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The cyclometalated nickel complex [(Phbpy)NiBr] (Phbpy$^-$ = 2,2′-bipyridine-6-phen-2-yl) − Synthesis, spectroscopic and electrochemical studies

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ABSTRACT

The new organometallic nickel complex [(Phbpy)NiBr] containing the anionic tridentate *N,N,C* ligand 6-(phen-2-yl)-2,2′-bipyridine (Phbpy$^-$) was synthesised from PhbpyBr and [Ni(COD)$_2$] in excellent yields and was fully characterised (MS, NMR, single crystal XRD). [(Phbpy)NiBr] was reacted with (CF$_3$)SiMe$_3$ giving the CF$_3$ complex [(Phbpy)Ni(CF$_3$)]. Both new complexes were studied in detail by electrochemical (CV) and spectroelectrochemical (UV/vis/NIR absorption) methods. For both complexes the first one-electron reduction and the first oxidation of the Br complex occur fully reversible in the CV, while spectroelectrochemistry shows decomposition reactions. The CF$_3$ complex is unstable in solution producing 2-CF$_3$-Phbpy. Reactivity patterns for these reactions were discussed, also in comparison with the non-cyclometalated complex [(bpy)Ni(Mes)Br].

Introduction

Organonickel(II) complexes with terpyridine ligands have recently entered the stage of nickel-catalysed C–C cross-coupling reactions [1–4]. Detailed mechanistic studies on reactions under Negishi-like conditions revealed that the terpy ligand contributes through its π-accepting ability to the stability or reactivity of reduced species. Thus, the catalytically crucial reduced species were better described as Ni(II) complexes bearing a reduced (radical anionic) terpy ligand [Ni(II)(terpy$^-$)(R)] (terpy = 2,2′:6′,2″-terpyridine; R = alkyl or aryl) than as Ni(I) species [Ni(I)(terpy)(R)] [3b,3e,4,5], while for the reduced complex [(terpy)NiBr] evidence for a metal centred [Ni(I)] description has been found [3b].

Quite similar findings have been obtained recently by us on organometallic complexes of the type [(N^N)Ni(R)Br] containing bidentate α-diimine ligands (N^N; R = aryl), which were able to perform electrocatalytic C–C or C–P coupling reactions with various aryl-, vinyl- or alkyl halides R–X [6–8]. Mechanistic studies on these systems, but also on the Cr/Ni catalysed vinylation of aldehydes (Nozaki–Hiyama–Kishi reaction) [9] showed that the Ni(II) pre-catalysts were reduced by one-electron steps to reactive Ni(II) species containing a reduced diimine ligand rather than having the character of a monovalent Ni(I) species [8,10]. Related diimine nickel complexes have also been applied in *i)* homogeneous electromediated reduction (HEMR) of olefins, ketons or alkyl halides [11]; *ii)* electrochemical carboxylation of bromostyrenes [12] or aziridines [13]; *iii)* electroreductive carbonylation of organic halides [14]; or *iv)* electroreductive coupling of olefins and polyhalo compounds [15].

To substantiate our previous findings on organometallic Ni terpy complexes we stepped on the idea to use the tridentate anionic *N,N,C* coordinating 2,2′-bipyridine-6-phen-2-yl (Phbpy$^-$) ligand instead of the neutral *N,N,N* coordinating terpy ligand. Corresponding Ni(II) complexes of the composition [(N^N^C)Ni(R)] (R = alkyl, aryl or halido) are neutral, compared with the cationic [(N^N^N)Ni(R)]$^+$ derivatives. This should largely change the electronic and catalytic properties. Also, from the expected coplanar arrangement of the phenyl moiety with the bpypart of the ligand these complexes should differ markedly from the previously thoroughly investigated complexes [(N^N)Ni(aryl)Br] [8,16]. To our knowledge nickel complexes containing the Phbpy$^-$ ligand or derivatives have not been reported yet, in contrast to numerous Pd(II) [17,18] and Pt(II) [18–20] complexes of this ligand. Pt complexes of Phbpy$^-$ represent a class of interesting luminescent materials [20].

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Experimental

General

All preparations and measurement were carried out in a dry argon atmosphere using Schlenk techniques. Solvents (CH_2Cl_2, THF, toluene, diethyl ether and MeCN) were dried using an MBRAUN MB SPS-800 solvent purification system.

Instruments

NMR spectra were recorded using a Bruker Avance II 300 MHz spectrometer (^{1}H: 300.13 MHz, ^{13}C: 75.47 MHz) using a triple resonance ^{1}H,^{19}F,BB inverse probehead. The unambiguous assignment of the ^{1}H and ^{13}C resonances was obtained from ^{1}H TOCSY, ^{1}H COSY, ^{1}H NOESY, gradient selected ^{1}H, ^{13}C HSQC and HMBC experiments. All 2D NMR experiments were performed using standard pulse sequences from the Bruker pulse program library. Chemical shifts were relative to TMS for ^{1}H and ^{13}C. The spectra analyses were performed by the *Bruker TopSpin 2* software. Elemental analyses were carried out using a Hekatech CHNS EuroEA 3000 Analyzer. EI-MS spectra were measured with a Finnigan MAT 900 S. Simulations were performed using ISOPRO 3.0. Electrochemical experiments were carried out in 0.1 M nBu$_4$NPF$_6$ solutions using a three-electrode configuration (glassy carbon electrode, Pt counter electrode, Ag/AgCl reference) and an Autolab PGSTAT30 potentiostat and function generator. Data were processed using GPES 4.9 (General Electrochemical System Version 4.9). The ferrocene/ferrocenium couple ($FeCp_2/FeCp_2^+$) served as internal reference. Spectroelectrochemical investigations (UV/vis/NIR) were performed at ambient temperature using an OTTLE (optical transparent electrochemical) cell designed by J. Fiedler, Prague [21]. UV/vis/NIR absorption spectra were recorded using Varian Cary50 Scan or Cary05E photospectrometers.

Crystal structure determination

The data collection was performed at $T = 100(2)$ K on a *STOE IPDS I* diffractometer with MoKα radiation ($\lambda = 0.71073$ Å) employing $\omega{-}2\theta$ scan technique. The structure was solved by direct methods using the SHELXTL package [22] and refinement was carried out with SHELXL97 employing full-matrix least-squares methods on F^2 [23] with $F_0^2 \geq 2\sigma(F_0^2)$ with the results shown in Table 1 (and Supplementary data). For the sake of a clear distinction between the Ni coordinated N2 and C12 atoms, the site occupancy factor for both atoms was freely refined and yielded unity. All non-hydrogen atoms were treated anisotropically; hydrogen atoms were included by using appropriate riding models.

Reagents

The complex [Ni(COD)$_2$] [24] was synthesised according to a literature procedure. All other chemicals were purchased by commercial suppliers and were used without further purification.

Synthesis of PhbpyH (adapted from Ref. [25])

To a solution of 4.68 g (30 mmol) 2,2′-bipyridine in dry diethyl ether were drop wise added 18 mL (36 mmol) of a 2 M phenyl lithium solution in diethyl ether at 0 C. After 2 h the deep red mixture was quenched with 50 mL of water whereupon the colour changed to green. After the aqueous layer was extracted with diethyl ether the combined organic layers were dried over magnesium sulphate. The solvent was evaporated and the remaining oil was diluted with 70 mL of acetone. A saturated potassium permanganate solution in acetone was added drop wise until the colour remained slightly purple. The formed dark solid was filtered off and the solvent of the filtrate was evaporated. The received brown oil was purified by column chromatography (silica gel, diethyl ether/petroleum 2/1) which led to a yellowish powder. After recrystallisation out of pentane the product was received as a colourless powder. Yield: 2.79 g (12 mmol, 40%). Anal.: $C_{16}H_{12}N_2$ ($M_W = 232.28$ g/mol): C, 82.73; H 5.21; N, 12.06%. Found: C, 82.04; H, 5.75; N, 10.94%. ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 8.71$ (d, 1H, H6), 8.66 (d, 1H, H3), 8.40 (d, 1H, H3′), 8.16 (d, 2H, Ha/He), 7.90 (m, 1H, H4′), 7.84 (m, 1H, H4), 7.78 (m, 1H, H5′), 7.54 (m, 1H, Hb), 7.49 (m, 1H, Hc), 7.45 (m, 1H, Hd), 7.35 (t, 1H).

Table 1
Details of the crystal structure determination and selected structural data of [(Phbpy)NiBr][a].

Formula/weight [g/mol]	$C_{16}H_{11}Br_1N_2Ni_1$/369.89
Crystal system/space group	Monoclinic/$P2_1/n$ (no. 14)
Cell [Å]	$a = 8.7252(7)$, $b = 16.4594(10)$, $c = 9.1139(5)$ $\beta = 95.560(4)°$
V [Å]^3/Z	1302.70(15)/4
ρ_{calc} [g/cm^3]/μ [mm^{-1}]	1.886/4.544
Limiting indices	$-11 < h < 11$, $-21 < k < 20$, $-11 < l < 11$
Refl. coll./uniq./R_{int}	8086/2820/0.0585
Data/restraints/param.	2820/0/181
Goof. on F^2	1.078
Final R_1, wR_2 [$I > 2\sigma(I)$]	0.0501/0.1416
R_1, wR_2 (all data)	0.0685/0.1501
$\Delta\rho_{min/max}$ [10^{-6} e/pm^3]	−1.011/1.442
Distances [Å]	
Ni–N1, Ni–Br	1.848(5), 2.300(1)
Ni–N2, Ni–C12,	1.969(5), 1.947(5)
C10–C11, C1–C2	1.475(7), 1.472(8)
Angles [°]	
N1–Ni–N2, N1–Ni–C12	82.6(2), 82.8(2)
N1–Ni–Br, N2–Ni–C12	178.7(1), 165.4(2)
Br–Ni–C12, Br–Ni–N2	96.9(1), 97.7(1)
Sum of angles around Ni	360.0(2)

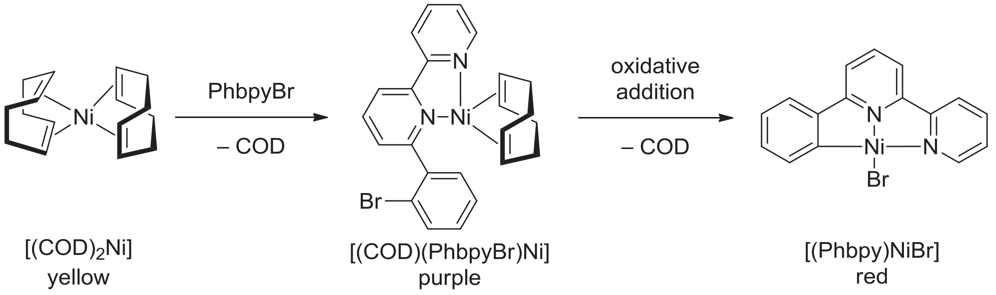
[a] Measured at 100(2) K at $\lambda = 0.71073$ Å.

Synthesis of PhbpyBr (adapted from Ref. [26])

36 mg (2.3 mmol) 6-Phenyl-2,2′-bipyridine, 497 mg (2.8 mmol) *N*-bromosuccinimide and 27 mg (5 mmol %) Pd(OAc)$_2$ were suspended in 25 mL of acetonitrile and heated for 14 h at 120 °C in an autoclave. After cooling to room temperature the yellow reaction mixture was filtered over celite and the solvent was evaporated. The yellow solid was extracted three times with 25 mL of hexane. The solvent was evaporated again to receive a yellow oil as the product. Yield: 660 mg (2.6 mmol, 93%). Anal. $C_{16}H_{11}N_2Br$ ($M_W = 311.18$ g/mol): C, 61.76%; H 3.56%; N, 9.00%. Found: C, 60.92%; H, 3.67%; N, 8.91%. ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 8.72$ (d, 1H, H6), 8.55 (d, 1H, H3), 8.44 (d, 1H, H3′), 7.92 (t, 1H, H4′), 7.83 (dt, 1H, H4), 7.77 (m, 1H, Hd), 7.75 (m, 1H, H5′), 7.70 (m, 1H, Ha), 7.46 (t, 1H, Hb), 7.33 (t, 2H, H5/Hc).

Synthesis of [(Phbpy)NiBr] (adapted from Ref. [27])

400 mg (1.4 mmol) [Ni(COD)$_2$] and 450 mg (1.4 mmol) PhbpyBr were dissolved in dry THF under argon atmosphere. The mixture immediately turned purple and after a short while intensive red. After 14 h of stirring at room temperature the solvent was evaporated in vacuum and the red residue was washed three times with 15 mL of pentane and once with 20 mL of heptane. The remaining red product was dried in vacuum. Yield: 430 mg (1.12 mmol, 80%). Anal. $C_{16}H_{11}N_2NiBr$ ($M_W = 369.87$ g/mol): C, 51.96; H, 3.00; N, 7.57%. Found: C, 52.44; H, 3.17; N, 7.42%. ^{1}H NMR (300 MHz, CD$_2$Cl$_2$): $\delta = 9.20$ (s, 1H, H6), 7.98 (m, 1H, H4), 7.89 (m, 1H, H3′), 7.84



Scheme 1. Preparation of the title complex.

(m, 1H, H3), 7.77 (m, 1H, Hd), 7.53 (m, 1H, H4′), 7.48 (m, 1H, H5), 7.42 (m, 1H, H5′), 7.29 (m, 1H, Hb), 7.05 (m, 1H, Ha), 7.01 (m, 1H, Hc). EI-MS: m/z = 370 $[M]^+$, 324 [[(Phbpy)NiCl]]$^+$, 289 $[M - Br]^+$, 232 $[M - Ni,Br + H]^+$.

Synthesis of [(Phbpy)Ni(CF$_3$)] (adapted from Ref. [28])

300 mg (0.8 mmol) [(Phbpy)NiBr] and 456 mg (3.0 mmol) CsF were dissolved in 20 mL of dry THF. 411 μL (3.0 mmol) of trimethyl(trifluormethyl)silane were added drop wise yielding a deep red solution that was stirred for 18 h at room temperature. Afterwards the solvent was evaporated which led to a brown solid that was dissolved in a mixture of pentane and CH_2Cl_2 1:1 and filtrated. The brown filtrate was dried and the received red solid was washed with 15 mL of pentane and 25 mL of heptane and dried in vacuum. Yield: 110 mg (0.3 mmol, 38%). Anal. $C_{17}H_{11}F_3N_2Ni_1$ (M_W = 757.8 g/mol): C, 56.88; H, 3.09; N, 7.08%. Found: C, 50.17; H, 2.92; N, 5.32%. ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta = 8.83$ (s, 1H, H6), 7.93 (m, 1H, Ha), 7.92 (m, 1H, H3′), 7.79 (m, 1H, H4), 7.78 (m, 1H, Hc), 7.51 (m, 1H, H4′), 7.49 (m, 1H, H5′), 7.48 (m, 1H, H3), 7.43 (m, 1H, H5), 7.43 (m, 1H, Hb), 7.43 (m, 1H, Hd). ^{19}F NMR (300 MHz, CD_2Cl_2) $\delta = -28$ (Ni–CF_3). EI-MS: m/z = 358 $[M]^+$, 324 [[(Phbpy)NiCl]]$^+$, 305, 300 $[M - Ni]^+$, 289 $[M - CF_3]^+$, 232 $[M - Ni, CF_3 + H]^+$.

Results and discussion

Preparations and analytical characterisation

The 6-phenyl-2,2′-bipyridine precursor PhbpyH was prepared through a variant of an established procedure [25]. The bromination of the 2 position in the phenyl ring was successfully carried out using N-bromosuccinimide, also following an established method. Upon mixing of PhbpyBr and $[Ni(COD)_2]$ in solution a deep purple colour was observed, which is due to the intermediate nickel(0) complex [(PhbpyBr)Ni(COD)] [10] (Scheme 1). During the next few minutes the colour of the mixture turn to bright red, which represents the cyclometalated product [(Phbpy)NiBr], formed through an oxidative addition (Scheme 1).

The complex [(Phbpy)NiBr] seem to be a very suitable starting material for further complexes $[(Phbpy)Ni(L)]^n$ (L = any ligand, n depends on the charge of L and is 0 for anionic ligands). As a first example for such derivatives, the bromido complex was successfully reacted with trimethyl-(trifluormethyl)silane in the presence of CsF to yield the CF_3 complex [(Phbpy)Ni(CF$_3$)].

The constitution of the new compounds was established through elemental analyses, EI-MS and ^{1}H (and ^{19}F) NMR spectroscopy (see Experimental Section). The two nickel complexes are well soluble in common organic solvents (toluene, CH_2Cl_2, THF, acetonitrile). While the Br complex is stable in these solutions (and in the solid state), the CF_3 complex turns out to be unstable in solution (although degassed and dry) but can be stored for longer times in the solid.

Crystal and molecular structures

Single crystals of [(Phbpy)NiBr] were obtained from THF solutions and the crystal and molecular structure (Fig. 1) was determined with the results summarised in Table 1.

In the crystal structure [(Phbpy)NiBr] does not exhibit any *pronounced* intermolecular interaction other than the coplanar stacking visible in Fig. 1. The shortest interplanar distances are about 3.3 Å and the tilt angles are almost zero [29], quite similar to what has been observed for the related complex [(terpy)NiBr] [3b] (see Supplementary data for details). The molecular structure shows a

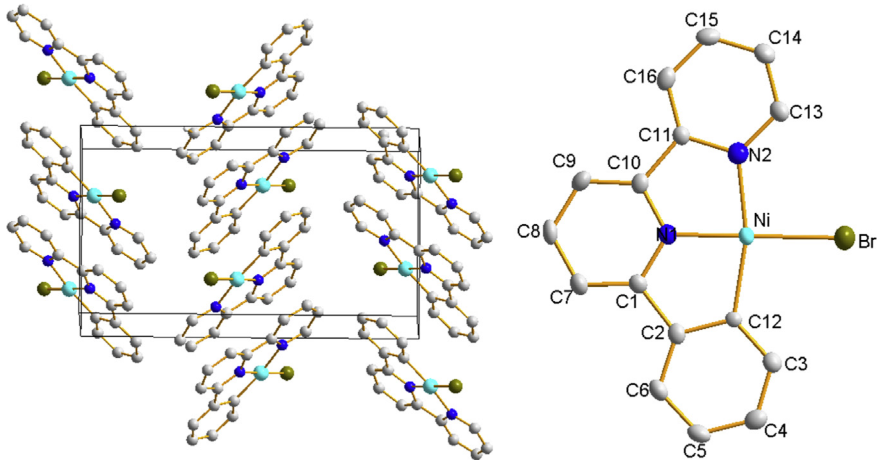


Fig. 1. Crystal structure of [(Phbpy)NiBr] (left; viewed along the crystallographic a axis) and molecular structure (right; at 50% probability level (with numbering); protons were omitted for clarity).

distorted square planar surrounding of the nickel atom with a short central Ni–N1 bond of 1.848(5) Å and markedly longer peripheral Ni–N2 (1.969(5) Å) and Ni–C12 (1.947(5) Å). Importantly, the structure solution in monoclinic $P2_1/n$ allowed to unequivocally assign the bonding N2 and C12 atoms in contrast to the Pd derivative [(Phbpy)PdCl] (space group C2/*c*) [18b]. For the Pt complex [(Phbpy)Pt(NCMe)][BF_4] (space group *Pcnb*) the M–C bond is markedly shorter than the M–N bond (7.8%) [18b], while in [(Phbpy)NiBr] this bond is only 1.1% shorter. For the Ni derivative the N1–Ni–C12 angle, which defines the distortion from a real square-type coordination, is highest with 165.4(2)° compared with the Pd (160.6(1)°) and Pt (160.2(9)°) derivatives. Interestingly, all three Phbpy complexes exhibit perfect planarity around the metal centre.

When comparing [(Phbpy)NiBr] with nickel complexes of 2,2′:6′,2″-terpyridine (terpy) it must be first noted that only the five-coordinated complex [(terpy)$NiBr_2$] exists for bromido-coordinated nickel(II) [3a,30]. For [(terpy)$NiBr_2$] no structure has been reported so far, instead structural data of the very related complex [(Rterpy)$NiBr_2$] with Rterpy = 6,6″-{(2,6-i-$Pr_2C_6H_3$)N=CH}$_2$-terpy [31] show a distorted trigonal bipyramidal coordination with a relatively long central Ni–N1 bond and very long peripheral Ni–N bonds (comparative data is provided in the Supplementary data, Table S6). To obtain a square-planar coordination for terpy nickel complexes the relatively weak coligand Br has to be replaced by one strong alkyl or aryl coligand, which leads to cationic complexes, such as [(terpy)Ni(Mes)]$^+$ (Mes = 2,4,6-trimethyl-phenyl) [5]. Here, the central Ni–N bond is shortened due efficient back-bonding of the electron density donated by the aryl coligand [5]. This effect can be also seen in [(Phbpy)NiBr] confirming the previous assumptions. Also in the one-electron reduced complexes [(terpy)Ni(Me)] [3b,3e,32] and [(terpy)NiBr] [3b], square planar coordination is found. While for the first no qualitatively satisfying crystal structure could be obtained [3e], the latter shows generally far longer Ni–N bonds, with the central Ni–N bond only slightly shorter than the peripheral ones. Based on this structure, quantum chemical calculations and spectroscopy it was concluded, that this complex is best described as a Ni(I) complex with a neutral terpy ligand, in contrast to the corresponding complexes [(terpy)Ni(R)] with R = methyl [3b,3e] or aryl [5], which are best described as Ni(II) complex bearing a reduced (radical anionic) terpy ligand [Ni(II)(terpy$^-$)(R)].

Electrochemical experiments

The bromido complex [(Phbpy)NiBr] exhibits three reversible reduction waves and one reversible oxidation wave (Fig. 2). While the first reduction wave accounts for exactly one electron, the second and third wave are slightly (2nd) or markedly (3rd) smaller. For the CF_3 derivative the same processes were observed, however, only the first reduction is reversible, the oxidation is only partly reversible and the 2nd and 3rd reductions are irreversible. Generally, the potentials for the CF_3 complex are more negative compared with the Br derivative, which probably accounts for the irreversibility of the 2nd and 3rd reduction. As outlined above, the complex [(Phbpy)Ni(CF_3)] decomposes upon standing in solution, a process which is accelerated when exposed to air. The rather irreversible oxidation wave is in line with this observation and points to an oxidatively initiated decomposition reaction, which does not happen for the Br derivative.

Table 2
Redox potentials of Phbpy Ni complexes and related bpy Ni complexes[a].

	E_{Ox}	E_{red1}	E_{red2}	E_{red3}	$\Delta E_{Ox}-E_{red1}$
[(Phbpy)NiBr]	0.08 rev	−1.90 rev	−2.52 rev	−2.70 rev	1.98
[(Phbpy)Ni(CF)$_3$]	−0.08 prev[b]	−2.04 rev	−2.71 irr	−2.97 irr	1.96
[(bpy)Ni(Mes)Br][c]	0.21 irr	−1.92 irr	−2.08 rev	−2.91 irr	2.13
[(bpy)Ni(Mes)$_2$][c]	−0.14 irr	−2.19 rev	−2.97 rev	–	2.05

[a] From cyclic voltammetry in THF/*n*Bu_4NPF_6. Potentials (in V) referenced vs. $FeCp_2/FeCp_2^+$. Potentials in V vs. $FeCp_2^{+/0}$. half-wave potentials for reversible processes (rev), cathodic peak potentials for irreversible reductions (irr).

[b] Partly reversible.

[c] From Ref. [8b].

When comparing the behaviour of the cyclometalated bromide complex with that of the thoroughly studied non-cyclometalated complex [(bpy)Ni(Mes)Br] (Mes = 2,4,6-trimethylphenyl = mesityl) (Table 2) it is remarkable, that both reduction and oxidation occur reversible for the cyclometalated complex, while for the complex [(bpy)Ni(Mes)Br] both processes are irreversible. For the reduction, which occurs at almost the same potential it has been established, that the cleavage of bromide after the first reduction is responsible for the irreversible behaviour (EC mechanism) [8]. This is in line with the reversible character of the reduction of the bis(mesityl) complex [(bpy)Ni(Mes)$_2$]. It thus seems that for [(Phbpy)NiBr] the cleavage of the Br ligand after reduction is hampered.

For the oxidation a mainly nickel-centred process [Ni(II)/Ni(III)] can be assumed from previous studies [8]. It seems, that the cyclometalated complex [(Phbpy)NiBr] is largely stabilised in the oxidised form (assumed trivalent nickel). A marked difference in the electronic structure of both complexes can be expected from the co-planar orientation or the aryl group for the cyclometalated complex in contrast to the non-cyclometalated derivative in which the aryl group displays a tilt angle of about 75° (XRD [16e,f] and

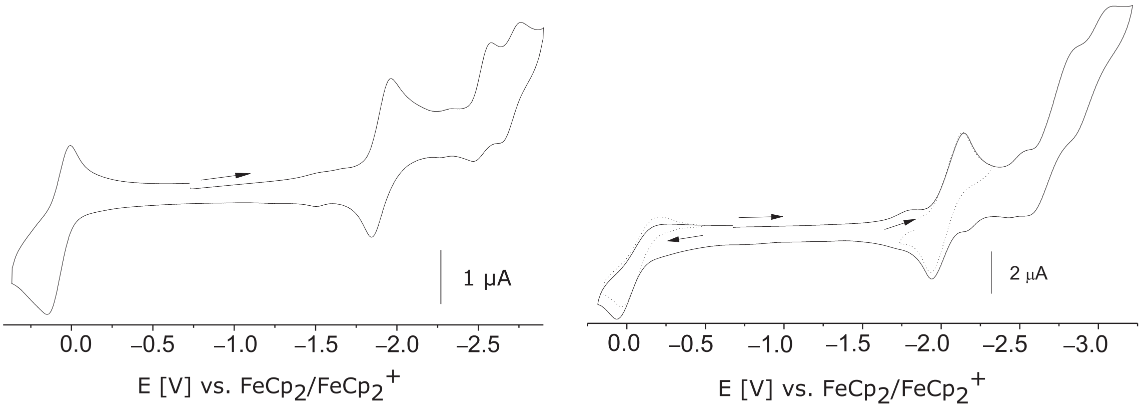


Fig. 2. Cyclic voltammogramms of [(Phbpy)NiBr] (left) and [(Phbpy)Ni(CF_3)] (right) in THF/*n*Bu_4NPF_6 at 298 K, 200 mV/s scan rate.

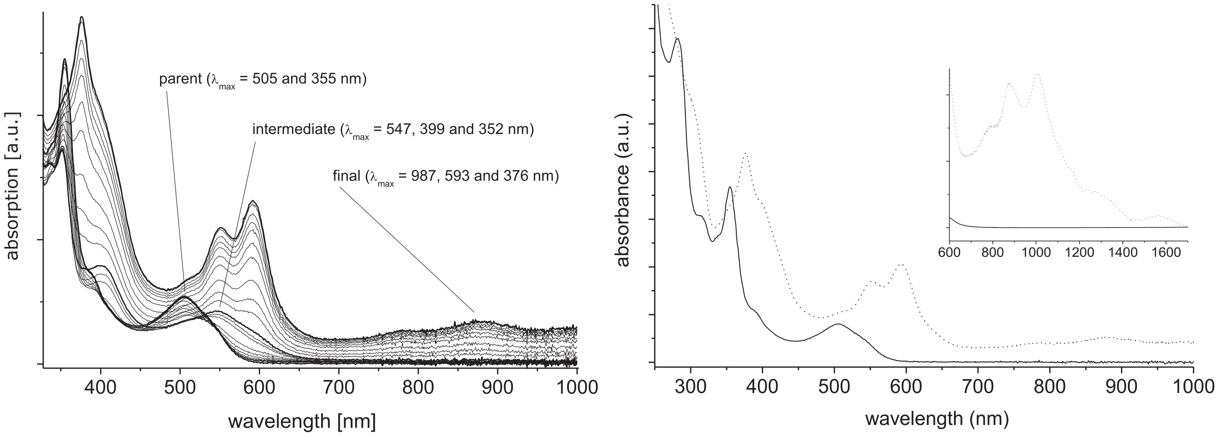


Fig. 3. Left: Absorption spectra recorded during cathodic electrolysis (spectroelectrochemistry) of [(Phbpy)NiBr] in THF/nBu$_4$NPF$_6$ solutions; right: spectra of the parent complex as solid line and the final reduced product dotted.

calculated [16d]). Previous calculations for [(bpy)Ni(Mes)Br] and [(bpy)Ni(Mes)$_2$] have revealed marked contributions of the Br and Mes coligands to the largely nickel-centred HOMO (highest molecular orbital) of the complexes. Maybe, the co-planar binding of the Ph group including an extended delocalisation in the Phbpy$^-$ ligand leads to a markedly increased contribution of the Phbpy ligand to the HOMO with a high delocalisation of the odd electron in the oxidised state over the nickel atom and the Phbpy ligand. Spectroelectrochemical experiments (see next paragraph) and quantum chemical calculations (in the future) might help to clarify this.

UV/vis absorption spectroscopy and spectroelectrochemistry

The parent complex [(Phbpy)NiBr] (Fig. 3) exhibits a long-wavelength band at 505 nm (19,800 cm^{-1}) lying between the maxima observed for [(bpy)Ni(Mes)Br] at 464 nm (21,550 cm^{-1}) and [(bpy)Ni(Mes)$_2$] at 564 nm (17,730 cm^{-1}) (λ_4 in Table 3). Assuming the same mixed MLCT/L'LCT transition for these bands [16c,d], we can conclude that the Phbpy anion exerts a stronger σ-donation effect (lifting the HOMO energy) than (bpy) + (Mes) but smaller than bpy + (Mes)$_2$. The complex [(Phbpy)Ni(CF$_3$)] exhibits markedly higher absorption energy (468 nm or 21,370 cm^{-1}) in line with the electron-withdrawing effect of CF$_3$ [28]. The second MLCT/L'LCT transitions, which are also observed in [(bpy)NiMes)$_2$] occur at around 390 nm (λ_3). The intense bands around 350 nm (λ_2) are partly structured, which points to intraligand (π–π^*) transitions of the Phbpy$^-$ ligand. They do not appear in the non-cyclometalated complexes [(bpy)Ni(Mes)Br] and [(bpy)Ni(Mes)$_2$]. The bands at very high energy at 282 nm are identical for both complexes can be unequivocally assigned to intraligand (π–π^*) transitions (λ_1).

Upon spectroelectrochemical reduction (Fig. 3) the same behaviour for both Phbpy complexes was observed. During the first step from 0 to −2.4 V (compare Fig. 2) both long-wavelength bands undergo red shifts, and the 350 bands lose markedly in intensity. The intraligand bands at 282 nm remain almost unchanged. Importantly, the conversion from the parent species to the so-called intermediate complexes does not show isosbestic points, thus no simple reaction occurs. These first reduction processes are partially reversible; approximately 50% of the original spectra could be recovered upon reverse sweep. Further reduction from −2.4 to −2.7 V goes along with the observation of three marked, partially structures bands with maxima at 376, 593 and 1006 nm for Br and 377, 572 and 946 nm for the CF$_3$ derivative. These processes seem to be fully reversible. Comparison with the spectrum of [(bpy)Ni(Mes)$_2$]$^-$ and the spectral features of reduced bpy (Table 3) clearly shows that these final species contain a reduced bpy-moiety.

For the related complex [(bpy)Ni(Mes)Br] quite similar behaviour has been observed and was explained by an ECE mechanism [8]. ECE means that the parent complex is one-electron reduced (E), then undergoes bromide cleavage (C) and the product can be further reduced (E). It can be assumed, that the two Phbpy complexes feature very similar mechanisms. However, the chemical

Table 3
UV/vis absorption spectral data of Phbpy nickel complexes and corresponding reduced and oxidised species[a,b].

		λ_1 (ε)	λ_2 (ε)	λ_3 (ε)	λ_4 (ε)	λ_5 (ε)
[(Phbpy)NiBr]^n	$n = 0$	282 (58.2)	355 (13.9)	388 (4.1)	505 (3.1)	–
[(Phbpy)NiBr]^n	$n = -1$ intermediate	276 (56.8)	352 (8.8)	399 (4.0)	547 (2.4)	–
[(Phbpy)NiBr]^n	$n = -1$ final	296 (51.3)	376 (11.8)	–	593 (6.0)	1006 (1.3)
[(Phbpy)NiBr]^n	$n = +1$	–	315 (17.4)	–	–	–
[(Phbpy)Ni(CF)$_3$]^n	$n = 0$	281 (22.7)	347 (12.7)	394 (4.6)	468 (2.7)	–
[(Phbpy)Ni(CF)$_3$]^n	$n = -1$ intermediate	279 (23.0)	346 (11.8)	397 (5.0)	542 (2.1)	–
[(Phbpy)Ni(CF)$_3$]^n	$n = -1$ final	297 (22.1)	377 (12.9)	–	572 (5.8)	946 (1.4)
[(Phbpy)Ni(CF)$_3$]^n	$n = +1$	–	308 (15.1)	–	–	–
[(bpy)Ni(Mes)Br]^n[c]	$n = 0$	310 (17.2)	–	–	464 (2.3)	
[(bpy)Ni(Mes)$_2$]^n[c]	$n = 0$	298 (15.1)	–	367 (3.2)	564 (3.1)	–
[(bpy)Ni(Mes)$_2$]^n[c]	$n = -1$	–	355 (14.9)	–	530 (2.6)	940 (1.7)
bpy$^-$		–	398	–	585	1230

[a] Wavelengths of absorption maxima λ in nm; molar absorption coefficient ε in 1000 Mol^{-1} cm^{-1}.

[b] Generated by *in situ* electrolysis in THF/0.1 M nBu$_4$NPF$_6$ at ambient temperatures.

[c] From Ref. [8b].

reactions (Br and CF_3 cleavage, respectively) seem to be markedly slower, allowing the observation of reversible redox waves in the CV. Furthermore, the mechanisms for both complexes might be different, since, while the generation of a Br^- anion in solution is likely to occur in such a reaction, the generation of a CF_3^- anion is probably less preferred and the cleavage of a $^{\cdot}CF_3$ radical is more likely [4].

The UV/vis absorption data for both intermediate complexes are quite similar (spectra of [(Phbpy)Ni(CF_3)] in the Supplementary data), and the formation of Phbpy Ni complexes can therefore be assumed. On the other hand, the absorption bands of the final reduced species for the Br and CF_3 complexes are different. The overall features in these spectra are the same and are very similar to reduced bpy. The product from the Br complex exhibits markedly lower energies for the corresponding absorption bands λ_2, λ_4 and λ_5 in Table 3 pointing to a different substitution pattern of a reduced Phbpy ligand. We therefore propose that the chemical reaction in the ECE sequence of these complexes does not (only) comprise the cleavage of the Br or CF_3 coligands to the solution but (also) their transfer to the 2-phenyl- moiety as radicals or in a kind of reductive elimination leading to coordinated Phbpy-Br or Phbpy-CF_3 ligands. Bulk electrolysis studies on the complexes will help to clarify this in the future.

Upon spectroelectrochemical oxidation (Fig. 4) of the two complexes almost all bands disappear and only one marked band at around 310 nm characterises the oxidised products. This time the process shows clear isosbestic points, however, the reversibility is only about 50–60% (Figures in the Supplementary data).

Thus, for both the first reduction of both Phbpy complexes and the oxidation of [(Phbpy)NiBr] the CV experiments show complete reversibility, while in the slower spectroelectrochemical experiments only partial reversibility is observed. Compared with the very similar but non-cyclometalated system [(bpy)Ni(Mes)Br], in which both oxidation and reduction occur completely irreversible under the same CV conditions, the Phbpy systems seem to be more stable after oxidation and reduction. For the non-cyclometalated system [(bpy)Ni(Mes)Br] reversibility for the first reduction process, thus, hampering of the Br^- cleavage is only observed at −60°, while the oxidation remains irreversible even at very low temperatures. Either the tridentate $Phbpy^-$ ligand provides some kind of electronic stabilisation of the mono-reduced or oxidised species or the decomposition reactions of these species differ markedly from the species generated from the non-cyclometalated complex [(bpy)Ni(Mes)Br]. Comparative quantum chemical calculations will give insight to the electronic situation, while further spectroelectrochemical studies (bulk electrolysis with isolation of products or trapping of intermediates) will clarify the underlying mechanisms. These experiments will be carried out in the near future.

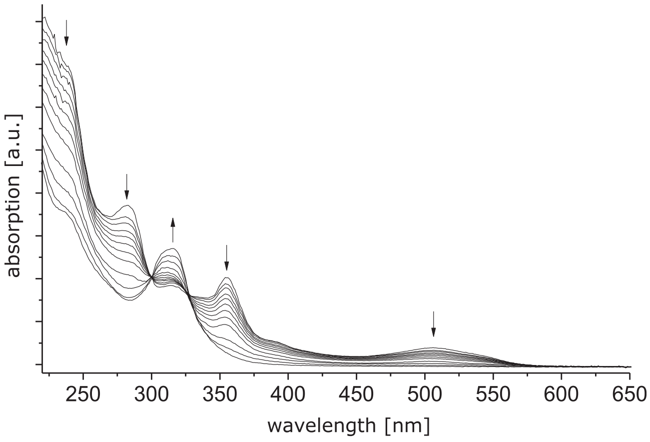
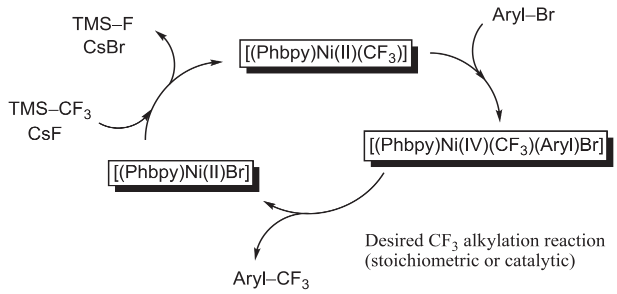


Fig. 4. Absorption spectra of [(Phbpy)NiBr] during anodic scan from 0 V to +0.8 V (spectroelectrochemistry) in THF/nBu$_4$NPF$_6$ solutions.



Scheme 2. Proposed mechanism for a CF_3 arylation reaction based on [(Phbpy)Ni].

Decomposition of the CF_3 complex

The CF_3 complex [(Phbpy)Ni(CF_3)] decomposes quite rapidly in solution. This was studied by ^1H and ^{19}F NMR spectroscopy, UV/vis absorption spectroscopy and EI-MS. The NMR and MS results clearly show the generation of the CF_3 alkylated Phbpy ligand (6-(2-(trifluoromethyl)phenyl)-2,2′-bipyridine) probably formed through an internal CF_3 transfer. UV/vis absorption and NMR spectroscopy reveal that the process requires about two to 3 h and involve several steps, e.g. intermediate nickel species were observed. For two reasons we will study this process in more detail in the future: *i)* we want to establish the underlying mechanisms which are probably strongly linked to the behaviour under electrolysis (concerted reductive elimination or radical reactions) and *ii)* we want to asses, if in a related process the CF_3 group could be transferred to other substrates and not to the Phbpy ligand, preferably in a catalytic fashion as depicted in Scheme 2.

Conclusions and outlook

The new cyclometalated complex [(Phbpy)NiBr] (Phbpy = 6-(phen-2-yl)-2,2′-bipyridine anion) can be easily prepared from the Br-Phbpy precursor and [Ni(COD)$_2$]. The molecular structure from single crystal XRD shows the tridentate *N,N,C* binding of the $Phbpy^-$ ligand. The bromido complex is probably a very suitable precursor for further Phbpy Ni complexes. In a first example, the complex was reacted with trimethyl(trifluormethyl)silane in the presence of CsF and gave [(Phbpy)Ni(CF_3)] in good yields. UV/vis absorption, electrochemical and spectroelectrochemical investigations of [(Phbpy)NiBr] show interesting differences to the non-cyclometalated but otherwise quite related complex [(bpy)Ni(Mes)Br] (Mes = 2,4,6-trimethylphenyl). On the timescale of the cyclic voltammetry experiments both oxidations and reductions were found to exhibit a high degree of reversibility for the Phbpy systems at ambient temperature, while for the non-cyclometalated derivative irreversible processes were observed throughout. While the Br complex is completely stable in the solid and in solution, the CF_3 complex undergoes cleavage of 2-(CF_3)Phbpy in solution. The product is in agreement with an overall reductive elimination. However, a closer look showed that the underlying mechanism is more complicate and will be subject to further studies. These studies seek to clarify the reactivity details of the mono-reduced or mono-oxidised species (anion cleavage or reductive elimination or radical mechanisms) and will link them to what is observed for the parent complexes. Also, it is intended to establish the bromido complex as “platform” to allow stoichiometric or catalytic CF_3

alkylations of various substrates. Finally, quantum chemical calculations will be carried out to assess the electronic structure of the cyclometalated complexes and shed light on the “stabilising” effect of the ligand Phbpy$^-$ on the products of one-electron oxidation and reduction.

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Appendix A. Supplementary material

CCDC 1017365 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Appendix B. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2014.10.013.

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