ni(COD)_2$ led to stable bis-ligand $Ni^0$ complexes **29** (Scheme 14) because the tetrahedral coordination of the metal decreased the steric interactions of bulky groups on phosphorus atoms.[72] Complexes **29** were oxidized by $[Fe(C_5Me_5)_2]BF_4$ to afford paramagnetic $Ni^I$ complexes **30a**,**b**




**Scheme 14**

(Scheme 14), which also contained pseudo-tetrahedral central ions and two ligands in chair–boat conformations. Similar $Co^I$ complex **30c** was obtained by the reduction of **28c** with zinc in the presence of $P_2^{Bu^t}N_2^{Ph}$ (Scheme 14). The overall solid-state structure of **30c** was close to that of **30a**, but one of the ligands had a chair–chair conformation. Stable hydride complexes **31** (Scheme 14) were prepared by the protonation of **29** with pyridinium and 2,6-lutidinium tetrafluoroborates, respectively, and isolated as pure products. The absence of the disproportionation of $Ni^I$ and hydride complexes is caused by the instability of usual bis-ligand $Ni^{II}$ complexes with bulky ligands. The double protonation of **29b** forms the *endo-endo*, *endo-exo* and *exo-exo* isomers of $[Ni^0(P_2^{Bu^t}N^{Bn}HN^{Bn})_2](BF_4)_2$, which are the analogues of catalytic intermediates **P** (Scheme 12), but they are more stable toward the loss of $H_2$ than similar unbulky complexes.[72]

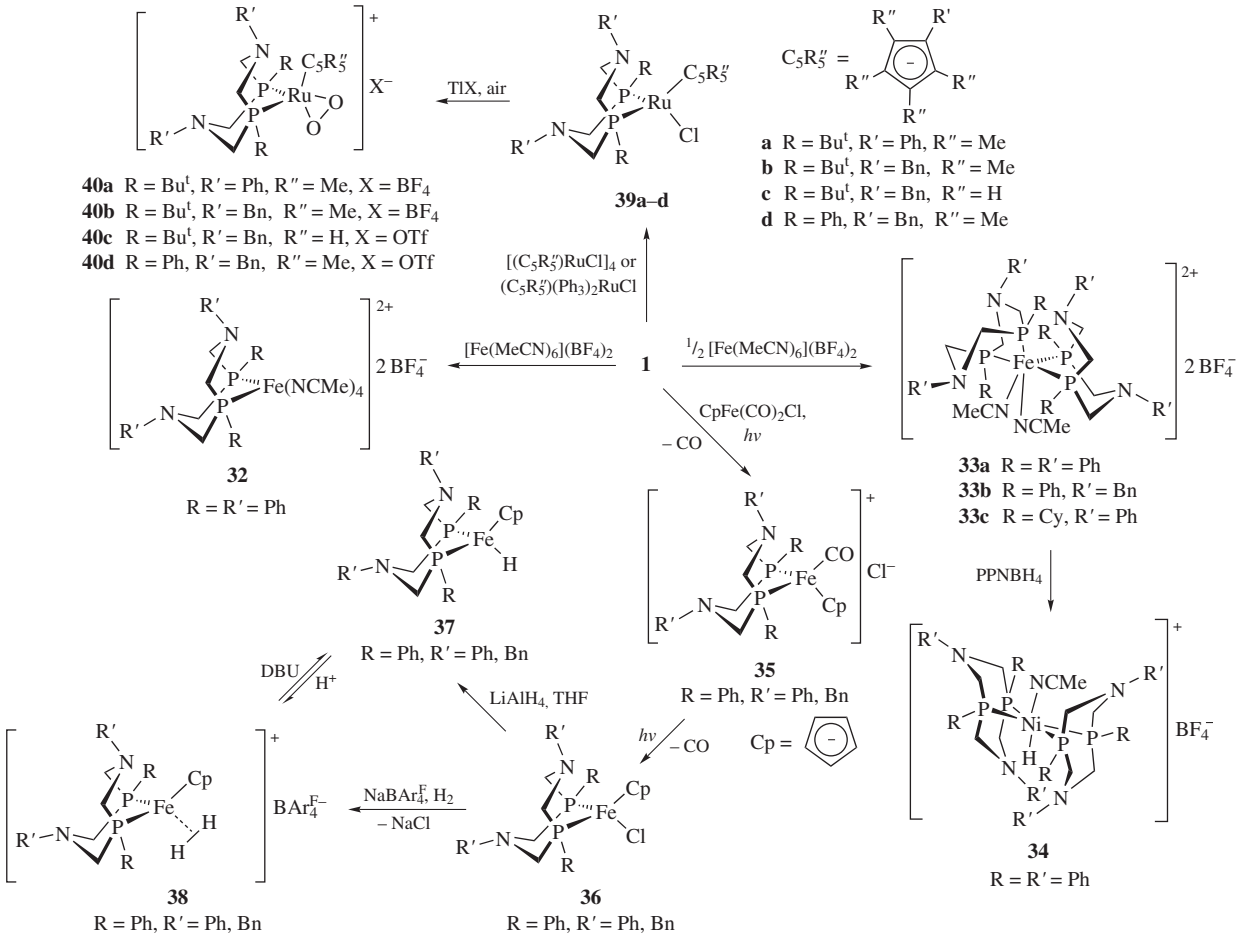
Nickel(II) complexes **20** are electrocatalysts for the oxidation of formate in solution to produce $CO_2$. A maximum turnover frequency of 15.8 $s^{-1}$ was observed for **20** (R = Ph, R′ = Me).[31]

The reaction of $P_2^{Ph}N_2^{Ph}$ with $[Fe(MeCN)_6](BF_4)_2$ in acetonitrile resulted in the formation of only monoligand complex **32**, whereas bis-ligand *cis*-complexes **33a–c** were obtained in acetone. The reaction of **33a** with bis(triphenyphosphino)iminium(PPN) borohydride gave hydride *trans*-complex **34** (Scheme 15). In a crystal, the iron ions of all types of complexes are in distorted octahedral environments with small P–Fe–P angles (79.1–81.7°). The ligands have chair–boat conformations and non-bonding distances N···Fe are 3.43–3.53 Å. The hydride ligand in **34** is located between nitrogen atoms of the boat parts of ligands; so distances N···H are only 2.60–2.68 Å.[73]

The photolysis of $P_2^{Ph}N_2^{R'}$ (R′ = Ph, Bn) and $CpFe(CO)_2Cl$ in toluene led to the consecutive formation of cationic and neutral monoligand complexes **35** and **36** (Scheme 15). The reduction of **36** with $LiAlH_4$ in THF gave hydride complexes **37** (Scheme 15). The abstraction of chloride with $NaBAr_4^F$ in fluorobenzene in an atmosphere of $H_2$ afforded dihydrogen complexes **38**. The deprotonation of **38** with DBU led to **37**, which could be reversibly protonated to give **38** (Scheme 15).[74] Rapid H/D exchange is observed for dihydrogen complexes **38** in an $H_2/D_2$ atmosphere, whereas under the same conditions HD formation is not observed for analogous dihydrogen complex with 1,5-diphenyl-1,5-diphosphacyclooctane ligand, which does not have a base incorporated in its second coordination sphere. Together with the DFT calculations, these experimental observations indicate that necessary structural features for the intramolecular heterolytic cleavage of $H_2$ are a $Fe^{II}$ center, a pendant amine, and matched hydride and proton acceptor abilities. These mononuclear iron dihydrogen complexes **38** with pendant amines in the ligands mimic the crucial features of the distal Fe site of the active site of [FeFe]-hydrogenase required for H–H bond formation and cleavage. Although the electrocatalytic oxidation of $H_2$ has not been observed for complexes **37** and **38**, this study provides a useful basis for catalyst development in this series of CpFe derivatives.[74]

Ruthenium complexes **39a–d** similar to complexes **36** were obtained according to Scheme 15. Complexes **39** react with $O_2$ to form $\eta^2$-peroxo complexes **40** which are protonated at the endocyclic nitrogen atom, forming a hydrogen bond with bound $O_2$.[75,76] Despite the favorable interaction between the protonated pendant amine and the $O_2$, the ruthenium peroxo complexes, both protonated and unprotonated, decompose upon reduction, precluding catalytic $O_2$ reduction.[76]

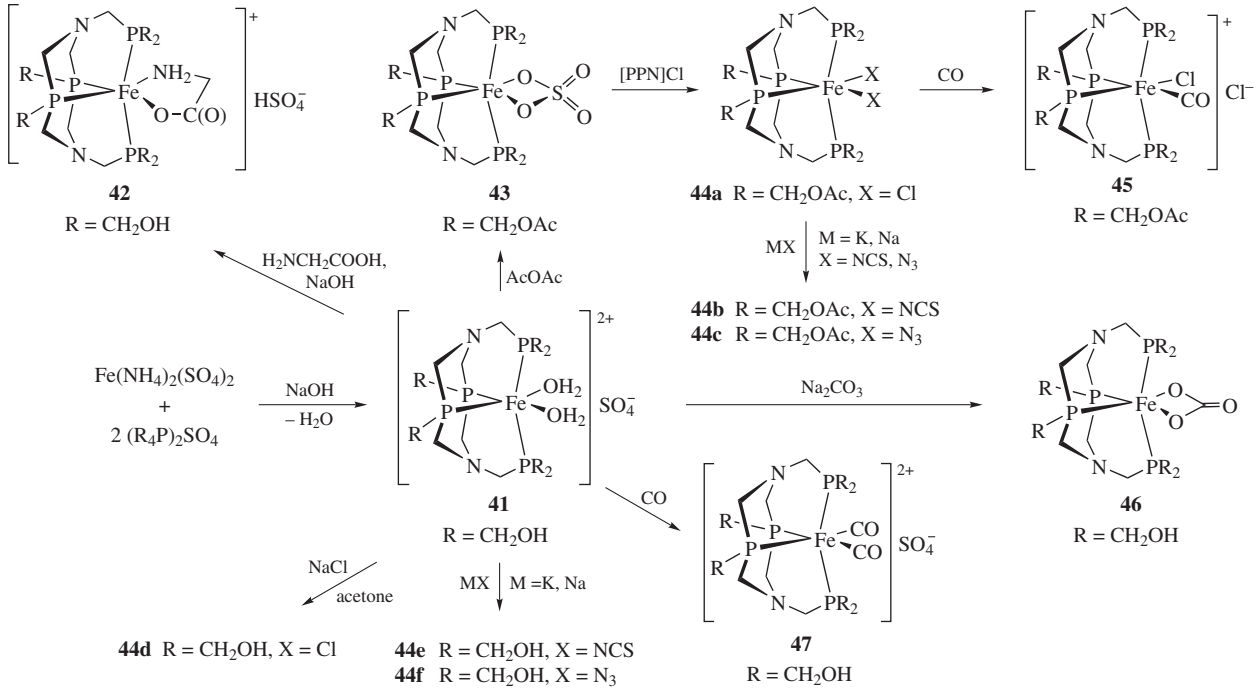
Note that a unique and remarkable example of the self-assembly of iron(II) complex with diazadiphosphacyclooctane ligand was described. The interaction of iron(II) ammonium sulfate with tetrakis(hydroxymethyl)phosphonium sulfate in water under basic conditions produced water-soluble monoligand cationic complex **41** (Scheme 16), where the iron ion is coordinated by two endo-




**Scheme 15**

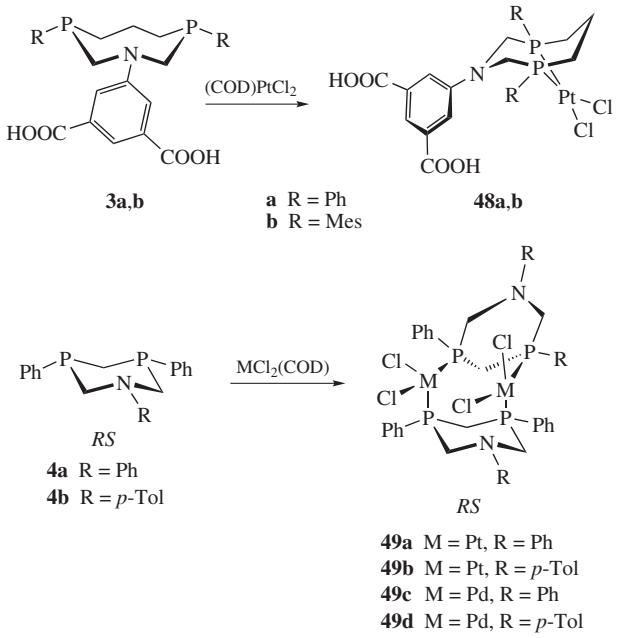
cyclic phosphorus atoms in equatorial positions and by two pendant phosphine groups in apical ones. The precise mechanism of the formation of **41** is uncertain. The ligand had forced chair–chair conformation; the bite P–Fe–P angle is 80.6°.[77] The ligand substitution reactions and the modification of hydroxymethyl fragments of **41** resulted in a whole family of similar complexes **42**–**47** (Scheme 16), but their applicable properties were not still reported.[78]

The coordination chemistry of other types of cyclic aminomethylphosphines is less studied. Only monoligand P,P-chelate platinum(II) complexes **48** of 1-aza-3,7-diphosphacyclooctanes (Scheme 17) were described. The structure of **48a** is closely




**Scheme 16**

related to that of the platinum complexes of 1,5-diaza-3,7-diphosphacyclooctanes. The heterocyclic ligand has a chair–boat conformation with a narrowed P–Pt–P bond angle of 84.5°. The sterically more demanding $CH_2N(aryl)CH_2$ fragment forms the boat part of the heterocycle, resulting in an N···Pt distance of 3.40 Å. The nitrogen atom has a nearly trigonal-planar coordination environment.[48]

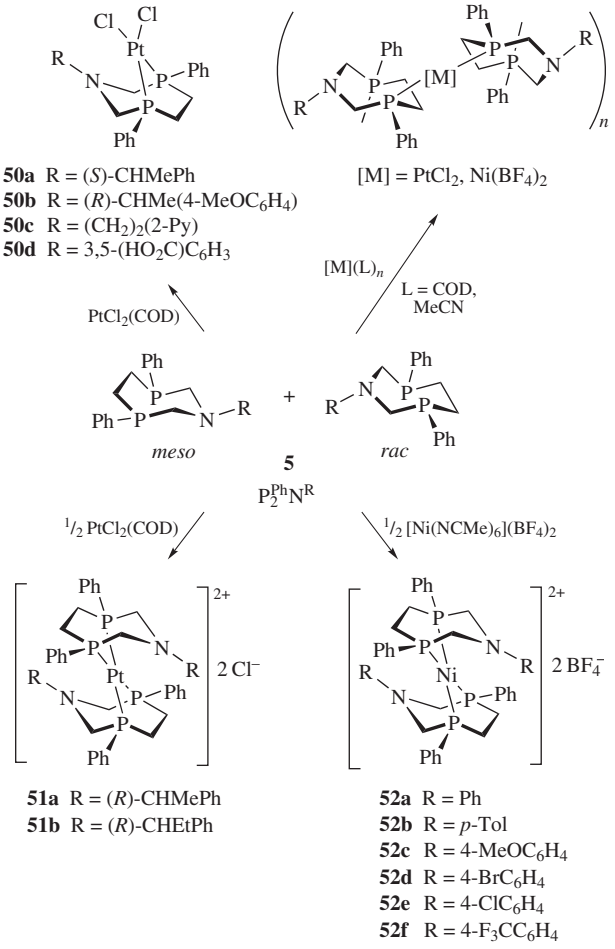



**3a**,**b** **a** R = Ph, **b** R = Mes; **48a**,**b**

**4a** R = Ph
**4b** R = *p*-Tol

**49a** M = Pt, R = Ph
**49b** M = Pt, R = *p*-Tol
**49c** M = Pd, R = Ph
**49d** M = Pd, R = *p*-Tol

**Scheme 17**




**50a** R = (*S*)-CHMePh
**50b** R = (*R*)-CHMe(4-MeOC$_6$H$_4$)
**50c** R = $(CH_2)_2$(2-Py)
**50d** R = 3,5-$(HO_2C)C_6H_3$

[M] = $PtCl_2$, $Ni(BF_4)_2$

**51a** R = (*R*)-CHMePh
**51b** R = (*R*)-CHEtPh

**52a** R = Ph
**52b** R = *p*-Tol
**52c** R = 4-MeOC$_6$H$_4$
**52d** R = 4-BrC$_6$H$_4$
**52e** R = 4-ClC$_6$H$_4$
**52f** R = 4-$F_3$CC$_6$H$_4$

**Scheme 18**

The *meso*-isomers of small and rigid 1-aza-3,5-diphosphacyclohexanes act only as bridging ligands to give binuclear complexes **49a**–**d** with platinum(II) and palladium(II) dichlorides (Scheme 17). The NMR and IR spectra evidenced that the metal ions of complexes **48** have *cis*-square-planar configurations.[51]

The complexation modes of the *rac* and *meso* isomers of 1-aza-3,6-diphosphacycloheptanes are completely different. The *rac* isomers with *anti*-oriented phosphorus lone electron pairs act as bridging ligands to give oligomeric complexes.[52,53,55] The structures of the *meso* isomers are very favorable for the formation of chelate complexes, and these ligands readily form both monoligand neutral P,P-chelate complexes **50a**–**d**[52–54] and bis-ligand cationic bis-P,P-chelate complexes **51a**,**b**[54] with platinum(II) dichloride according to used metal–ligand ratios (Scheme 18). The formation of chelate complexes proceeds faster than the formation of oligomeric ones, and it has been used for the separation of the stereoisomers of the $P_2^{Ph}N^{rCHEtPh}$ ligand.[54]

The nickel(II) complexes of 1-aza-3,6-diphosphacycloheptanes were prepared starting from *rac*/*meso* stereoisomeric mixtures, but bis-ligand cationic complexes **52a**–**f** (Scheme 18) could be successfully isolated in pure forms by fractional crystallization in reasonable yields (26–75%).[55,79] Unlike analogous diazadiphosphacyclooctane complexes **20**, the central ions of **52** have a slightly distorted square planar geometry. The P–Ni–P bite angles vary from 79.7° to 80.1° (*vs.* 82–84° for diazadiphosphacyclooctane complexes). For **52**, one five-membered and one six-membered ring are formed upon chelation of the ligand. The smaller bite angles of **52** result in a decrease in the steric interactions between the substituents on adjacent phosphorus atoms of the two ligands and more planar structures in comparison with corresponding complexes **20**. The dihedral angles between two P–Ni–P planes in **52** are 0.0°. Thus, the replacement of one six-membered chelate with a five-membered ring has significant structural consequences for these complexes. Two six-membered rings containing the nitrogen atoms are *trans* to each other across the metal center, and, except for **52f**, adopt boat conformations, so that in all complexes except **52f** the conformations of the ligands are similar to the chair conformations of free ligands. The chair conformations of the six-membered rings observed in **52f** likely result from the interaction of the $BF_4^-$ anions with the metal center in a solid state. The nonbonding Ni···N distances are 3.17–3.23 Å for **52a**–**e** and 3.68 Å for **52f**.[55,79]

The cyclic voltammograms of **52a**–**f** indicate two overlapping one-electron reversible redox couples, with observed $E_{1/2}$ values ranging from –1.05 to –1.14 V. The potentials of the $Ni^{II/I}$ couples of complexes **52** shift to more negative values in comparison with complexes **20** as complexes **51** become more planar, approaching the potentials of the $Ni^{I/0}$ couples.[55,79]

All complexes **52a**–**f** are efficient electrocatalysts for hydrogen production at the potential of the $Ni^{II/I}$ couple, with turnover frequencies ranging from 2400 to 33 000 $s^{-1}$ with $[(DMF)H]^+$ as a proton source in acetonitrile. The addition of water accelerates the catalysis, giving turnover frequencies ranging from 4100 to 106 000 $s^{-1}$. The highest catalytic rates have been found for complexes **52a**,**b**. The activity of **52** as catalysts for hydrogen production is dramatically higher than that of complexes **20**, but overpotentials required for electrocatalysis by complexes **52** are relatively high (550–640 mV *vs.* ~300 mV for complexes **20** and < 100 mV for hydrogenases).[55,79] The possible explanations of the increased catalytic rates for complexes **52** in comparison with **20** are greater hydride donor abilities of the catalytic intermediates $[HNi(P_2^{Ph}N^R)_2]^+$ due to the planarity of the metal environment in complexes **52** and the increased stability of *endo*- (with respect to the metal center) *vs. exo*-protonation of the $Ni^I$ species due to the absence of the stabilizing NH···N 'pinch' interaction

that occurs in protonated complexes with diazadiphosphacyclooctane ligands[15,70,71] (see Scheme 12). The *endo*-protonation is essential to attain the suitable proximity to the reduced metal center to generate $H_2$. Computational studies carried out for complexes **52** also indicate that the catalytic rates reach a maximum when the electron-donating character of substituents on nitrogen results in the p$K_a$ of the $Ni^I$ protonated pendant amine matching that of the acid used for proton delivery.[55,79]

Different factors responsible for the catalytic activities of the metal complexes of cyclic aminomethylphosphines complicate their predictions at the present time; thus, both a targeted design and a wide catalytical screening of these complexes are necessary.

The data summarized in this survey clearly show that chelating cyclic aminomethylphosphine ligands have a great potential as the basis for the design of effective catalysts for reactions with the participation of small molecules (especially, hydrogen). The advantage of the metal complexes of these ligands is their ability to mimic the crucial functional features of natural hydrogenase enzymes. A key feature of these enzyme systems is channels that regulate the delivery/removal of protons and $H_2$. The relatively rigid cyclic structures of nitrogen-containing diphosphine ligands are crucially important because they provide the necessary positioning of nitrogen centers (pendant amines) incorporated into the cyclic framework in close proximity to the metal over or/and under the mean $P_4M$ planes of complexes. Properly positioned nitrogen atoms serve as proton relays that accelerate intramolecular and intermolecular proton mobility. In addition to the role of accelerating proton transfer reactions, the nitrogen centers of aminomethylphosphine ligands also have such favorable effects as enhancement of the binding of $H_2$ to a metal, lowering the barrier to the heterolytic cleavage of $H_2$, and involvement in proton-coupled electron-transfer reactions. The additional advantage of the cyclic structures of these ligands is a decrease in bite P–M–P angles due to short P–P distances in their conformations, which are most favorable for chelation (chair–boat one for 1,5-diaza-3,7-diphosphacyclooctanes and chair one for 1-aza-3,7-diphosphacycloheptanes). The narrowed bite angles decrease the steric interactions of two ligands and the resulting tetrahedral distortions of the planar metal environment, which is more favorable for the catalysis.

Although the reactions including hydrogen as a key participant have been mainly studied, the use of nitrogen atoms in the second coordination sphere of a metal as proton relays for the acceleration of proton transfer reactions should be applicable to many other processes that involve the transfer of multiple protons and electrons. The reactions of these types are of interest for both energy storage/utilization and synthetic chemistry.

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## References

1 G. Märkl, G. Yu. Jin and C. Schoerner, *Tetrahedron Lett.*, 1980, **21**, 1409.
2 B. A. Arbuzov, O. A. Erastov and G. N. Nikonov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1980, 735 (in Russian).
3 A. A. Karasik and G. N. Nikonov, *Zh. Obshch. Khim.*, 1993, **63**, 2775 (in Russian).
4 A. A. Karasik, G. N. Nikonov, A. S. Dokuchaev and I. A. Litvinov, *Koord. Khim.*, 1994, **20**, 300 (in Russian).
5 A. A. Karasik, S. V. Bobrov, G. N. Nikonov, A. P. Pisarevskii, I. A. Litvinov, A. S. Dokuchaev, Yu. T. Struchkov and K. M. Enikeev, *Koord. Khim.*, 1995, **21**, 574 (in Russian).
6 J. C. Kane, E. H. Wong, G. P. A. Jap and A. L. Rheingold, *Polyhedron*, 1999, **18**, 1183.
7 A. A. Karasik, A. V. Krashilina, A. T. Gubaidullin, I. A. Litvinov, V. K. Cherkasov, O. G. Sinyashin and G. A. Abakumov, *Russ. Chem. Bull., Int. Ed.*, 2000, **49**, 1782 (*Izv. Akad. Nauk, Ser. Khim.*, 2000, 1806).
8 A. A. Karasik, R. N. Naumov, R. Sommer, O. G. Sinyashin and E. Hey-Hawkins, *Polyhedron*, 2002, **21**, 2251.
9 A. A. Karasik, R. N. Naumov, O. G. Sinyashin, G. P. Belov, H. V. Novikova, P. Lönnecke and E. Hey-Hawkins, *Dalton Trans.*, 2003, 2209.
10 A. A. Karasik, Yu. S. Spiridonova, D. G. Yakhvarov, O. G. Sinyashin, P. Lönnecke, R. Sommer and E. Hey-Hawkins, *Mendeleev Commun.*, 2005, 89.
11 A. A. Karasik, R. N. Naumov, A. S. Balueva, Yu. S. Spiridonova, O. N. Golodkov, H. V. Novikova, G. P. Belov, S. A. Katsyuba, E. E. Vandyukova, P. Lönnecke, E. Hey-Hawkins and O. G. Sinyashin, *Heteroatom Chem.*, 2006, **17**, 499.
12 A. D. Wilson, R. H. Newell, M. J. McNevin, J. T. Muckerman, M. Rakowski DuBois and D. L. DuBois, *J. Am Chem. Soc.*, 2006, **128**, 358.
13 M. Rakowski DuBois and D. L. DuBois, *Acc. Chem. Res.*, 2009, **42**, 1974.
14 D. L. DuBois and R. M. Bullock, *Eur. J. Inorg. Chem.*, 2011, 1017.
15 S. Raugei, S. Chen, M.-H. Ho, B. Ginovska-Pangovska, R. J. Rousseau, M. Dupuis, D. L. DuBois and R. M. Bullock, *Chem. Eur. J.*, 2012, **18**, 6493.
16 M. D. Doud, K. A. Grice, A. M. Lilio, C. S. Seu and C. P. Kubiak, *Organometallics*, 2012, **31**, 779.
17 S. Wiese, U. J. Kilgore, D. L. DuBois and R. M. Bullock, *ACS Catal.*, 2012, **2**, 720.
18 A. A. Karasik, I. O. Georgiev, O. G. Sinyashin and E. Hey-Hawkins, *Polyhedron*, 2000, **19**, 1455.
19 B. A. Arbuzov, O. A. Erastov, G. N. Nikonov, R. P. Arshinova, I. P. Romanova and R. A. Kadyrov, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1983, **32**, 1672 (*Izv. Akad. Nauk SSSR, Ser. Khim.*, 1983, 1846).
20 G. N. Nikonov, A. S. Balueva, O. A. Erastov and B. A. Arbuzov, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1989, **38**, 1223 (*Izv. Akad. Nauk SSSR, Ser. Khim.*, 1989, 1340).
21 U. J. Kilgore, J. A. S. Roberts, D. H. Pool, A. M. Appel, M. P. Stewart, M. Rakowski DuBois, W. G. Dougherty, W. S. Kassel, R. M. Bullock and D. L. DuBois, *J. Am. Chem. Soc.*, 2011, **133**, 5861.
22 S. E. Smith, J. Y. Yang, D. L. DuBois and R. M. Bullock, *Angew. Chem. Int. Ed.*, 2012, **51**, 3152.
23 J. Y. Yang, R. M. Bullock, W. G. Dougherty, W. S. Kassel, B. Twamley, D. L. DuBois and M. Rakowski DuBois, *Dalton Trans.*, 2010, **39**, 3001.
24 J. S. Spiridonova, A. A. Karasik and O. G. Sinyashin, *Phosphorus Sulfur Silicon Relat. Elem.*, 2011, **186**, 764.
25 A. Jain, S. Lense, J. C. Linehan, S. Raugei, H. Cho, D. L. DuBois and W. J. Shaw, *Inorg. Chem.*, 2011, **50**, 4073.
26 P. D. Tran, A. Le Goff, J. Heidkamp, B. Jousselme, N. Guillet, S. Palacin, H. Dau, M. Fontecave and V. Artero, *Angew. Chem. Int. Ed.*, 2011, **50**, 1371.
27 U. J. Kilgore, M. P. Stewart, M. L. Helm,W. G. Dougherty, W. S. Kassel, M. Rakowski DuBois, D. L. DuBois and R. M. Bullock, *Inorg. Chem.*, 2011, **50**, 10908.
28 E. I. Musina, R. M. Kuznetsov, E. F. Gubanov, A. S. Balueva and G. N. Nikonov, *Russ. J. Gen. Chem.*, 1999, **69**, 891 (*Zh. Obshch. Khim.*, 1999, **69**, 928).
29 S. N. Ignatieva, A. S. Balueva, A. A. Karasik, S. K. Latypov, A. G. Nikonova, O. E. Naumova, P. Lönnecke, E. Hey-Hawkins and O. G. Sinyashin, *Inorg. Chem.*, 2010, **49**, 5407.
30 E. S. Wiedner, J. Y. Yang, W. G. Dougherty, W. S. Kassel, R. M. Bullock, M. Rakowski DuBois and D. L. DuBois, *Organometallics*, 2010, **29**, 5390.
31 B. R. Galan, J. Schöffel, J. C. Linehan, C. Seu, A. M. Appel, J. A. S. Roberts, M. L. Helm, U. J. Kilgore, J. Y. Yang, D. L. DuBois and C. P. Kubiak, *J. Am. Chem. Soc.*, 2011, **133**, 12767.
32 J. Y. Yang, S. Chen, W. G. Dougherty, W. S. Kassel, R. M. Bullock, D. L. DuBois, S. Raugei, R. Rousseau, M. Dupuis and M. Rakowski DuBois, *Chem. Commun.*, 2010, **46**, 8618.
33 E. I. Musina, I. D. Strelnik, T. I. Fesenko, D. B. Krivolapov, A. A. Karasik, E. Hey-Hawkins and O. G. Sinyashin, *Phosphorus Sulfur Silicon Relat. Elem.*, 2013, **188**, 59.
34 A. A. Karasik, I. O. Georgiev, E. I. Musina, J. Heinicke and O. G. Sinyashin, *Polyhedron*, 2001, **20**, 3321.
35 F. Z. Baimukhametov, V. F. Zheltukhin, G. N. Nikonov and A. S. Balueva, *Russ. J. Gen. Chem.*, 2002, **72**, 1754 (*Zh. Obshch. Khim.*, 2002, **72**, 1858).
36 B. A. Arbuzov, O. A. Erastov, G. N. Nikonov, I. A. Litvinov, D. S. Yufit and Yu. T. Struchkov, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1981, **30**, 1872 (*Izv. Akad. Nauk SSSR, Ser. Khim.*, 1981, 2279).
37 S. K. Latypov, A. G. Strelnik, S. N. Ignatieva, E. Hey-Hawkins, A. S. Balueva, A. A. Karasik and O. G. Sinyashin, *J. Phys. Chem. A*, 2012, **116**, 3182.

38 A. S. Balueva, R. M. Kuznetsov, I. A. Litvinov, A. T. Gubaidullin and G. N. Nikonov, *Mendeleev Commun.*, 2000, 120.

39 R. M. Kuznetsov, A. S. Balueva, I. A. Litvinov, A. T. Gubaidullin, G. N. Nikonov, A. A. Karasik and O. G. Sinyashin, *Russ. Chem. Bull., Int. Ed.*, 2002, **51**, 151 (*Izv. Akad. Nauk, Ser. Khim*., 2002, 142).

40 A. S. Balueva, R. M. Kuznetsov, S. N. Ignat'eva, A. A. Karasik, A. T. Gubaydullin, I. A. Litvinov, O. G. Sinyashin, P. Lönnecke and E. Hey-Hawkins, *Dalton Trans*., 2004, 442.

41 D. V. Kulikov, A. A. Karasik, A. S. Balueva, O. N. Kataeva, I. A. Litvinov, E. Hey-Hawkins and O. G. Sinyashin, *Mendeleev Commun.*, 2007, **17**, 195.

42 D. V. Kulikov, A. S. Balueva, A. A. Karasik, A. V. Kozlov, Sh. K. Latypov, O. N. Kataeva, P. Lönnecke, E. Hey-Hawkins and O. G. Sinyashin, *Phosphorus Sulfur Silicon Relat. Elem*., 2008, **183**, 667.

43 A. A. Karasik, D. V. Kulikov, A. S. Balueva, S. N. Ignat'eva, O. N. Kataeva, P. Lönnecke, A. V. Kozlov, S. K. Latypov, E. Hey-Hawkins and O. G. Sinyashin, *Dalton Trans*., 2009, 490.

44 A. A. Karasik, A. S. Balueva and O. G. Sinyashin, *C. R. Chimie*, 2010, **13**, 1151.

45 A. S. Balueva, S. N. Ignatieva, A. A. Karasik, P. Lönnecke, E. Hey-Hawkins and O. G. Sinyashin, *Phosphorus Sulfur Silicon Relat. Elem*., 2011, **186**, 891.

46 A. A. Karasik, D. V. Kulikov, R. M. Kuznetsov, A. S. Balueva, A. A. Akhmetgaliev, O. N. Kataeva, P. Lönnecke, O. R. Sharapov, Y. A. Zhelezina, S. N. Ignat'eva, E. Hey-Hawkins and O. G. Sinyashin, *Macroheterocycles*, 2011, **4**, 324.

47 S. K. Latypov, A. V. Kozlov, E. Hey-Hawkins, A. S. Balueva, A. A. Karasik and O. G. Sinyashin, *J. Phys. Chem. A*, 2010, **114**, 2588.

48 A. A. Karasik, R. N. Naumov, Yu. S. Spiridonova, O. G. Sinyashin, P. Lönnecke and E. Hey-Hawkins, *Z. Anorg. Allg. Chem.*, 2007, **633**, 205.

49 R. N. Naumov, A. A. Karasik, O. G. Sinyashin, P. Lönnecke and E. Hey-Hawkins, *Dalton Trans*., 2004, 357.

50 R. N. Naumov, A. A. Karasik, K. B. Kanunnikov, A. V. Kozlov, S. K. Latypov, K. V. Domasevich, E. Hey-Hawkins and O. G. Sinyashin, *Mendeleev Commun*., 2008, **18**, 80.

51 A. A. Karasik, S. V. Bobrov, A. I. Akhmetzyanov, R. N. Naumov, G. N. Nikonov and O. G. Sinyashin, *Koord. Khim*., 1998, **24**, 530 (in Russian).

52 A. A. Karasik, A. S. Balueva, E. I. Moussina, R. N. Naumov, A. B. Dobrynin, D. B. Krivolapov, I. A. Litvinov and O. G. Sinyashin, *Heteroat. Chem*., 2008, **19**, 125.

53 T. I. Fesenko, I. D. Strelnik, E. I. Musina, A. A. Karasik and O. G. Sinyashin, *Russ. Chem. Bull., Int. Ed.*, 2012, **61**, 1792 (*Izv. Akad. Nauk, Ser. Khim*., 2012, 1776).

54 E. I. Musina, A. A. Karasik, A. S. Balueva, I. D. Strelnik, T. I. Fesenko, A. B. Dobrynin, T. P. Gerasimova, S. A. Katsyuba, O. N. Kataeva, P. Lönnecke, E. Hey-Hawkins and O. G. Sinyashin, *Eur. J. Inorg. Chem*., 2012, 1857.

55 M. P. Stewart, M.-H. Ho, S. Wiese, M. L. Lindstrom, C. E. Thogerson, S. Raugei, R. M. Bullock and M. L. Helm, *J. Am. Chem. Soc.*, 2013, **135**, 6033.

56 M. T. Mock, S. Chen, R. Rousseau, M. J. O'Hagan, W. G. Dougherty, W. S. Kassel, D. L. DuBois and R. M. Bullock, *Chem. Commun.*, 2011, **47**, 12212.

57 K. D. Welch, W. G. Dougherty, W. S. Kassel, D. L. DuBois and R. M. Bullock, *Organometallics*, 2010, **29**, 4532.

58 A. Fihri, D. Luart, C. Len, A. Solhy, C. Chevrin and V. Polshettiwar, *Dalton Trans*., 2011, **40**, 3116.

59 R. Z. Khairullina, A. A. Karasik and E. Yu. Musakova, *Neftekhimiya*, 1994, **34**, 332 (in Russian).

60 V. V. Yanilkin, N. I. Maksimyuk, E. I. Strunskaya, A. A. Karasik and Yu. M. Kargin, *Russ. Chem. Bull*., 1994, **43**, 372 (*Izv. Akad. Nauk, Ser. Khim*., 1994, 414).

61 E. V. Novikova, A. A. Karasik, E. Hey-Hawkins and G. P. Belov, *Russ. J. Coord. Chem.*, 2005, **31**, 260 (*Koord. Khim.*, 2005, **31**, 280).

62 G. M. Jacobsen, J. Y. Yang, B. Twamley, A. D. Wilson, R. M. Bullock, M. Rakowski DuBois and D. L. DuBois, *Energy Environ. Sci.*, 2008, **1**, 167.

63 A. D. Wilson, K. Fraze, B. Twamley, S. M. Miller, D. L. DuBois and M. Rakowski DuBois, *J. Am. Chem. Soc*., 2008, **130**, 1061.

64 R. M. Galimullina, M. I. Valitov, Yu. S. Spiridonova, E. I. Musina, S. A. Krasnov, M. K. Kadirov, A. A. Karasik, Yu. G. Budnikova and O. G. Sinyashin, *Russ. J. Phys. Chem. A*, 2011, **85**, 2214 (*Zh. Fiz. Khim.*, 2011, **85**, 2370).

65 Yu. H. Budnikova, V. V. Khrizanforova, R. M. Galimullina, A. A. Karasik, E. I. Musina, A. R. Burilov and O. G. Sinyashin, *Phosphorus Sulfur Silicon Relat. Elem.*, 2013, **188**, 84.

66 K. Fraze, A. D. Wilson, A. M. Appel, M. Rakowski DuBois and D. L. DuBois, *Organometallics*, 2007, **26**, 3918.

67 J. Y. Yang, R. M. Bullock, W. J. Shaw, B. Twamley, K. Fraze, M. Rakowski DuBois and D. L. DuBois, *J. Am. Chem. Soc.*, 2009, **131**, 5935.

68 M. Dupuis, S. Chen, S. Raugei, D. L. DuBois and R. M. Bullock, *J. Phys. Chem. A*, 2011, **115**, 4861.

69 A. M. Appel, D. H. Pool, M. O'Hagan, W. J. Shaw, J. Y. Yang, M. Rakowski DuBois, D. L. DuBois and R. M. Bullock, *ACS Catal*., 2011, **1**, 777.

70 M. O'Hagan, W. J. Shaw, S. Raugei, S. Chen, J. Y. Yang, U. J. Kilgore, D. L. DuBois and R. M. Bullock, *J. Am. Chem. Soc*., 2011, **133**, 14301.

71 M. O'Hagan, M.-H. Ho, J. Y. Yang, A. M. Appel, M. Rakowski DuBois, S. Raugei, W. J. Shaw, D. L. DuBois and R. M. Bullock, *J. Am. Chem. Soc*., 2012, **134**, 19409.

72 E. S. Wiedner, J. Y. Yang, S. Chen, S. Raugei, W. G. Dougherty, W. S. Kassel, M. L. Helm, R. M. Bullock, M. Rakowski DuBois and D. L. DuBois, *Organometallics*, 2012, **31**, 144.

73 G. M. Jacobsen, R. K. Shoemaker, M. J. McNevin, M. Rakowski DuBois and D. L. DuBois, *Organometallics*, 2007, **26**, 5003.

74 T. Liu, S. Chen, M. O'Hagan, M. Rakowski DuBois, R. M. Bullock and D. L. DuBois, *J. Am. Chem. Soc*., 2012, **134**, 6257.

75 T. A. Tronic, M. Rakowski DuBois, W. Kaminsky, M. K. Coggins, T. Liu and J. M. Mayer, *Angew. Chem. Int. Ed*., 2011, **50**, 10936.

76 T. A. Tronic, W. Kaminsky, M. K. Coggins and J. M. Mayer, *Inorg. Chem*., 2012, **51**, 10916.

77 J. C. Jeffery, B. Odell, N. Stevens and R. E. Talbot, *Chem. Commun.*, 2000, 101.

78 A. D. Burrows, D. Dodds, A. S. Kirk, J. P. Lowe, M. F. Mahon, J. E. Warren and M. K. Whittlesey, *Dalton Trans*., 2007, 570.

79 M. L. Helm, M. P. Stewart, R. M. Bullock, M. Rakowski DuBois and D. L. DuBois, *Science*, 2011, **333**, 863.


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