Synthetic procedures

General technique

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 known procedures[1,2]. (DME)$NiBr_2$ was prepared by reaction of Ni powder with Br_2 in dimethoxyethane[3]. All synthetic procedures with o-semiquinones were carried out in the evacuated ampoules using freshly purified solvents[4] (except 95% aqueous ethanol which was used as received).

^{1}H- and ^{31}P-NMR spectra were obtained on “Bruker” DPX-200 spectrometer (200 MHz, $CDCl_3$, δ/ppm). EPR spectra were recorded on Bruker EMX spectrometer, operating in X-band (work frequency ~ 9.6 GHz) and equipped by NMR-gaussmeter and variable temperature unit. HFC constants and g-factor values have been obtained by simulation in WINEPR SimFonia (v. 1.25).

Synthetic procedures

2,6-bis-(dicyclohexylphosphinomethyl)phenyl-bromonickel (Cy_2PCP)NiBr[5].

The solution of 4.87 g (18.4 mmol) of 1,3-bis-bromomethylbenzene and 7.30 g (36.8 mol) of Cy_2PH in 30 ml of acetone have been heated to 55°C during 1h and cooled to 5°C. Precipitated phosphonium salt was separated by decantation, washed with cold acetone, dissolved in 10 ml of water and added to solution of 4 g (48 mmol) of CH_3COONa in 15 ml of water. 1,3-bis-(dicyclohexylphosphinomethyl)benzene (Cy_2PCP)H was extracted with Et_2O and isolated after solvent removal as viscous residue which slowly crystallize.

NMR ^{1}H (δ, ppm): 7.62 s (1H, o,o-H of C_6H_4), 7.30 s (3H, 2 o,p-H + m-H of C_6H_4), 2.89 s (4H, 2 CH_2); 1.96-1.20 (м, 44H, 4 C_6H_{11}). Lit: 7.51 s (1H, C_6H_4 (o’-H)), 7.18 m (2H, C_6H_4 (o-H)), 7.17 m (1H, C_6H_4 (m-H)), 2.77 s (4H, CH_2), 1.84–1.16 m (44H, Cy).

Ethanolic solution of 1 eq of (Cy_2PCP)H and 0.8 eq of (DME)$NiBr_2$ was heated to 75°C during 2h and cooled to 5°C giving (Cy_2PCP)NiBr as golden needles.

Anal.(%) found: C 60.32, H 8.15, Br 12.65, Ni 9.19; $C_{32}H_{51}BrNiP_2$ calc.: C 60.40, H 8.08, Br 12.56, Ni 9.22.

2,6-bis-(di*iso*propylphosphinomethyl)phenyl-bromonickel (i-Pr_2PCP)NiBr[6], 2,6-bis-(di-*tert*-butylphosphinomethyl)phenyl-3,5-dimethyl-bromonickel (t-Bu_2PCP)NiBr[7].

Desired products were obtained as previously described, but without isolation of intermediate phosphinated products.

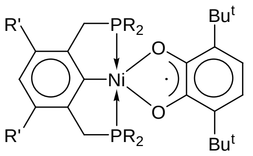
(i-Pr_2PCP)NiBr

NMR ^{1}H (δ, ppm): 1.17 dt (12H, 4 CH3, $J_{HH} \approx J_{HP}$=6.8Hz), 1.44 dt (12H, 4 CH3, J_{HH}=8.7Hz, J_{HP}=7.3Hz), 2.36 m (4H, 4 CH), 3.07 t (4H, 2Ar-CH_2-P, J_{HP}=4.0Hz), 6.90 s (3H, C_{Ar}H). Lit: 1.17 dt (12H, 4 CH3, $J_{HH} \approx J_{HP}$=6.9Hz), 1.44 dt (12H, 4 CH3, $J_{HH} \approx J_{HP}$=7.7Hz), 2.36 m (4H, 4 CH), 3.09 t (4H, 2Ar-CH_2-P, J_{HP}=4.0Hz), 6.90 m (3H, C_{Ar}H).

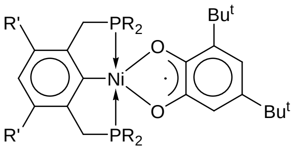
(t-Bu_2PCP)NiBr

NMR ^{1}H (δ, ppm): 1.48 t (36H, 4 $C(CH_3)_3$, J_{HP}=6.4Hz), 2.19 s (6H, 2 Ar-CH_3), 2.97 t (4H, 2Ar-CH_2-P, J_{HP}=2.8Hz), 6.59 s (1H, C_{Ar}H). Lit. for 2,6-bis-(di*tert*butylphosphinomethyl)phenyl-chloronickel: 1.48 t ($C(CH_3)_3$, $^3J_{HP}+^5J_{HP}$=12.8Hz), 3.08 t (Ar-CH_2-P, $^2J_{HP}+^4J_{HP}$=7.4Hz).

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



1a R = Cy, R' = H
2a R = Pr^i, R' = H
3a R = Bu^t, R' = Me
4a R = Ph, R' = H



1b R = Cy, R' = H
2b R = Pr^i, R' = H
3b R = Bu^t, R' = Me
4b R = Ph, R' = H

Syntheses of **4a** and **4b** were described earlier[8]. Other compounds were obtained using the same procedure.

THF solution of 0.5 eq of o-quinone have been shaken with thallium amalgam (~35 % wt of Tl, at least 10-fold excess) until colour unchanged. Forming solution (or suspension depending from quinone nature) of dithallium catecholate was decanted; amalgam was carefully washed with THF, and combined solution was added to 0.5 eq of o-quinone giving a solution of 1 eq of thallium o-semiquinolate Tl(SQ), which was used *in situ*.

Solution of 1 eq of Tl(SQ) was added to THF solution of 1 eq of (R_2PCP)NiBr. The mixture was kept for 30 min, and THF was replaced by toluene. After completion of the reaction (1-2 week, monitored by EPR) solution was filtered. Complex **1a** was isolated from hexane as greenish-brown needles (32% yield).

Anal.(%) found: C 71.05, H 9.25, Ni 7.59; $C_{46}H_{71}NiO_2P_2$ calc.: C 71.13, H 9.21, Ni 7.56.

IR (nujol, cm^{-1}): 1569w, 1550s, 1456s, 1431s, 1419s, 1406s, 1381s, 1356s, 1294m, 1275m, 1269m, 1244m, 1206m, 1188m, 1169m, 1119s, 1106m, 1069w, 1038w, 1000s, 969m, 956m, 950m, 913m, 888m, 856m, 844s, 831s, 818m, 756w, 731s, 663w, 656w, 581w, 506m, 456m, 444w, 419w.

Other complexes have been investigated without isolation.

EPR spectral data

EPR spectra of **1a**, **1b**, **2a**, **2b** and some simulated spectra are represented at Fig. 1 – 4 correspondingly. To reduce the number of spectra at one figure the including of simulated ones were restricted to doubtable cases (unresolved hyperfine structure, superposition of several spectra, etc.). The simulation parameters are listed as well. Because the software restrictions the tumbling effect simulation is possible only for one nucleus. So, separate simulations were made for each phosphorus components but only one of simulated spectra is represented, but all of them are listed.

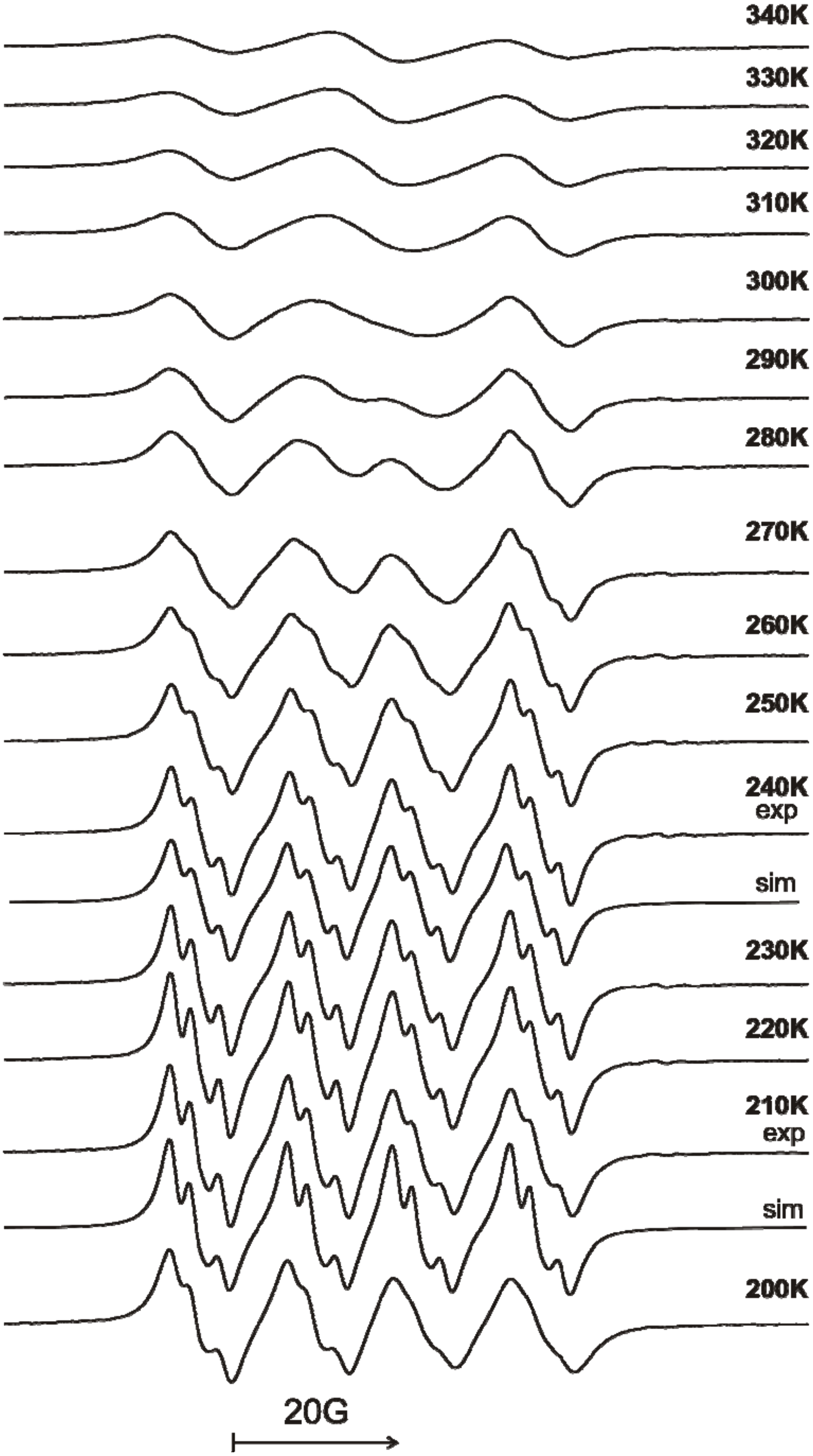


Fig. 1. EPR spectrum of **1a** (toluene). Simulation parameters:

210K – g_i=2.0071, a_{P1}=27.8G, a_{P2}=14.7G, a_{H1}=3.6G, a_{H2}=2.2G, for components left to right, simulating tumbling effect on nuclei H1: Γ=2.2-0.4m_i, Γ=2.35-0.4m_i, Γ=2.5-0.4m_i, Γ=2.7-0.4m_i.

240K – g_i=2.0071, a_{P1}=27.8G, a_{P2}=14.7G, a_{H1}=3.6G, a_{H2}=2.2G, Γ=2.30G.

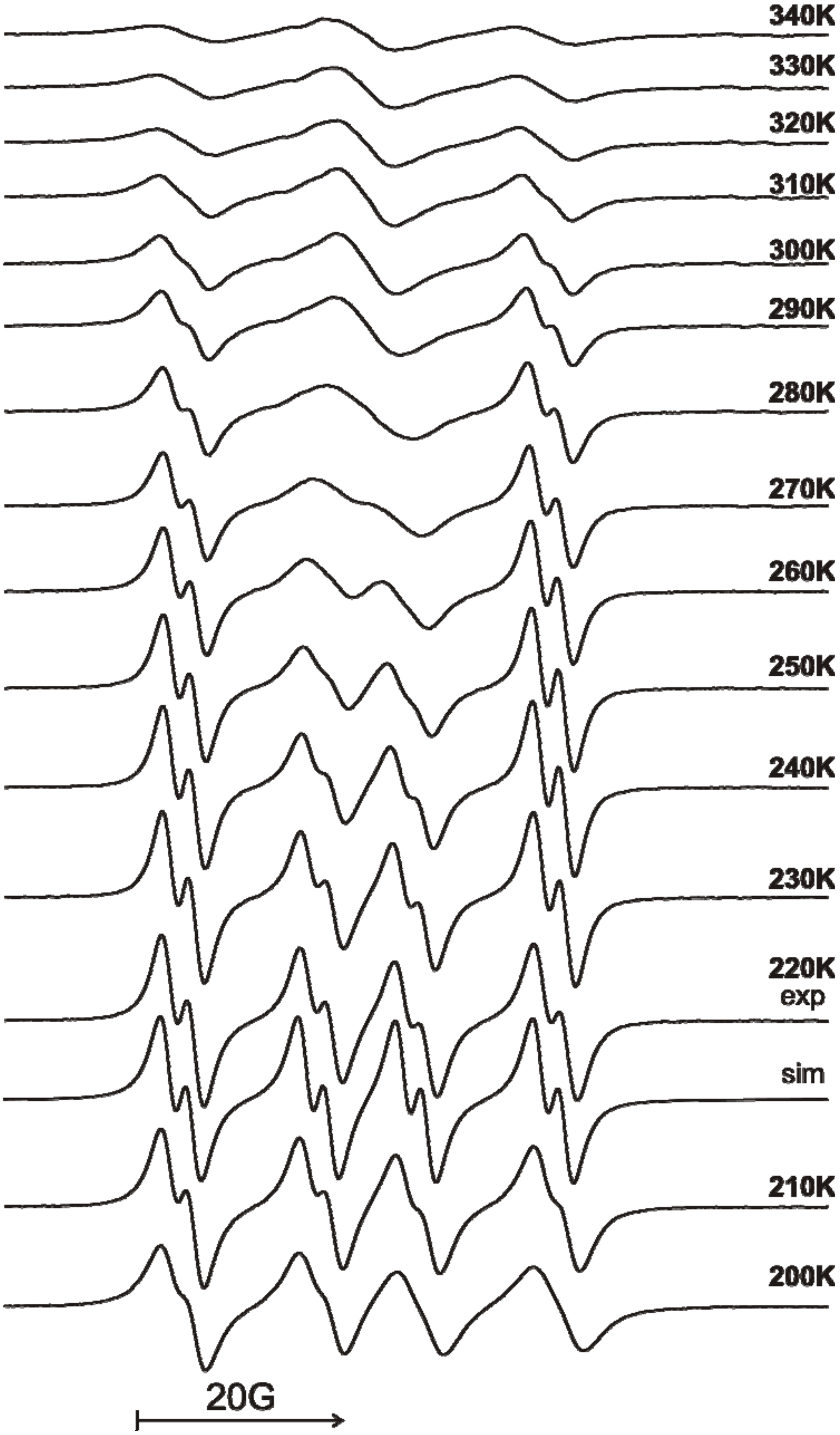


Fig. 2. EPR spectrum of **1b** (toluene). Simulation parameters: g_i=2.0054, a_{P1}=22.7G, a_{P2}=13.4G, a_H=2.5G, for components left to right: Γ=1.85G, Γ=2.0G, Γ=2.1G, Γ=1.95G.

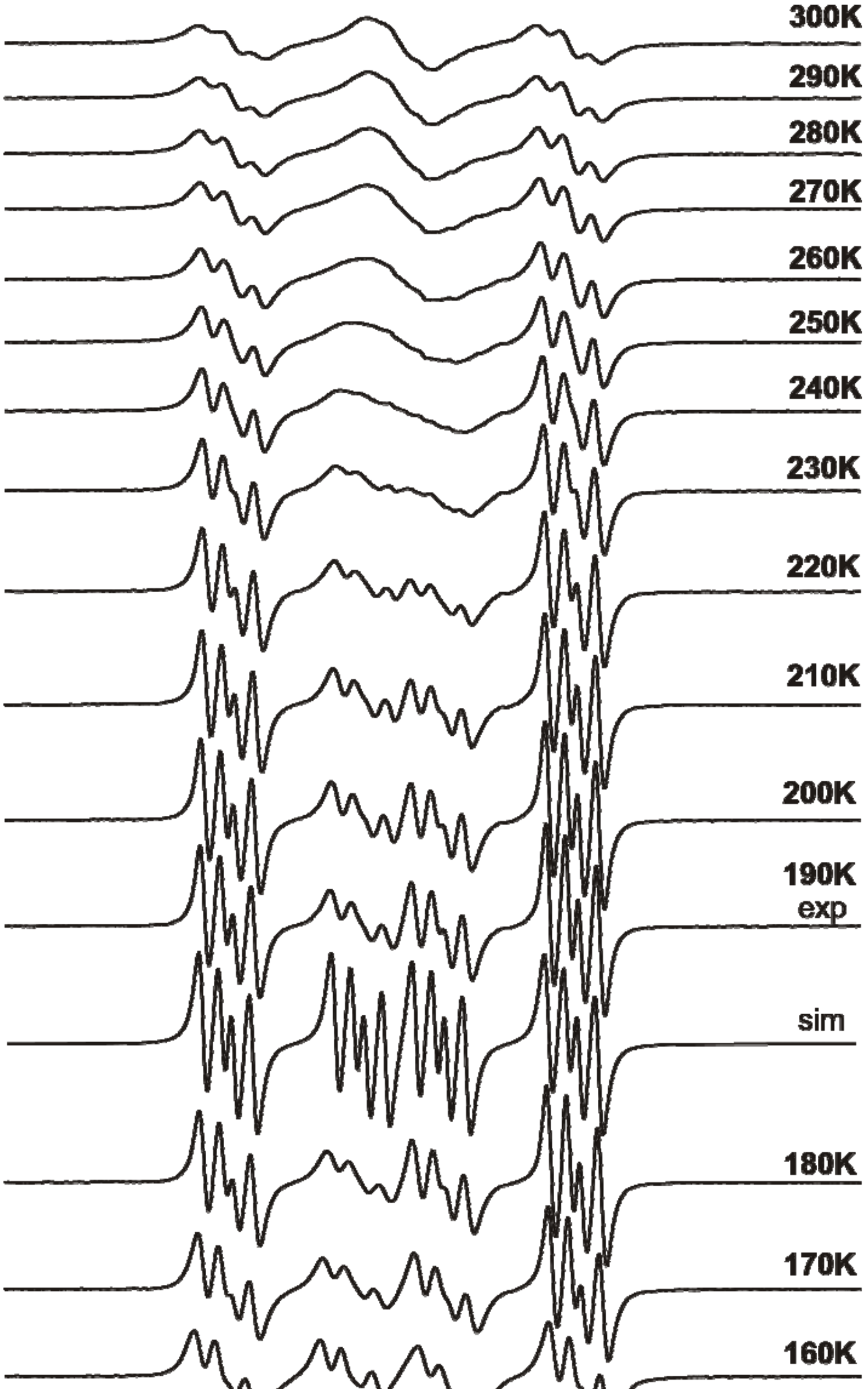


Fig. 3. EPR spectrum of **2a** (Et_2O). Simulation parameters: g_i=2.0054, a_{P1}=25.3G, a_{P2}=15.7G, a_{H1}=3.8G, a_{H2}=2.2G, for components left to right: Γ=1.2G, Γ=2.0G, Γ=1.5G, Γ=1.0G.

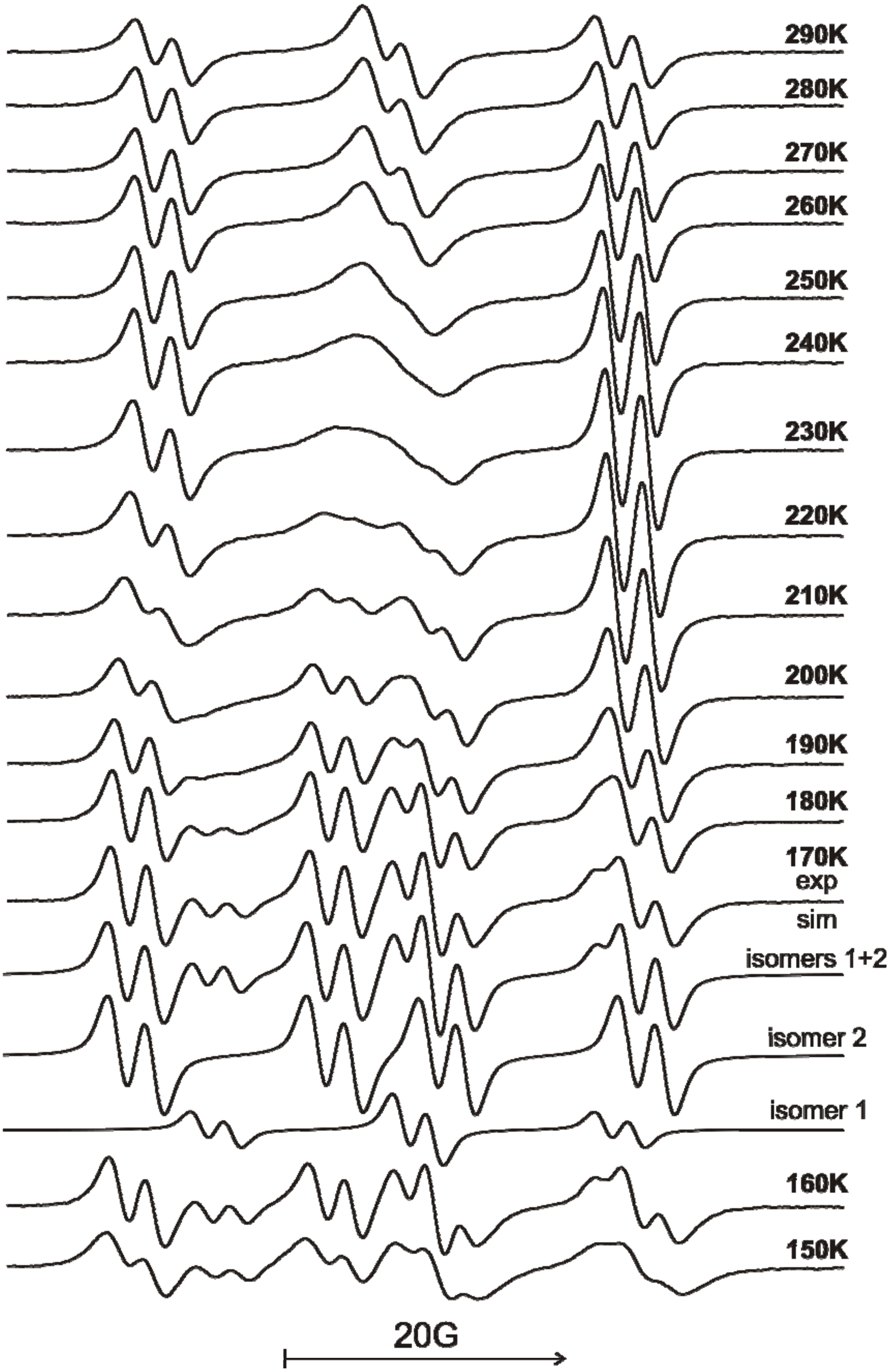


Fig. 4. EPR spectrum of **2b** (Et_2O). Simulation parameters:
Isomer 1 – g_i=2.0043, a_{P1}=a_{P2}=14.4G, a_H=2.2G, Γ=1.50G.
Isomer 2 – g_i=2.0054, a_{P1}=22.2G, a_{P2}=14.2G, a_H=2.5G, Γ=1.60G.

Kinetic calculations

The broadening of central component in high temperature spectra of **1a** and **1b** caused by fast interconversion is described by follow equation[9]:

$\Delta\Gamma=\gamma_e\tau P_1P_2(\delta H)^2$, where γ_e is the electron hyromagnetic constant, τ is the reduced lifetime ($1/\tau = 1/\tau_1 + 1/\tau_2$, τ_i are lifetimes of exchanging particles), P_i are probabilities of corresponding particle formation, δH is mean-square distance between particles lines. In our case lifetimes of both tautomers are equal, so $\Delta\Gamma=\gamma_e\tau(\delta H)^2/4$ and $\tau_1=\tau_2=2\tau$. Also, outer components of phosphorus triplet are recorded at the same field, so only central component is broadened, and $\Delta\Gamma$ is a difference between central line width and extreme lines one.

Using these considerations we calculated tautomers lifetimes at different temperatures:

T,K	$\tau_1=\tau_2$, s **1a**	 **1b**
340	$1.35\cdot10^{-09}$	$8.41\cdot10^{-10}$
330	$2.66\cdot10^{-09}$	$1.21\cdot10^{-09}$
320	$3.25\cdot10^{-09}$	$1.38\cdot10^{-09}$
310	$8.95\cdot10^{-09}$	$2.76\cdot10^{-09}$
300	$1.9\cdot10^{-08}$	$6.01\cdot10^{-09}$
290	n/a	$9.21\cdot10^{-09}$
280	n/a	$1.92\cdot10^{-08}$

Using lifetime temperature dependence we estimated $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ of "fan" motion, using follow equation:

$1/\tau_1=1/\tau_2=(k_BT/h)\exp(\Delta S^{\ddagger}/R)\exp(-\Delta H^{\ddagger}/RT)$, where k_B, h, R are Boltzmann, Planck and absolute gas constants.

After linearization of the equation and linear regression analysis the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were estimated. The sqrt($1-r^2$) value, where r is linear regression correlation coefficient, was used as a relative error in both cases.

For **1a** $\Delta H^{\ddagger}=53\pm7$kJ/mole, $\Delta S^{\ddagger}=79\pm14$J/mole*K and for **1b** $\Delta H^{\ddagger}=40\pm6$kJ/mole, $\Delta S^{\ddagger}=46\pm7$J/mole*K.

Molecular modelling

Molecular modelling was provided using "Hyperchem 8.0" software. Molecular mechanics "MM+" method with "bonds dipoles" options and all of force field components using "Fletcher-Reeves" algorithm were applied for geometry optimization. Results of the geometry optimization are shown at Fig. 5 and Table 1.

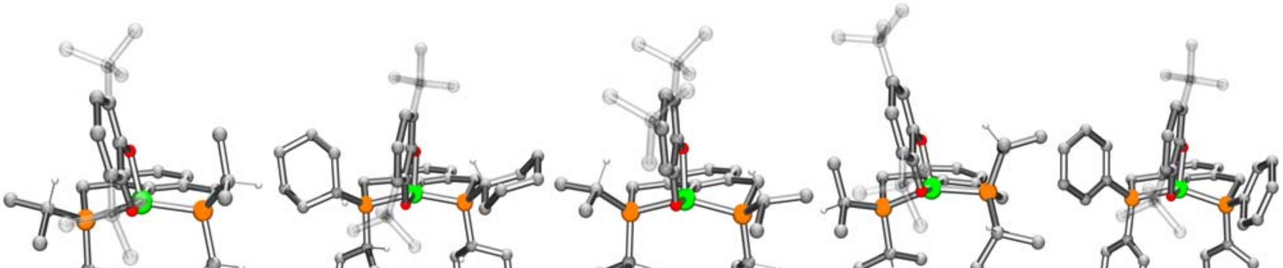


Fig. 5. Results of computer modeling for (from left to right): **2a**, **1a**, **2b** isomer 1, **2b** isomer 2, **4a**. Hydrogens (except methine ones of phosphorus substituents) are omitted for clarity, *tert*-butyls of *o*-semiquinone are translucent for better view.

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Table 1 Results of molecular modelling (energies and angles O-Ni-P)

Complex	Energy, kcal/mole	Angles, deg. 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[a]	51.67	96.46	103.57	94.59	105.21
2b-2[a]	53.51	100.52	99.81	92.3	104.54
4a	95.16	96.06	107.47	95	111.47

[a] Isomers 1 and 2 of **2b** correspondingly.
[b] O1 is basal oxygen, O2 is apical one.

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