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ORIGINAL RESEARCH

Theoretical study of cobalt and nickel complexes involved in methyl transfer reactions: structures, redox potentials and methyl binding energies

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Abstract

Cobalamins, cobalt glyoximate complexes and nickel complexes with Triphos (bis(diphenylphosphinoethyl)phenylphosphine) and $PPh_2CH_2CH_2SEt$ ligands were studied with the DFT/BP86 method in connection with methyl transfer reactions. Geometries, methyl binding energies and redox potentials were determined for the studied complexes. Three- and four-coordinate structures were considered for nickel complex with $PPh_2CH_2CH_2SEt$ ligand, whereas four- and five-coordinate for its methyl derivative. On the basis of calculations, the possible mechanism of methyl transfer reaction between cobalt and nickel complexes was considered.

Keywords Nickel complexes · Cobalt complexes · DFT · Redox potentials · Methyl transfer

Introduction

The B_{12} vitamin derivatives (cobalamins) present in methyltransferases take part in many enzymatic methyl transfer reactions [1–3]. A unique methyl transfer reaction, where metals act as donors and acceptors of the methyl group, is found in the acetyl-CoA (Ljungdahl-Wood) pathway of autotrophic carbon fixation in various bacteria and archaea [4]. Acetyl-CoA is synthesized at the Ni-Ni-[4Fe-4S] cluster (the A-cluster) of acetyl-CoA synthase (ACS) through condensation of coenzyme-A (CoASH) with CO and the methyl group from CH_3-Cob(III)alamin of the corrinoid-iron-sulfur protein (CoFeSP) [5, 6]. A key step of such synthesis is the transfer of the methyl group from CoFeSP to the proximal Ni atom in the active site of ACS [7]. This reaction proceeds according to the equation:

$$CH_3 - Co(III)FeSP + CO + CoASH \rightleftharpoons CH_3CO - SCoA + Co(I)FeSP + H^+ \quad (1)$$

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The occurrence of Ni(0) [8, 9] or Ni(I) [10] in reaction (1) of ACS was postulated. Since the mechanism of catalytic action of the ACS enzyme is not fully understood [8, 11–13], models of methylation reactions involving nickel complexes and various methylation factors are being examined experimentally [9, 14–19]. Likewise, many complexes relevant to ACS enzyme are investigated experimentally [20–24] and computationally [25–29]. Examples of methylation reactions with nickel participation are [10, 28]:

$$Ni(Triphos)PPh_3 + CH_3 - Co(dmgBF_2)_2py + sol \longrightarrow Ni(Triphos)CH_3^+ + Co(dmgBF_2)_2sol^- + PPh_3 + py, \quad (2)$$

where Triphos stands for bis(diphenylphosphinoethyl)phenylphosphine ligand, and

$$Ni(PPh_2CH_2CH_2SEt)_2 + CH_3J \longrightarrow Ni(PPh_2CH_2CH_2SEt)_2CH_3^+ + J^-. \quad (3)$$

In general, two mechanisms—S_N2 and radical—are possible in methyl transfer reactions with cobalamin participation [28, 30, 31]. Both reactions (2) and (3) involve methylation of nickel(0) complexes. In the first step of the radical reaction, the methyl derivative should be reduced by the methyl acceptor; thus, the homolytic cleavage of Co-CH_3 bond is initiated by electron transfer between reactants. The radical mechanism is therefore possible when methyl acceptor is able to reduce methyl donor.

For theoretical modelling of such reactions with the use of DFT method, it is extremely important to apply a functional which properly describes electronic structure of the reactants, giving the results comparable with experiment. This is especially important for methyl-metal binding energy and oxidation—reduction properties of the reacting complexes. In this work, the calculational study was carried out for nickel and cobalt complexes pertinent to biological (1) and model (2), (3) methyl transfer reactions with the use of DFT method and nonhybrid functional BP86. This functional allows to get a good description of the cobalt-methyl bond in alkylcobalamins, while the hybrid functionals significantly underestimate the energy of this bond [32–35]. Calculations for transition metal complexes show that BP86 functional gives also good estimation for redox potentials [36–38]. In the present study, BP86 is used to determine geometry, methyl binding energies and redox potentials for the investigated cobalt and nickel complexes. The results are compared with the experimental data.

Method of calculations

The calculations were carried out with the use of Gaussian16 program [39]. The DFT method with BP86 [40, 41] functional and TZVP [42] basis sets were used in the calculations. The effect of environment was taken into account by PCM solvent model [43–45], with water (for Co complexes) and acetonitrile (for Ni complexes) as solvents. The geometry of all studied complexes was fully optimized. The zero point energy (ZPE) and G3 dispersion correction [46, 47] were added to the calculated binding energies.

Methylcobalamin (MeCbl) is a methyl derivative of vitamin B_{12} which is uses in methyltransferases enzymes as a methylation factor. In CoFeSP protein it exists as a base-off form. The base-on form of methylcobalamin has dimethylbenzimidazole (DMB) as a ligand trans to methyl [2]. In the base-off form, DMB is replaced by a water ligand. The base-on and base-off forms are shown in Fig. S1 (Supporting Material).

In the present study, the base-on and base-off structures were examined in the form of simplified models, in which all the corrin (denoted further as Cor) side chains were replaced by hydrogen atoms and for base-on methylcobalamin the 5,6-dimethylbenzimidazole trans axial base was replaced by imidazole [48]. The base-off form without trans axial base and with water molecule as ligand was also considered. The calculations for cobalt complexes without methyl ligand were also performed for the sake of comparison with the experimental data.

The calculations for cobalt dimethylglyoxime complexes and nickel complexes were carried out, in reference to the reactions (2) and (3). The $Ni(PPh_2CH_2CH_2SEt)_2$ complex was examined with nickel in three oxidation states: Ni(II), Ni(I) and Ni(0) which were studied experimentally [10]. In the case of the one and two-electron reduced complex the four and three coordinated complexes were investigated. For $Ni(Triphos)PPh_3$ complex, the calculations were performed in the neutral and oxidized state. The relevant methyl derivatives of nickel complexes were also studied.

Results and discussion

The aim of this work is to compare the properties of nickel and cobalt methyl derivatives in relation to methyl transfer reactions. It is essential in context of reactions (1) and (2), where the methyl group is transferred between the two metal centers, from cobalt to nickel. The important question is what properties of these complexes cause the reaction to run in this direction, what is the relative strength of methyl binding and other electron properties. It could help to explain the occurrence of nickel in the ACS enzyme and the unique biological properties of ACS enzyme. To the best of our knowledge, there are no studies with theoretical methods for methyl nickel complexes in the literature. The cobalamin-methyl complexes were extensively investigated theoretically [3, 32, 33, 35, 49–61] due to their enormous significance in biological processes. We performed also the calculations for cobalt complexes to have consistent data set obtained with the same method, basis set, solvent and other computational conditions.

Structure

The axial ligand distances for cobalt complexes and methyl-nickel bond lengths for nickel complexes are collected in Table 1. The obtained structures are presented in Figs. 1, 2, 3, 4, and 5. In Supporting Information, the total energies and selected geometrical parameters of the investigated complexes are given in Table S1 and Tables S2, S3, S4, and S5, respectively.

Cobalt complexes

For cobalamin and dimethylglyoxime complexes the geometry of optimized structures are shown in Figs. 1 and 2, respectively. The axial ligand bond lengths are gathered in Table 1. Other selected geometrical parameters for cobalamins and cobaloximes are presented in Tables S1 and S2, respectively and the numbering of atoms in Fig. S2.

For cobalamins, the most notable features are related to geometry changes occurring upon reduction. After reduction of the five-coordinated complex CoCorIm, the imidazole ligand dissociates and the four-coordinated CoCor(I) complex is formed. This is in agreement with the experimental

Table 1 Selected distances (Å) in Co and Ni complexes

			Calc.	Exp.
$CH_3CoCorIm^+$		Co-C_{CH_3}	1.990	1.972[a]
		Co-N_{Im}	2.178	2.093[a]
$CH_3CoCorIm$		Co-C_{CH_3}	1.981	
		Co-N_{Im}	2.169	
CH_3CoCor^+		Co-C_{CH_3}	1.971	
CH_3CoCor		Co-C_{CH_3}	1.959	
$CoCorIm^+$		Co-N_{Im}	2.160	
CoCorIm		Co-N_{Im}	19.745	
$CH_3CoCorH_2O^+$		Co-C_{CH_3}	1.974	
		Co-O_{H_2O}	2.370	
$CH_3CoCorH_2O$[d]		Co-C_{CH_3}	1.960	
		Co-$H2_{H_2O}$	3.073	
		N1-$H1_{H_2O}$	2.588	
		N2-$H2_{H_2O}$	2.654	
$CoCorH_2O^+$		Co-O_{H_2O}	2.304	
$CoCorH_2O$		Co-H_{H_2O}	2.218	
$CH_3Co(dmgBF_2)_2py$		Co-C_{CH_3}	2.033	2.007[b]
		Co-N_{py}	2.082	2.119[b]
$CH_3Co(dmgBF_2)_2py^-$		Co-C_{CH_3}	2.003	
		Co-N_{py}	2.269	
$CH_3Co(dmgBF_2)_2$		Co-C_{CH_3}	1.980	
$CH_3Co(dmgBF_2)_2^-$		Co-C_{CH_3}	2.001	
$Co(dmgBF_2)_2py$		Co-N_{py}	2.050	
$Co(dmgBF_2)_2py^-$		Co-N_{py}	1.993	
$CH_3Ni(PPh_2CH_2CH_2SEt)_2^+$	**MeVI**[e]	Ni-C_{CH_3}	1.981	
$CH_3Ni(Triphos)^+$		Ni-C_{CH_3}	1.975	1.963[c]

[a]Ref. [82]

[b]Ref. [19]

[c]Ref. [28]

[d]Numbering of atoms is presented in Fig. S1

[e]For the lowest energy conformer (Fig. 4 and Table S1)

data and theoretical calculation results [3, 48, 51, 62–64]. In the reduced base-off methylcobalamin with a water molecule as an axial ligand the water is coordinated to cobalt by the oxygen atom. The reduction of $CH_3Co(III)CorH_2O$ leads to a system with water linked by hydrogen bond to corrin nitrogens ($CH_3Co(II)CorH_2O$). In contrast to that, in the reduced methyl-free cobalt complex $CoCorH_2O$, the water molecule is bound by hydrogen bond to the cobalt atom (see Fig. 1 and Table 1). The existence of cobalt-water hydrogen bonding was predicted theoretically [64].

In the dimethylglyoxime complexes, the axial base coordinated to cobalt is pyridine (Fig. 2). The BP86 results reveal that upon reduction pyridine is not detached both in methylated and methyl-free complexes.

Nickel complexes

The structures of nickel complexes are depicted in Figs. 3, 4, 5, whereas methyl-nickel bond lengths and other selected optimized geometrical parameters are collected in Tables 1, S4, and S5.

For $Ni(PPh_2CH_2CH_2SEt)_2^{2+}$ a planar structure was obtained (Fig. 3, structure $\mathbf{I}^{2+}$) which is in agreement with the crystal structure [10, 15]. The one- and two-electron reduced complexes $\mathbf{I}^+$ and **I** are characterized by a distorted tetrahedral coordination (Fig. 3 and Table S3). For the two-electron reduced molecule $Ni(PPh_2CH_2CH_2SEt)_2$ which is a Ni(0) complex, the possibility of ligand dissociation was suggested [15]; hence, the calculations for three-coordinated

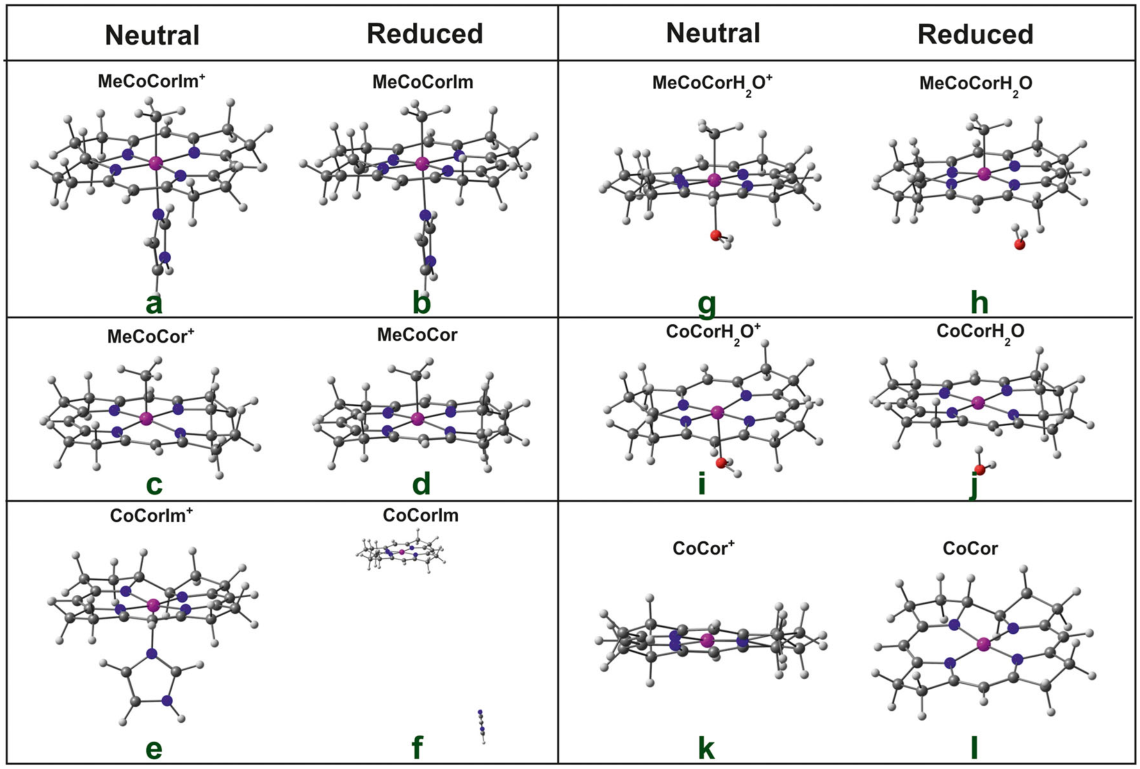

Fig. 1 The optimized structures of cobalamin complexes: **ab**, **cd**, **kl** reduction does not change the geometry of the complexes; **ef** – after reduction the imidazole ligand is detached; **gh** – after reduction the water ligand is bonded by hydrogen bond with nitrogen atoms of the corrin ring; **ij** – after reduction the water ligand is bonded by hydrogen bond with the cobalt atom

forms of the one- and two-electron reduced complexes were also performed (**II**$^+$-**III**$^+$ and **II-III**). **II** and **III** differ in the nickel coordination mode, in **II** nickel is coordinated by two phosphorus and one sulfur atom while in **III** by two sulfur and one phosphorus atom (Fig. 3 and Fig. S3). Optimized geometry reveals that the coordination of the nickel atom in two-electron reduced three-coordinate structures approximately corresponds to vertices of an almost equilateral triangle, while in the case of One-electron reduced two-coordinate phosphorus or sulfur atoms are almost linear (Fig. 3 and Table S3).

The computed energies (Fig. 3) show that the lowest energy complex is a four-coordinate one for both reduced states, **I**$^+$ and **I**. The three-coordinated complex with two phosphines (**II**) is 6.9 kcal/mol higher in energy (14.3 kcal with dispersion correction) than four-coordinate **I**. The three-coordinate complexes in which the nickel atom is coordinated by two sulfur atoms and one phosphorus are much higher in energy.

The methylated complex $CH_3Ni(PPh_2CH_2CH_2SEt)_2^+$ was examined in the form of five- and four-coordination structures. The obtained structures **MeI**–**MeVI** are shown in Fig. 4. These structures differ in mutual position of sulfur and phosphorus atoms and metal coordination number where **MeI** and **MeII** are five-coordinate and **MeII**–**MeVI** are four-coordinate. The lowest energy structure is **MeVI**, where nickel is coordinated by two phosphorus and one sulfur atoms and where sulfur is in trans position to the methyl group. BP86 functional gives five-coordinated structure, **MeII**, as a second one in energy (6.2 kcal/mol, and 1.6 kcal/mol higher with dispersion correction). Basing on the NMR spectra, the five-coordinated geometry is suggested [10]. Taking into account a small energy difference calculated with D3 correction, it is possible that sulfur ligands undergo very fast exchange process.

The nickel complexes with Triphos ligand are depicted in Fig. 5 and the optimized geometry parameters are gathered in Table S5. The Ni(Triphos)PPh_3 which is a Ni(0) complex has a distorted tetrahedral structure, which is in agreement with the crystal structure [28]. Similarly the distorted tetrahedral geometry was obtained for Ni(Triphos)PPh_3^+. The methyl derivative, CH_3Ni(Triphos)$^+$ which is a Ni(II) complex, has a planar structure, which is also in accordance with the experiment [28].

Methyl-metal bonding

The methyl binding energy in the investigated cobalt and nickel complexes was computed according to the formula:

$$E_B = \Delta E + ZPE + D3 + BSSE, \quad (4)$$

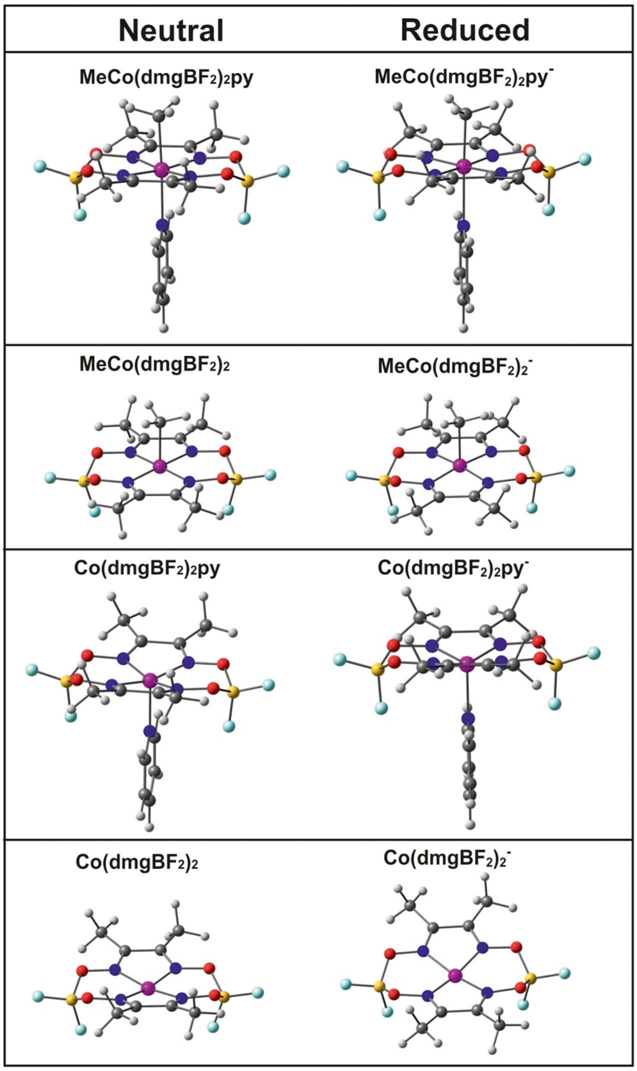

Fig. 2 The optimized structures of dimethylglyoxime cobalt complexes

where

$$\Delta E = E(CH_3) + E(ML) - E(CH_3 - ML),$$

and ML, ZPE, D3 and BSSE denote metal complex, zero point energy, dispersion correction and basis set superposition error correction, respectively.

The obtained results are collected in Table 2 with the experimental data for comparison, where available.

There were many theoretical studies in which Co-C binding energy was calculated [3, 32–35, 49–61, 64–74]. It was shown that gradient functional BP86 gives binding energy close to experimental, while the hybrid functionals significantly underestimate its value. The TPSS functional was found to perform well in binding energy calculations for adenosylcobalamin system [73, 74]. We use BP86 as it gives good results for E_B and reduction potentials as well, as shown further. As mentioned earlier our binding energy calculations for cobalamins are performed to have consistent data set of computational results allowing for systematic comparison between cobalt and nickel complexes. Inspection of data in Table 2 reveals that the binding energies without dispersion correction are generally underestimated. The good agreement of the BP86+D3 calculated binding energies for methylcobalamin and its reduced form with experimental data [59, 75] is also found in the present calculations. The BSSE error is rather small (about 1.5 kcal) and of similar value for all complexes studied.

From the data in Table 2, it can be noted that for the reduced cobalamins (**3** and **5**, Table 2), the methyl binding energy is smaller than in the case of oxidized ones. The mechanism of methyl dissociation in the reduced methylcobalamin was studied theoretically, and it was shown that the reduction occurs on the corrin ring [76]. When looking at the spin density values collected in Table 3, one can find that indeed the unpaired electron is localized on the corrin ring in the reduced methylcobalamin. Similar pattern emerges from the electron density difference plots shown in Fig. 6, where the largest values are found on corrin carbons in the reduced methylcobalamin base-on and base-off forms. As mentioned in the "Cobalt complexes" section, the reduced cobalamin occurs in the base-off form where the axial base is missing or replaced by a water molecule.

The results from the calculations show that for dimethylglyoxime cobalt complex with the axial pyridine ligand the Co-CH_3 bond energy is somewhat larger (about 3.5 kcal) than in methylcobalamin. After the reduction methyl binding energy decreases of about 10 kcal (to 33 kcal, Table 2). Unlike as in cobalamins, after reduction of Co$(dmgBF_2)_2$py, the pyridine ligand is not detached. When the pyridine ligand is missing (for **8** and **9**), the methyl-cobalt binding energy for the oxidized and reduced forms are very similar (about 40 kcal), which is also different than in the case of MeCbl. These differences can be explained by inspecting the spin densities of the reduced cobalt complexes gathered in Table 3. The spin densities in reduced glyoximate complexes show that reduction occurs partially on the dimetyloglyoxime ligand and partially on cobalt atom, which is in contrast to cobalamins, where it occurs solely on corrin. This can be traced to more negatively charged cobaloxime than corrin ring (−2 vs. −1). This is also visible in Fig. 6 where pronounced values of electron density differences are present on cobalt and methyl. The calculated methyl binding energy in **6** from Table 2 (42 kcal) is larger than measured for CH_3Co$(dmgh)_2$py [52] amounting to 33.1 kcal; on the other hand, it is close to calculated value of 41.06 kcal for CH_3Co$(dmgH)_2NH_3$ [77] and 40.7 kcal for CH_3Co$(dmgH)_2NHCH_2$ [68].

For the nickel complex with the $PPh_2CH_2CH_2$SEt ligand, the methyl binding energy is given only for the lowest energy conformer (**MeVI** in Fig. 3 and in Table S1),

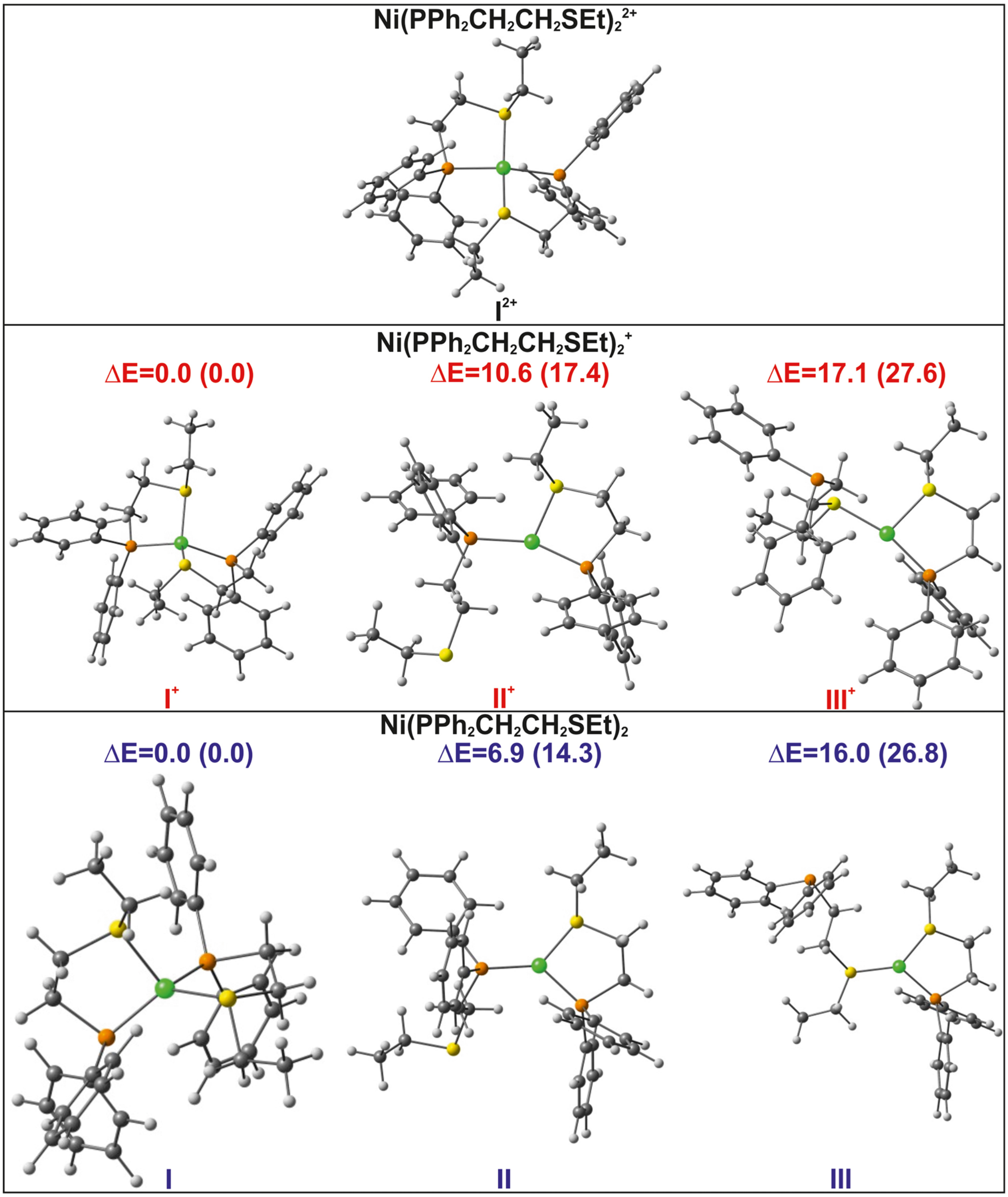

Fig. 3 The optimized structures of nickel complexes with $PPh_2CH_2CH_2SEt$ ligand. ΔE (in kcal/mol) denotes relative energy obtained from BP86 optimization, in parentheses the G3 correction is taken into account

and it amounts to 50.1 kcal/mol. The Ni-CH_3 bond energy calculated for the $CH_3Ni(Triphos)^+$ complex is 52.3 kcal/mol and is the largest among all calculated E_B values. To the best of our knowledge, the nickel–methyl binding energies were not determined experimentally. For both nickel complexes, the calculated methyl binding energies are larger than those for cobalt cobaloximes and cobalamins. This accounts for the fact that the methyl is transferred from cobalt to nickel complex.

In Table 4, the NBO bonding analysis for metal-methyl bond is given for cobalt and nickel complexes. Concerning the cobalt complexes it can be seen that the bonding σ_{Co-CH_3} orbital has approximately equal percentage participation of cobalt and carbon hybridized atomic orbitals (between 47% and 53%). The larger deviation is for $CH_3Co(dmgBF_2)_2$ with 43% and 57% cobalt and carbon orbital participation, respectively. For nickel complexes, the metal contribution to the bonding orbital amounts to 35%

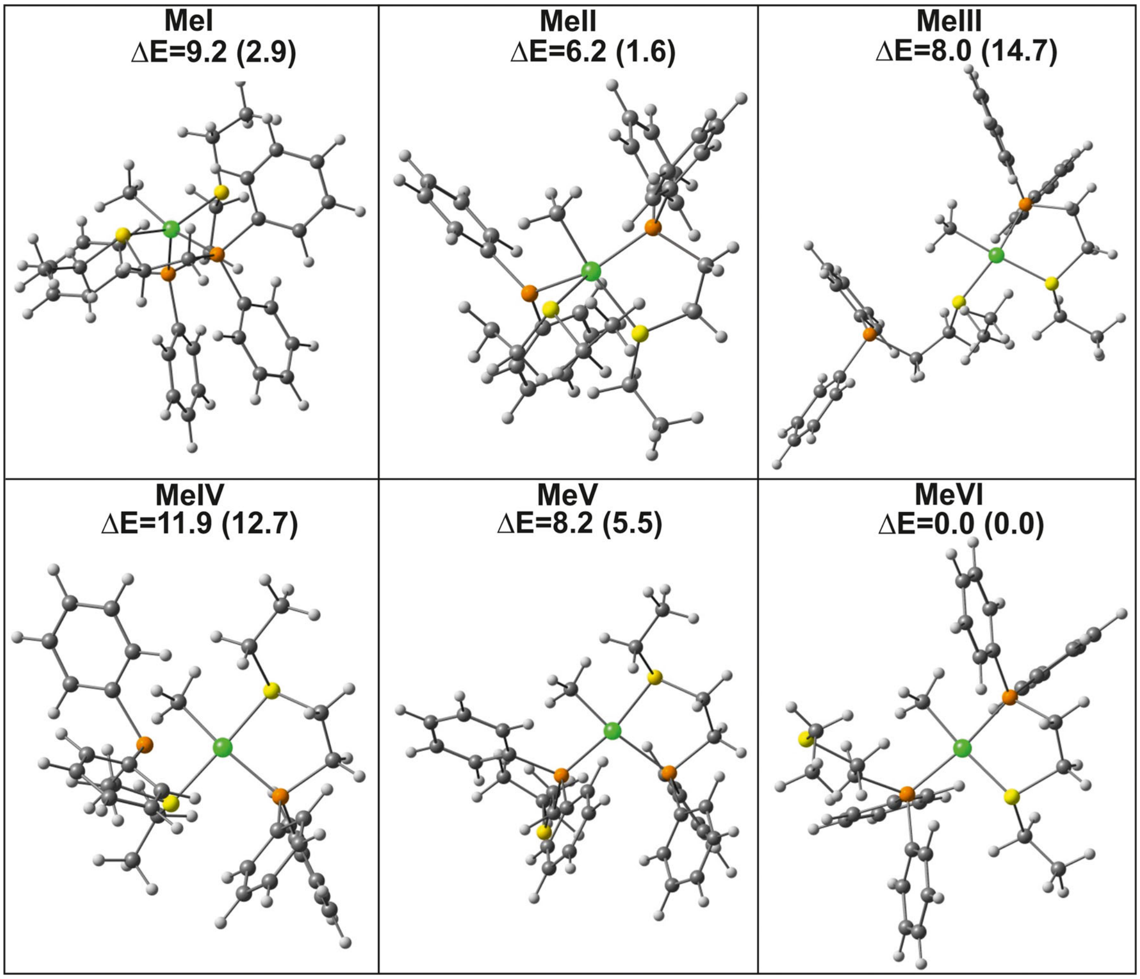

Fig. 4 The optimized structures of methyl-nickel $CH_3Ni(PPh_2CH_2CH_2SEt)_2^+$ complex. ΔE (in kcal/mol) denotes relative energy obtained from BP86 optimization, in parentheses the G3 correction is taken into account

and carbon to 65%. Thus, some ionic character in Ni–CH_3 bonding can be inferred with participation of formally CH_3^- ion. In turn, the cobalt–methyl bond can be viewed as basically covalent.

In Table S5, NBO charges are collected for methyl-nickel and methyl-cobalt complexes. For cobalt complexes, the charge on the metal and the methyl group is positive, except for the reduced base-on glyoxime complex, where the metal is negative. The charge on metal and methyl in reduced and non-reduced cobalamin complexes is practically the same, indicating that the reduction occurs predominantly on the corrin ring. On the other hand, metal and methyl group are both more negative in the cobalt glyoximate reduced complexes. This corroborates with data in Table 3 and confirms the different behaviors of glyoximate and corrinate cobalt-methyl complexes upon reduction. These differences are due to the charge of the macrocyclic ligand, minus one for corrin and minus two for glyoxime, so the corrin ligand can accept a larger charge as a result of the reduction. In turn, in the methyl nickel complexes, the methyl group and nickel have negative charges.

Redox potentials

Redox potentials were calculated according to the equation:

$$E_{redox} = E(M^{n+1})_{sol} - E(M^{n})_{sol} - 4.34(SHE) \qquad (5)$$

The value of standard hydrogen electrode potential was taken from [78]. The obtained results are summarized in Table 5 and compared with experimental data. Because redox potentials were measured with the use of different reference electrodes, we converted all values to the standard hydrogen electrode (SHE). There were several measurements of redox potentials for various cobalamin forms [72, 75, 79–81]. The cobalamin redox potentials were also calculated theoretically [56, 64]. The calculations performed with BP86 functional show that it gives good

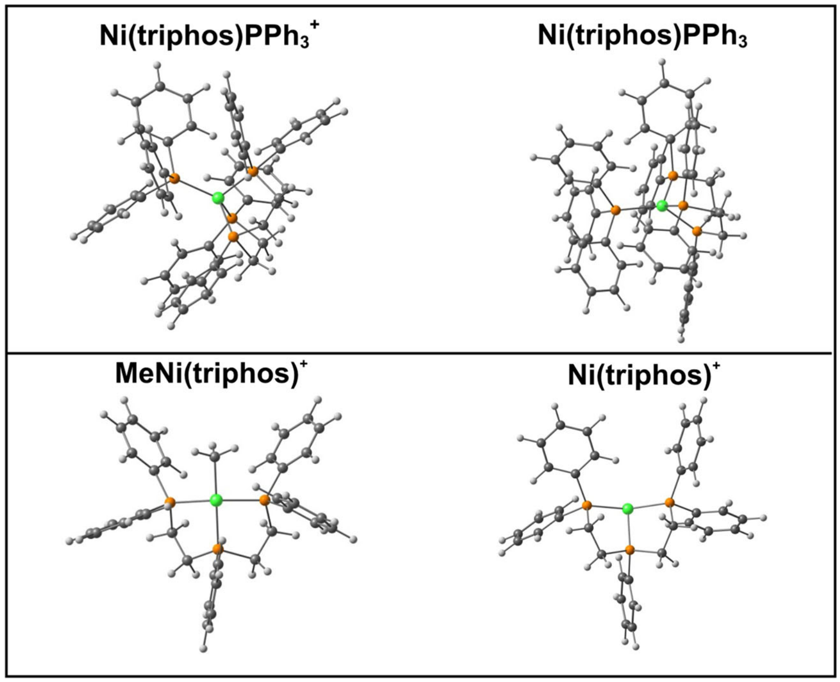

Fig. 5 The structure of Ni(Triphos) complexes

results for redox potentials of transition metal complexes [36–38].

Generally, it can be noted (Table 5) that the BP86 calculated redox potentials are in good agreement with the experimental data (maximum difference up to 0.2 eV). From the results it can be seen that for base-off cobalamins the redox potentials are more positive that for the base-on ones. For cobaloxime complexes, calculated values of redox potentials are significantly more positive in comparison with similar forms of cobalamin complexes.

In regard to the reactions (2) and (3), there may be S_N2 or radical mechanisms involved, the latter one with electron transfer from the nickel complex to methylcobalamin or methyl derivative of cobalt dimethylglyoximate. Looking

Table 2 Methyl binding energy E_B (kcal/mol)

	Molecule	ΔE+ZPE	ΔE+ZPE +D3	ΔE+ZPE +D3+BSSE	Exp.
1	$CH_3CoCorIm^+$	30.4	40.0	38.7	37±3[a], 36±4[b], 39 ± 5[c]
2	CH_3CoCor^+	34.9	44.4	43.0	
3	CH_3CoCor	13.0	21.7	20.2	
4	$CH_3CoCorH_2O^+$	32.1	41.4	40.0	44.6[d], 42 ± 5[c]
5	$CH_3CoCorH_2O$	9.6	19.8	18.4	19.0[e]
6	$CH_3Co(dmgBF_2)_2py$	33.8	43.5	42.2	33.1[f]
7	$CH_3Co(dmgBF_2)_2py^-$	19.0	34.4	33.0	
8	$CH_3Co(dmgBF_2)_2$	32.5	41.1	39.7	
9	$CH_3Co(dmgBF_2)_2^-$	31.5	39.7	38.1	
10	$CH_3Ni(PPh_2CH_2CH_2SEt)_2^{+}$[g]	40.0	51.8	50.1	
11	$CH_3Ni(Triphos)^+$	44.5	54.6	52.9	

[a]Ref. [60]
[b]Ref. [83]
[c]Ref. [84]
[a]Gas phase, Ref. [61]
[e]Ref. [75]
[f]For $CH_3(dmgH)_2py$, Ref. [52]
[g]For the lowest energy conformer **MeVI** (Fig. 4 and Table S1)

Table 3 Spin densities in the reduced cobalamin and dimethylglyoxime cobalt complexes

	Co	Cor	CH_3
$CH_3CoCorIm$	−0.052	−0.949	0.003
CH_3CoCor	−0, 046	−0.958	0.004
$CH_3CoCorH_2O$	−0.048	−0.944	0.004
	Co	$(dmgBF_2)_2$	CH_3
$CH_3Co(dmgBF_2)_2py^-$	−0.300	−0.644	0.023
$CH_3Co(dmgBF_2)_2^-$	−0.333	−0.590	−0.077

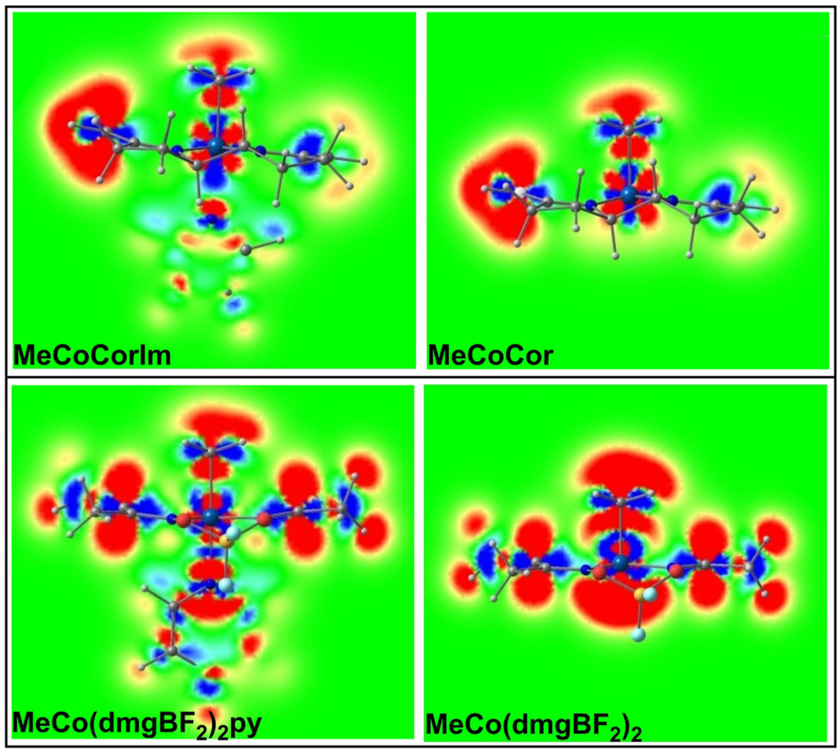

Fig. 6 Cross-sectional contours along the axial bonding for electron density difference between the oxidized and reduced form of selected cobalamin and dimethylglyoxime cobalt complexes, contour values between − 0.001 a.u (blue) and 0.001 a.u. (red)

Table 4 NBO analysis of axial bonds for cobalamin and dimethylglyoxime cobalt complexes (the hybridization of the atoms is indicated with the percent contribution of the metal-centered *d* or (and) *p* orbitals as a superscript, LP denotes an electron lone pair)

NBO	Occupancy	
$CH_3CoCorIm^+$		
$\sigma_{Co-C_{CH_3}}$	1.8093	$[47\%]0.6848(sp^{13.19}d^{54.29})_{Co} + [53\%]0.7287(sp^{81.11})_C$
$\sigma^*_{Co-C_{CH_3}}$	0.1326	$[53\%]0.7287(sp^{13.19}d^{54.29})_{Co} - [47\%]0.6848(sp^{81.11})_C$
$LP(N_{Im})$	1.6858	$sp^{62.99}$
$CH_3CoCorH_2O^+$		
$\sigma_{Co-C_{CH_3}}$	1.8167	$[49\%]0.7033(sp^{8.29}d^{57.87})_{Co} + [51\%]0.7109(sp^{82.37})_C$
$\sigma^*_{Co-C_{CH_3}}$	0.1161	$[51\%]0.7109(sp^{8.29}d^{57.87})_{Co} - [49\%]0.7033(sp^{82.37})_C$
$LP(O_{H_2O})$	1.9908	$sp^{69.75}$
$LP(O_{H_2O})$	1.8715	$sp^{76.39}$
CH_3CoCor^+		
$\sigma_{Co-C_{CH_3}}$	1.8258	$[51\%]0.7176(sp^{4.43}d^{60.81})_{Co} + [49\%]0.6965(sp^{83.72})_C$
$\sigma^*_{Co-C_{CH_3}}$	0.1245	$[49\%]0.6965(sp^{4.43}d^{60.81})_{Co} - [51\%]0.7176(sp^{83.72})_C$

Table 4 (continued)

NBO	Occupancy	
$CH_3Co(dmgBF_2)_2py$		
$\sigma_{Co-C_{CH_3}}$	1.6952	$[43\%]0.6594(sp^{45.18}d^{38.00})_{Co} + [57\%]0.7518(sp^{81.67})_C$
$\sigma_{Co-N_{py}}$	1.8863	$[17\%]0.4147(sp^{54.68}d^{29.42})_{Co} + [83\%]0.9099(sp^{71.82})_N$
$\sigma^*_{Co-C_{CH_3}}$	0.0805	$[57\%]0.7518(sp^{45.18}d^{38.00})_{Co} - [43\%]0.6594(sp^{81.67})_C$
$\sigma^*_{Co-N_{py}}$	0.1686	$[83\%]0.9099(sp^{54.68}d^{29.42})_{Co} - [17\%]0.4147(sp^{71.82})_N$
$CH_3Co(dmgBF_2)_2$		
$\sigma_{Co-C_{CH_3}}$	1.8241	$[52\%]0.7203(sp^{5.13}d^{61.09})_{Co} + [48\%]0.6936(sp^{84.94})_C$
$\sigma^*_{Co-C_{CH_3}}$	0.0691	$[48\%]0.6936(sp^{5.13}d^{61.09})_{Co} - [52\%]0.7203(sp^{84.94})_C$
$CH_3Ni(PPh_2CH_2CH_2SEt)_2^{+a}$		
$\sigma_{Ni-C_{CH_3}}$	1.7679	$[35\%]0.5907(sp^{42.99}d^{34.48})_{Ni} + [65\%]0.8069(sp^{79.18})_C$
$\sigma_{Ni-S_{trans}}$	1.9082	$[20\%]0.4481(sp^{56.68}d^{22.53})_{Ni} + [80\%]0.8940(sp^{80.19})_S$
$\sigma^*_{Ni-C_{CH_3}}$	0.1237	$[65\%]0.8069(sp^{42.99}d^{34.48})_{Ni} - [35\%]0.5907(sp^{79.18})_C$
$\sigma^*_{Ni-S_{trans}}$	0.1295	$[80\%]0.8940(sp^{56.68}d^{22.53})_{Ni} - [20\%]0.4481(sp^{80.19})_S$
$CH_3Ni(Triphos)^+$		
$\sigma_{Ni-C_{CH_3}}$	1.7856	$[35\%]0.5894(sp^{42.73}d^{33.16})_{Ni} + [65\%]0.8078(sp^{79.23})_C$
$\sigma_{Ni-P_{trans}}$	1.8443	$[28\%]0.5258(sp^{57.18}d^{22.48})_{Ni} + [72\%]0.8506(sp^{70.42})_P$
$\sigma^*_{Ni-C_{CH_3}}$	0.1290	$[65\%]0.8078(sp^{42.73}d^{33.16})_{Ni} - [35\%]0.5894(sp^{79.23})_C$
$\sigma^*_{Ni-P_{trans}}$	0.1311	$[72\%]0.8506(sp^{57.18}d^{22.48})_{Ni} - [28\%]0.5258(sp^{70.42})_P$

[a]For the lowest energy conformer (**MeVI**, Fig. 4 and Table S1)

Table 5 Redox potentials E_{redox} (V)

		Calculated	Exp.	**SHE**	ΔE_0^a
$CH_3CoCorIm^+/CH_3CoCorIm$		− 1.58	− 1.60[b,f]	− 1.36	(− 0.22)
CH_3CoCor^+/CH_3CoCor		− 1.41	− 1.45[b,g]	− 1.21	(− 0.20)
$CoCorIm^+/CoCorIm$		− 0.78	− 0.85[b,g]	− 0.61	(− 0.17)
$CH_3CoCorH_2O^+/CH_3CoCorH_2O$		− 1.40			
$CoCorH_2O^+/CoCorH_2O$		− 0.36	− 0.74[b,g]	− 0.50	(0.14)
$CoCor^+/CoCor$		− 0.38			
$CH_3Co(dmgBF_2)_2py/CH_3Co(dmgBF_2)_2py^-$		− 0.99	− 1.10[c,h]	− 1.10	(0.11)
$CH_3Co(dmgBF_2)_2/CH_3Co(dmgBF_2)_2^-$		− 0.15			
$Co(dmgBF_2)_2py/Co(dmgBF_2)_2py^-$		− 0.14			
$Co(dmgBF_2)_2/Co(dmgBF_2)_2^-$		− 0.08	− 0.55[b,j]	− 0.31	(0.23)
$Ni(PPh_2CH_2CH_2SEt)_2^{2+}/Ni(PPh_2CH_2CH_2SEt)_2^+$		0.01	− 0.56[d,i]	− 0.02	(0.03)
$Ni(PPh_2CH_2CH_2SEt)_2^+$/ $Ni(PPh_2CH_2CH_2SEt)_2$	**I**[e]	− 0.65	− 1.14[d,i]	− 0.60	(− 0.05)
$Ni(Triphos)PPh_3^+$/ $Ni(Triphos)PPh_3$		− 0.30	− 0.10[c,h]	− 0.10	(− 0.20)

[a] $\Delta E_0 = E_0^{calc} - E_0^{SHE}$

[b]SCE = the standard calomel electrode

[c]SHE = the standard hydrogen electrode

[d] $Ag/AgNO_3$ = the standard silver electrode

[e]For the lowest energy conformers (Table S1)

[f]Ref. [72]

[g]Ref. [79]

[h]Ref. [28]

[i]Ref. [10]

[j]Ref. [85]

at the calculated reduction potentials of these complexes in Table 5, one can see that the reduction potentials of nickel complexes are in most cases much higher than for the base-on and base-off cobalamins and higher than for the methyl-cobalt dimethylglyoxime complexes with a pyridine ligand (base-on). This makes the radical reductive mechanism unlikely. On the other hand, the reduction potential of methyl cobalt glyoximate without pyridyne (base-off) is significantly higher than that for the base-on, contrary than in cobalamnis. Thus, the radical-reductive mechanism in principle could be possible for base-off glyoximate. This is probably not the case, because a pyridine or solvent molecule is attached to the cobalt atom in glyoximate complexes.

Conclusions

Several cobalt and nickel complexes involved in the methyl transfer reactions were examined with the DFT method using BP86 functional. The geometries, methyl binding energies and redox potentials of all the species were studied. For reduced cobalamins axial base undergo dissociation, which is consistent with experiment. In the base-off forms with water as an axial ligand, water molecule is linked by hydrogen bond to corrin nitrogen ($CH_3CoCorH_2O$). In methyl-free cobalamin ($CoCorH_2O$), the water molecule forms a hydrogen bond with cobalt atom.

Experimentally the five-coordinate structure for methylated nickel complex with $PPh_2CH_2CH_2SEt$ ligand is suggested. Our calculations give small energy difference between five- and four-coordinate forms (1.6 kcal) which may imply fast interconversion between them.

There are noticeable differences in geometry, Co-CH_3 binding energies and redox potentials between cobalamin and dimethylglyoxime complexes, which indicates that chemical properties of these two systems are different. On the basis of the experimental redox potentials (−1.1 for $CH_3Co(dmgBF_2)_2py/CH_3Co(dmgBF_2)_2py^-$ redox couple and −0.1 for $Ni(Triphos)PPh_3^+/Ni(Triphos)PPh_3$), it was suggested that the reaction (2) takes place according to the S_N2 mechanism [28]. In the case of radical mechanism reduction of $CH_3Co(dmgBF_2)_2py$ by $Ni(Triphos)PPh_3$ would be required. Our calculated redox potentials confirm such a statement, the calculated redox potential are equal to −0.99 V and −0.3 V, respectively.

Reaction (2) is fast [28] which can be attributed to the fact that the binding energy of methyl in the $CH_3Ni(Triphos)^+$ complex is about 10 kcal/mol higher than in the $CH_3Co(dmgBF_2)_2py$ complex.

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Compliance with ethical standards This study complied with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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