o-Semiquinonic PCP-pincer nickel complexes with alkyl substituents: versatile coordination sphere dynamics[†]

Konstantin A. Kozhanov,^{*a} Michael P. Bubnov,^a Vladimir K. Cherkasov,^a Nina N. Vavilina,^a Larisa Yu. Efremova,^a Oleg. I. Artyushin,^b Irina L. Odinets^b and Gleb A. Abakumov^a

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o-Semiquinonic nickel pincer complexes (R₂PCP)Ni(SQ) show a versatile coordination sphere dynamics *via* "swing" or "fan" oscillations depending on the steric properties of the phosphorus substituents.

Introduction

Pincer complexes have been of a great interest in recent decades. Being fine catalysts of certain reactions they have an excellent chemical stability.¹

Previously we have reported a number of spin-labeled *o*-semiquinonic nickel complexes with diphenylphosphine pincer ligands.² An unusual structural isomerisation of these complexes *via* unique "swing" oscillation has been reported (Scheme 1).²



Scheme 1 Structural isomerism of *o*-semiquinonic PCP-pincer nickel complexes.

Since the coordination sphere rearrangements play the certain role in the catalytic processes, the studies of the factors having an effect on the coordination sphere dynamics deserve consideration.

In present work we have obtained and thoroughly investigated a number of new *o*-semiquinonic pincer complexes (R_2PCP)Ni(SQ), where R = t-Bu, *i*-Pr or *cyclo*-C₆H₁₁ (Cy), and SQ = 3,6- or 3,5- di-*tert*-butyl-*o*-benzosemiquinone.



^aG. A. Razuvaev Institute of Organometallic Chemistry of Russian Academy of Sciences, Tropinina str., 49, Nizhny Novgorod, 603950, Russia. E-mail: kostik@iomc.ras.ru; Fax: +7(831)4627497; Tel: +7(831)4627682 ^bA. N. Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences, Vavilova str. 28, 119991, Moscow, Russia. E-mail: odinets@ineos.ac.ru; Fax: 7(495)1355085

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Experimental

Materials and methods

Starting materials are commercially available (Aldrich, Dalchem, Strem) and were used without purification unless otherwise noted. The quinones and 1,5-bis(bromomethyl)-2,4-dimethylbenzene were obtained according to known procedures.^{3,4} (DME)NiBr₂ was prepared by reaction of Ni powder with Br₂ in dimethoxyethane.⁵ All synthetic procedures were carried out in evacuated ampoules using freshly purified solvents⁶ (except 95% aqueous ethanol which was used as received).

¹H and ³¹P NMR spectra were obtained on a "Bruker" DPX-200 spectrometer (200 MHz, CDCl₃, δ /ppm). EPR spectra were recorded on Bruker EMX spectrometer, operating in X-band (working frequency ~9.6 GHz) and equipped with an NMRgaussmeter and variable-temperature unit. HFC constants and *g*factor values were obtained by simulation in WINEPR SimFonia (v. 1.25).

Molecular modelling was provided using "Hyperchem 8.0" software. The molecular mechanics "MM+" method with "bonds dipoles" options and all of force field components using the "Fletcher–Reeves" algorithm was applied for geometry optimization.

Synthetic procedures

2,6-Bis(dialkylphosphinomethyl)arylbromonickel complexes (R_2PCP)NiBr were obtained by metallation using (DME)NiBr₂⁷ of the corresponding PCP-ligands. The latter were in turn obtained by dialkylphosphine addition to the corresponding 2,6-bis(bromomethyl)arene followed by dehydrobromination of the intermediate phosphonium salt formed.⁷ Thallium *o*-benzosemiquinonates Tl(SQ) were obtained by reaction of the corresponding *o*-benzoquinones with the thallium amalgam⁸ and were used *in situ*.

o-Semiquinonic nickel pincer complexes 1a-b, 2a-b, 3b

To THF solution of 1 eq. of $(R_2PCP)NiBr$ a solution of 1 eq. of Tl(SQ) was added. The mixture was kept for 30 min, and THF was replaced by toluene. After completion of the reaction (1–2 week, monitored by EPR) the solution was filtered. Complex **1a** was isolated from hexane as greenish-brown needles (32% yield), while other complexes were investigated without isolation.

spectra for investigated complexes
spectra for investigated complexe

Complex	T/K		Hyperfine coupling constants/	G
		$g_{ m i}$	³¹ P	SQ back proton
1a	320	2.0071	$a_{\rm P1} = a_{\rm P2} = 21.7$	a
	210	2.0071	$a_{\rm P1} = 27.8, a_{\rm P2} = 14.7$	$a_{\rm H1} = 3.6, a_{\rm H2} = 2.2$
1b	320	2.0054	$a_{\rm P1} = a_{\rm P2} = 17.9$	
	220	2.0054	$a_{\rm P1} = 22.7, a_{\rm P2} = 13.4$	$a_{\rm H} = 2.5$
2a	300	2.0055	$a_{\rm P1} = a_{\rm P2} = 19.8$	$a_{\rm H1} = a_{\rm H2} = 2.8$
	190	2.0054	$a_{\rm P1} = 25.3, a_{\rm P2} = 15.7$	$a_{\rm H1} = 3.8, a_{\rm H2} = 2.2$
2b	290	2.0054	$a_{\rm P1} = a_{\rm P2} = 16.6$	$a_{\rm H} = 2.7$
	200 (isomer 1)	2.0043	$a_{\rm P1} = a_{\rm P2} = 14.4$	$a_{\rm H} = 2.2$
	200 (isomer 2)	2.0054	$a_{\rm P1} = 22.2, a_{\rm P2} = 14.2$	$a_{\rm H} = 2.5$
3b	300	2.0062	$a_{\rm P1} = a_{\rm P2} = 17.0$	$a_{\rm H} = 2.5$
4a	290	2.0060	$a_{\rm P1} = a_{\rm P2} = 24.2$	$a_{\rm H1} = a_{\rm H2} = 2.8$
	180	2.0056	$a_{\rm P1} = a_{\rm P2} = 25.6$	$a_{\rm H1} = 3.4, a_{\rm H2} = 2.2$
4b	330	2.0052	$a_{\rm P1} = a_{\rm P2} = 20.3$	$a_{\rm H} = 2.6$
	200 (isomer 1)	2.0064	$a_{\rm P1} = a_{\rm P2} = 18.4$	$a_{\rm H} = 2.4$
	200 (isomer 2)	2.0041	$a_{\rm P1} = a_{\rm P2} = 24.4$	$a_{\rm H} = 3.4$

Results and discussion

The reactivity of initial (R_2PCP)NiBr towards Tl(SQ) is much lower in comparison with the earlier studied (Ph_2PCP)NiBr.² Moreover, complex **3b** is unstable§ and complex **3a** is not formed. This fact is in a good agreement with steric protection of the metal centre.⁹

Surprisingly, the temperature dependence of the EPR spectrum of **1a** (Fig. 1, Table 1) drastically differs from that for **4a**.² So, while at low temperatures **4a** demonstrates hyperfine splitting on two equivalent phosphorus nuclei $(a_{P1} = a_{P2} = 25.6 \text{ G})$, for **1a** the phosphorus nuclei are not equivalent $(a_{P1} = 27.8 \text{ G}, a_{P2} = 14.7 \text{ G})$. Moreover, with increasing temperature, nonequivalent semiquinonic proton HFC constants for **4a** $(a_{H1} = 3.4 \text{ G}, a_{H2} = 14.7 \text{ G})$.



Fig. 1 EPR spectra of 1a

 \S Full decomposition of $\mathbf{3b}$ occurred during two months after synthesis in solution at r.t.

2.2 G) become averaged ($a_{H1} = a_{H2} = 2.8$ G) due to fast tautomeric interconversion. In the case of 1a these protonic HFC constants remain unchanged with temperature (210-280 K), but the phosphorus constants become averaged in the temperature range 210-320 K. In general, the size of HFC constants of the magnetic nucleus of the ligand (³¹P) bonded to the metal-o-semiquinone fragment arises from two mechanisms:10 spin polarization of σ bonds O-Ni-P and direct interaction of the Ni-P orbital with π^* orbital of the semiguinone containing unpaired electron. The second path is more effective and in the case of pincer-osemiquinonato-nickel complexes it determines the phosphorus splitting constants. As the consequence this value is very sensitive to geometrical features and particularly to the angle between the Ni-P axis and the o-semiquinonic plane¹¹ (particularly to the normal to this plane). For complex 1a EPR structural perturbations can be explained by "fan" oscillations (Scheme 2) without "swing" oscillation (Scheme 1). In fact, different phosphorus splitting constants are the consequence of different positions of phosphorus nuclei relative to o-semiquinonic ring. Rapid "fan" oscillations result in averaged phosphorus splitting constants. Decreasing of temperature slows down interconversion and both phosphorus nuclei can be observed separately.



Scheme 2 "Fan" oscillation in 1a.

The same is true for complex **1b**. In its EPR spectrum at low temperatures (Fig. 2, Table 1) only one signal with nonequivalent phosphorus atoms is observed ($a_{\rm H} = 2.5$ G, $a_{\rm P1} = 22.7$ G, $a_{\rm P2} = 13.4$ G) whereas for its analog² **4b** a superposition of two spectra is observed ($a_{\rm H} = 2.4$ G, $a_{\rm P1} = a_{\rm P2} = 18.4$ G and $a_{\rm H} = 3.4$ G, $a_{\rm P1} = a_{\rm P2} = 24.4$ G) indicating the presence of two structural isomers. The temperature dependence of the spectrum of **1b** (Fig. 2) is similar to that for **1a** (Fig. 1).



Fig. 2 EPR spectrum of 1b.

It should be noted that the central component of the phosphorus triplet in the high-temperature spectra of **1a** and **1b** is broadened. Such broadening is caused by a fast interconversion process (on the EPR time scale) and can be described by eqn (1) (with regard to equal concentration of interconverting tautomers):¹²

$$\Delta \Gamma = \gamma_{\rm e} \tau (\delta H)^2 / 4 \tag{1}$$

where γ_e is the electron magnetogyric ratio, τ is the reduced lifetime of exchanging particles, δH is root-mean-square field difference between exchanging lines. In our case the outer components of the phosphorus triplet are not broadened due to interconvertion, so $\Delta \Gamma$ is the difference between line widths of the central and the outer components. So it is possible to calculate the tautomer lifetime ($t = 2\tau$ with regard to equal life times of the interconverting tautomers) at different temperatures and, correspondingly, activation parameters (ΔH^{\ddagger} and ΔS^{\ddagger}) of the interconversion reaction (eqn (2)):²

$$1/t = (k_{\rm B}T/h)\exp(\Delta S^{\ddagger}/R)\exp(\Delta H^{\ddagger}/RT)$$
(2)

where $k_{\rm B}$, *h* and *R* are the Boltzmann, Planck and absolute gas constants, respectively. After linearization and linear regression analysis (ESI[†]) the following values were obtained: for **1a**: $\Delta H^{\ddagger} =$ 53 ± 7 kJ mol⁻¹, $\Delta S^{\ddagger} = 79 \pm 14$ J mol⁻¹ K⁻¹, for **1b** $\Delta H^{\ddagger} =$ 40 ± 6 kJ mol⁻¹, $\Delta S^{\ddagger} = 46 \pm 7$ J mol⁻¹ K⁻¹. These values are quite different from earlier obtained ones for "swing" motion of **4b** molecules: $\Delta H^{\ddagger} = 16.1 \pm 0.8$ kJ mol⁻¹, $\Delta S^{\ddagger} = -33.2 \pm 2.0$ J mol⁻¹ K⁻¹ for direct reaction and $\Delta H^{\ddagger} = 15.9 \pm 0.8$ kJ mol⁻¹, $\Delta S^{\ddagger} =$ -28.3 ± 2.0 J mol⁻¹ K⁻¹ for reverse reaction.² This can serve as an additional evidence for different interconversion mechanisms for **1a** and **1b** in comparison with **4a** and **4b**.

In the case of **2a** and **2b** the coordination sphere dynamics is more complicated. In the EPR spectrum of **2a** at low temperature (Fig. 3, Table 1) hyperfine splitting on two nonequivalent phosphorus atoms ($a_{P1} = 25.3$ G, $a_{P2} = 15.7$ G) and two nonequivalent



Fig. 3 EPR spectrum of 2a.

protons ($a_{H1} = 3.8$ G, $a_{H2} = 2.2$ G) is observed. With an increase in temperature the averaging of phosphorus constants in observed (as for 1a), but the same process is observed also for the protonic constants (as for 4a) indicating that both "swing" and "fan" oscillations take place (Scheme 3).



Scheme 3 "Swing" and "fan" motions for 2a (schematic view along the basal O–Ni–C direction).

A similar transformation of the EPR spectrum is observed for **2b** (Fig. 4, Table 1). At low temperature the superposition of two spectra is observed indicating the coexistence of two structural isomers: one with equivalent and another one with nonequivalent phosphorus nuclei (isomer 1: $a_{P1} = a_{P2} = 14.4$ G, $a_H = 2.2$ G; isomer 2: $a_{P1} = 22.2$ G, $a_{P2} = 14.2$ G, $a_H = 2.5$ G). The temperature increase leads to averaging of the central part of the spectrum (Fig. 4). Conclusions made for **4b**² allow to attribute each low-temperature spectrum to each structural isomer (Scheme 4). "Swing" oscillation is responsible for interconversion of isomers. The presence of two spectra (both isomers) at low temperature means that "swing" oscillation occurs. At the same time nonequivalence of phosphorus in isomer 2 reflects a "sloped" conformation and averaging of the spectrum indicates the presence of "fan" oscillations for isomer 2. Equivalence of the phosphorus



Fig. 4 EPR spectrum of **2b** (A) and simulated spectrum for the 170 K spectra of separate isomers and their sum (B).



Scheme 4 "Swing" and "fan" motions for 2b

nuclei in isomer 1 corresponds to an orthogonal configuration of ligand planes without "fan" oscillation. Complex **2b** thus exists as a mixture of two isomers, interconverting through a "swing"

oscillation; but only one of isomers exists as a mixture of two tautomers which interconvert through a "fan" oscillation.

Absence of "fan" oscillation for isomer 1 can be explained by steric reasons, particularly relatively small *i*-Pr substituents at the phosphorus atom together with the absence of *tert*-Bu groups in *ortho*-position to oxygen *trans*- to the Ni–C bond.

Unfortunately, the complicated character of molecular dynamics of **2a** and **2b** leads to transformation of all the central part of the EPR spectra upon temperature change making it impossible to separate the individual processes and hence evaluation of the activation parameters of the two different tautomeric interconversions.

Finally, in the case of **3b** no considerable perturbations in the EPR spectrum upon temperature change were observed. Moreover, the phosphorus HFC constants remain unchanged with temperature ($a_{P1} = a_{P2} = 17.0$ G, $a_{H} = 2.5$ G). Neither "fan" nor "swing" movements in the metal coordination sphere appear to operate, and the *o*-semiquinonic ring occupies an orthogonal position relative to the pincer fragment, as in complexes **4a–b**.²

Thus, two conformations of the complexes (R_2PCP)Ni(SQ) are possible: with "sloped" (**1a–b**, **2a–b**) and orthogonal (**3b**, **4a– b**) positions of *o*-semiquinonic and pincer fragments relative to each other. Such difference cannot be described only in terms of the substituent bulkiness. Most probably, the difference in configuration of chelate fragments is a result of axial asymmetry of *i*-Pr and Cy-substituents along the C–P-bond (in contrast to Ph and *t*-Bu). Asymmetry leads to concerted rotation of both substituents at the phosphorus atom and consequently appearance of local energy minima.

In order to investigate the driving force of forming of the "sloped" configuration which results in the "fan" type of motion we made some structural calculations for **1a**, **2a**, **2b** and **4a** in the molecular model system "HyperChem 8.0" (see ESI†). Geometry optimization of molecules of **1a**, **2a** and isomer 2 of **2b** leads to "sloped" configuration in contrast to **4a** and isomer 1 of **2b** which have geometries close to orthogonal. Table 2 presents the resulting O–Ni–P angles of the inner coordination core of the geometry optimized molecules. These angles determine the HFC constants in the EPR spectra.

Thus, results of the modelling are in a good agreement with EPR data and our suggestions about the structure of these complexes.

On the contrary, the "swing" oscillations ability is in good agreement with the steric considerations.⁹ So, complexes **4a–b** and **2a–b** having small substituents at phosphorus atoms reveal this dynamics, whereas **1a–b** and **3b** do not.

Conclusions

A new type of coordination sphere dynamics have been observed. Some spin-labeled *o*-semiquinonato-pincer nickel complexes possess "fan" additionally to "swing" oscillations of the *o*-semiquinone fragment relative to the pincer ligand. "Fan" oscillations are proposed to be connected with axial asymmetry of substituents at the phosphorus atoms in the pincer ligand. "Swing" oscillations occur when the substituents at the phosphorus atom are relatively small. Additionally, an unusual case was observed: one of structural isomers of complex bearing *i*-Pr substituents at the phosphorus atom shows "fan" oscillations of the ligands whereas the other one do not.

Complex	Energy/kcal mol ⁻¹	Angles/°				
		P1–Ni–O1 ^b	P1–Ni–O2 ^b	P2–Ni–O1 ^b	P2–Ni–O2 ^b	
1a	118.52	91.22	109.81	97.48	96.02	
2a	72.06	96.02	96.91	95.96	109.69	
2b -1 ^{<i>a</i>}	51.67	96.46	103.57	94.59	105.21	
2b -2 ^{<i>a</i>}	53.51	100.52	99.81	92.3	104.54	
4a	95.16	96.06	107.47	95	111.47	

Table 2 Results of molecular modelling (energies and angles O-Ni-P)

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