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Article

Electrochemistry and Spectroscopy of Organometallic Terpyridine Nickel Complexes

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Organonickel complexes [(R′terpy)Ni(aryl)]X (R′terpy=derivatives of 2,2′;6′,2′′-terpyridine; aryl=2,6-dimethylphenyl= Xyl or 2,4,6-trimethylphenyl=Mes; X=Br or PF_6) have been investigated by multiple electrochemical methods as well as combined electrochemical/spectroscopic techniques (spectroelectrochemistry). Reversible electrochemical reduction fills successively π^* orbitals in the terpy ligand. Some of the occurring species were characterized spectroscopically (EPR and UV/vis/NIR spectroelectrochemistry). The presumably nickel-centered oxidation occurs irreversibly.

Introduction

Organometallic nickel complexes with α-diimine ligands like 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen), or diazabutadienes (R-DAB) have gained an enormous interest in the past decade. This is mainly due to their success as effective catalysts in olefin polymerization or olefin/CO co-polymerization,[1−4] as well as their role in catalytic electro-chemically[4,5] or chemically driven[6] C−C cross-coupling reactions. Associated with this development, an increasing interest in the fundamental investigation of structures, spectroscopic, and electrochemical properties of such organonickel complexes can be stated.[7−13]

During a recent extended study on the use of various α-diimine ligands for nickel catalyzed alkyl−alkyl cross-coupling reactions, Vicic et al. reported that nickel complexes of the potentially tridentate diimine ligand 2,2′;6′,2′′-terpyridine (terpy) and its derivatives turned out to be good candidates, although not dramatically better than some bidentate diimines.[6a] Attempts to isolate and characterize species crucial to the reaction mechanism yielded the reduced methylnickel species [(terpy)Ni(Me)], which is presumably an active species in the catalytic cycle. The nature of this complex can either be described as monovalent nickel [Ni(I)] bound to a neutral terpy ligand (form A in eq 1) or as a reduced terpy ligand bound to a Ni(II) atom (form B). Preliminary electron paramagnetic resonance (EPR) and UV/vis spectra of the reduced species combined with density functional theory

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(DFT) calculations of the singly occupied molecular orbital (SOMO)[6a] and comparison to related platinum systems[14] suggested form B, although further support by spectroelectrochemical measurements is still needed.

$$[(\hat{N}\hat{N}N)Ni(I)(Me)](A) \leftrightarrow [(\hat{N}\hat{N}N^{\cdot-})Ni(II)(Me)(Solv)](B)$$

$$(1)$$
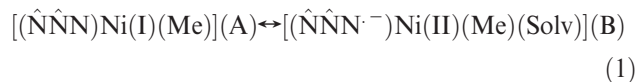
For the related complexes $[(\hat{N}\hat{N})Ni(Mes)Br]$ (N^N = various bidentate α-diimine ligands like bpy, Mes = mesityl) we have recently shown by a combination of electrochemical and spectroelectrochemical experiments that the reduced states can be characterized as mainly diimine ligand centered.[5a,12] Nevertheless, chemical reactivity in these species is centered on the nickel atom: the reduced complexes quickly releases a bromide ligand (Br⁻) to form the radical complexes $[(N^N)Ni(Mes)]^{\cdot}$ which have to be described as diimine anion radicals $N^N^{\cdot-}$ bound to $[Ni(Mes)]^{+}$. As a part of these investigations we have synthesized the complex $[(terpy)Ni(Mes)]Br$ which exhibits two reversible reduction steps because the mesityl co-ligand is not a leaving group.[12] However, the character of the two reduction steps remained unclear.

Having recently prepared a number of arylnickel complexes of terpy and derivatives $[(R'terpy)Ni(aryl)]X$ (R'terpy = terpy, 4'-Cl-terpy (Clterpy), 4'-p-tolyl-terpy (Tolterpy) or $4,4',4''$-^{t}Bu$_3$terpy (Bu$_3$terpy); aryl = 2,6-dimethylphenyl (Xyl) or 2,4,6-trimethylphenyl (Mes); X = Br or PF$_6$),[15] we started a thorough electrochemical and spectroelectrochemical investigation of the reduced states of the parent Ni(II) complexes. Since related Ni(III) species are also supposed to play a role in such C−C coupling reactions,[5,6] we investigated also the oxidized states of the parent Ni(II) complexes. The spectroelectrochemical approach (in situ electrolysis combined with EPR or UV/vis/NIR spectroscopy) has several advantages over bulk chemical or electrochemical synthesis and subsequent spectroscopic investigation. The electrochemical behavior (e.g., cyclic voltammetry) can be directly correlated to spectroscopic responses, the reversibility of electrochemical processes can be easily assessed because of the thin-layer conditions, and additionally, the investigations can be carried out at various temperatures in thermostatted cells.[16]

Experimental Section

General Information. Commercially available reagents (solvents and ligands) from Aldrich or Acros were used without further purification. Solvents were dried by standard procedures. All reactions involving metal complexes were conducted under argon by standard Schlenk techniques. The nickel complexes $[(R'terpy)Ni(aryl)]X$ were prepared as recently described.[15] Their purity was checked by elemental analysis and ^{1}H NMR spectroscopy (full EA, ^{1}H NMR and UV/vis data in the Supporting Information).

Instrumentation. Elemental analyses were obtained using a HEKAtech CHNS EuroEA 3000 analyzer. NMR spectra were recorded on a Bruker Avance 400 spectrometer using a triple resonance ^{1}H,^{19}F,BB inverse probe head. Chemical shifts were
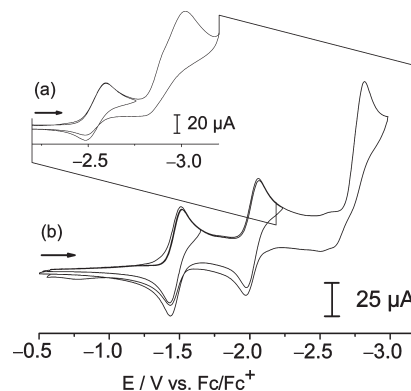
Figure 1. Cyclic voltammograms of terpy (a) and [(terpy)Ni(Xyl)]PF$_6$ (b) in ^{n}Bu$_4$NPF$_6$/MeCN solution at ambient temperature; Potentials vs Fc/Fc$^+$.
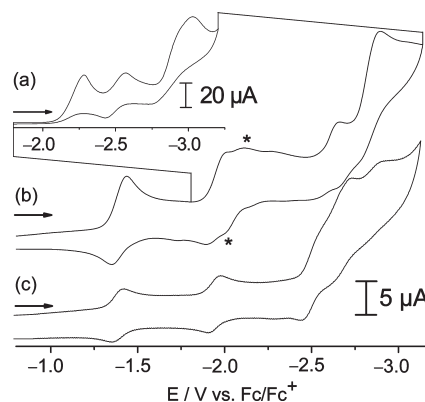
Figure 2. Cyclic voltammograms of Clterpy (a) and [(Clterpy)Ni-(Xyl)]PF$_6$ (b) in ^{n}Bu$_4$NPF$_6$/MeCN solution at ambient temperature and of [(Clterpy)Ni(Xyl)]PF$_6$ at −30 °C (c), potentials vs Fc/Fc$^+$. The * mark a wave corresponding to a decomposition product.

reported relative to tetramethylsilane (SiMe$_4$) as the internal standard. UV/vis/NIR absorption spectra were recorded on Varian Cary 05E or Cary50 Scan spectrophotometers. Cyclic voltammetry was carried out at 100 mV/s scan rate in 0.1 M ^{n}Bu$_4$NPF$_6$ solutions using a three-electrode configuration (glassy carbon electrode, Pt counter electrode, Ag/AgCl reference) and a Autolab PG STAT 30 potentiostat and function generator. The ferrocene/ferrocenium (Fc/Fc$^+$) couple served as internal standard. Spectroelectrochemical measurements (in 0.1 M ^{n}Bu$_4$NPF$_6$ solutions) were performed using optically transparent thin-layer electrode (OTTLE) cells at ambient temperature[17] or at −30 °C (LT-OTTLE cell)[18] for UV/vis/NIR spectra and a two-electrode capillary for EPR studies. EPR spectra were recorded in the X band on a Bruker System ELEXSYS 500E, with a Bruker Variable Temperature Unit ER 4131 VT (500 to 100 K). The g values were calibrated using a dpph sample. GC/MS were obtained using an Agilent 6890 N Network GC system equipped with an Agilent 7683B Series Injector and Agilent 5975 inert mass selective detector, H$_2$ as carrier gas, a HP-5MS column (Macherey-Nagel), and operating in EI mode.

Results and Discussion

Electrochemistry. The free terpy ligands and the complexes $[(R'terpy)Ni(aryl)]X$ both exhibit an irreversible oxidation process and two or more reduction processes.

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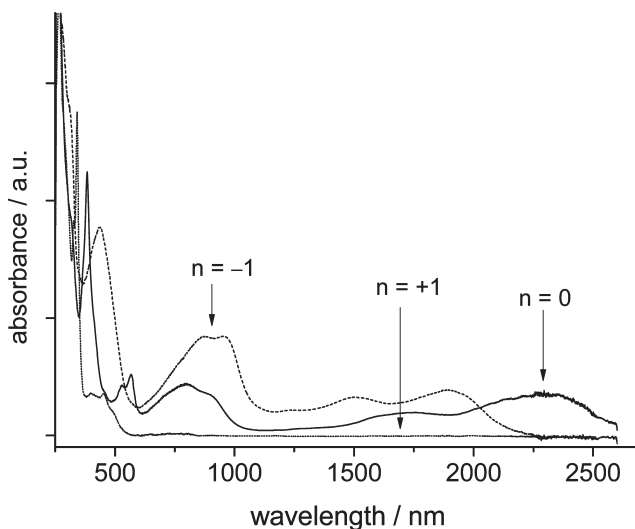
Table 1. Selected Electrochemical Data for Complexes [(R′terpy)Ni(aryl)]X and Free Ligands R′terpy[a]

| compound	$E_{5\ (Ox\ 1)}$ irr.	$E_{1(Red\ 1)}\ (\Delta E_{pp})$[b]	$E_{2\ (Red\ 2)}\ (\Delta E_{pp})$[b]	$E_{3\ (Red\ 3)}$	$E_{Red\ 1} - E_{Red\ 1}$Lig	$E_{Red1} - E_{Red2}$
Bu$_3$terpy	0.97	−2.66 (98)	−3.15 irr. [c]			0.49
Terpy	0.99	−2.55 (62)	−3.06 irr. [c]			0.51
Tolterpy	1.09	−2.44 (68)	−3.02 irr. [c]			0.58
Clterpy	0.77	−2.28 irr. [c]	−2.55 (83)[d]	−3.06 irr.[d]		0.51
[(Bu$_3$terpy)Ni(Xyl)](PF$_6$)	1.21	−1.61 (62)	−2.17 (66)	−3.00 irr.	1.05	0.56
[(terpy)Ni(Xyl)]Br	0.78	−1.48 (60)	−2.03 (62)	−2.86 irr.	1.07	0.55
[(terpy)Ni(Xyl)](PF$_6$)	1.12	−1.48 (63)	−2.02 (64)	−2.85 irr.	1.07	0.54
[(Tolterpy)Ni(Xyl)](PF$_6$)	0.94	−1.46 (59)	−1.99 (62)	−2.78 irr.	0.98	0.53
[(Clterpy)Ni(Xyl)](PF$_6$)	1.13	−1.40 (63)	−1.95 (64)	−2.67 irr.	0.89	0.55
[(Bu$_3$terpy)Ni(Mes)](PF$_6$)	1.08	−1.60 (66)	−2.16 (67)	−2.92 irr.	1.06	0.56
[(terpy)Ni(Mes)]Br	0.76	−1.50 (80)	−2.04 (89)	−2.86 irr.	1.05	0.54
[(terpy)Ni(Mes)](PF$_6$)	0.91	−1.49 (61)	−2.00 (60)	−2.78 irr.	1.06	0.51
[(Tolterpy)Ni(Mes)](PF$_6$)	0.90	−1.47 (64)	−2.01 (63)	−2.80 irr.	0.97	0.54
[(Clterpy)Ni(Mes)](PF$_6$)	1.09	−1.40 (64)	−1.97 (63)	−2.67 irr.	0.89	0.57

[a] From cyclic voltammetry in 0.1 M ^{n}Bu$_4$NPF$_6$/MeCN solutions at 100 mV/s scan rate. Potentials in V vs FeCp$_2^{+/0}$. [b] Half-wave potentials $E_{1/2}$ for reversible processes, peak potential differences $\Delta E_{pp} = E_{pa} - E_{pc}$ in mV in parentheses. [c] Irreversible. [d] These waves correspond to the terpy molecule which is formed after the first irreversible reduction (see text).

Figures 1 and 2 show representative examples, complete cyclic voltammograms including the irreversible oxidation processes are provided in the Supporting Information, and the collected data is summarized in Table 1. Each process comprises one electron, which was established using the Baranski method.[19] The first two reductions were reversible for the nickel complexes, while the third reduction is usually irreversible.

For the free ligands the first reduction process is reversible, while the second is irreversible (Figure 1). For the Clterpy derivative the situation is different. Here the first reduction of the free ligand occurs irreversibly, while the second is fully reversible. A closer inspection reveals that the second and third potential are identical to those of the terpy ligand. Therefore, we assume that after reduction the Clterpy ligand undergoes cleavage of a chloride, and the resulting terpy radical abstracts a hydrogen atom from its surrounding (probably from the solvent). To support this we examined an electrolyzed solution by GC/MS. We found high yields of terpy, but no evidence for the formation of the C−C coupling product bisterpy (6′,6″-bis(2-pyridyl)-2,2′:4,4″:2″,2‴-quaterpyridine) (for details see Supporting Information). Such electrochemical dehalogenation of halogen-containing aromatic systems is not uncommon.[20] Coordination of the Clterpy ligand to Ni(II) leads to a fully reversible first reduction process followed by a second reversible wave (Figure 2). At ambient temperature a small third (reversible) wave very close to the second is observed. Experiments at −30 °C reveal the absence of this small feature (Figure 2, bottom), and we assume that after the second reduction the complex undergoes the same kind of Cl-cleavage reaction observed for the free ligand, however to a much smaller extend. The peculiar electrochemistry of the Clterpy ligand will be further substantiated by spectroelectrochemical (UV/vis/NIR or EPR) experiments (see below).

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Figure 3. Absorption spectra of [(terpy)Ni(Mes)]^n ($n = +1$, dotted line; 0, solid line; and −1, dashed line) from UV/vis/NIR spectroelectrochemistry in DMF/^{n}Bu$_4$NPF$_6$ solutions.
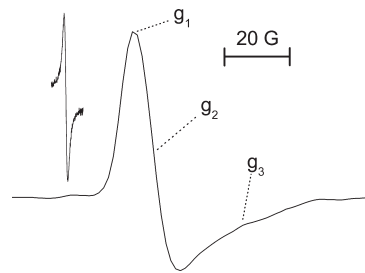
Figure 4. EPR spectra obtained during electrochemical reduction of Tolterpy in THF/Bu$_4$NPF$_6$ (narrow signal at high field, measured at 293 K) and of [(Tolterpy)Ni(Mes)]$^+$ in THF/Bu$_4$NPF$_6$ (rhombic spectrum at lower field with g_1, g_2, and g_3, measured at 110 K).

Table 1 reveals two important things for the assignment of the observed electrochemical processes. First, the nickel complexes undergo two consecutive reductions at electrode potentials which are less negative by approximately 1 V compared to those for the free R′terpy ligands ($E_{Red\ 1} - E_{Red\ 1}$Lig in Table 1). Second, the difference between first and second reduction potential of free

Table 2. Selected UV/vis/NIR Spectroelectrochemical Data of Reduced Species[a,b]

		λ_1 (ε)	λ_2 (ε)	λ_3 (ε)	λ_4 (ε)	λ_5 (ε)
[(Bu$_3$terpy)Ni(Mes)]^n	$n = +1$	324 (17.4)	335 (21.4)	399 (2.7)	448 (2.8)	487sh (1.5)
	$n = 0$	378 (14.5)	575 (4.0)	797 (2.7)	1722 (1.2)	2405 (2.0)
	$n = -1$	315sh (15.2)	430 (10.5)	932 (4.6)	1561 (2.2)	2001 (2.3)
[(terpy)Ni(Mes)]^n	$n = +1$	324 (14.1)	337 (18.4)	401 (2.3)	452 (2.4)	483sh (1.1)
	$n = 0$	392 (13.8)	570 (3.2)	802 (2.6)	1678 (1.2)	2245 (2.1)
	$n = -1$	320sh (17.0)	420 (10.4)	880 (5.0)	1458 (2.0)	1847 (2.2)
[(Tolterpy)Ni(Mes)]^n	$n = +1$	^{c}	337 (20.3)	420 (2.2)	458 (2.3)	505sh (1.1)
	$n = 0$	384 (3.5)	450 (2.3)	797 (2.9)	1529 (0.9)	2008 (0.8)
	$n = -1$	306 (10.5)	464 (3.8)	950 (3.7)	1490 (1.4)	1869 (1.2)
[(Clterpy)Ni(Mes)]^n	$n = +1$	323 (16.8)	332 (20.3)	392 (2.7)	457 (2.8)	480sh (1.6)
	$n = 0$ ^{d}	385 (3.8)	635 (0.9)	1070 (1.8)	1511 (0.6)	1990 (0.4)
	$n = -1$ ^{d}	305 (8.4)	382 (3.7)	1077 (4.3)	1278sh (1.2)	1632 (0.8)

^{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 DMF/0.1 M ^{n}Bu$_4$NPF$_6$ at ambient temperatures. ^{c} Obscured by $\pi-\pi^*$ absorption bands localized in the Tolyl substituent. ^{d} Qualitatively the same spectra were obtained at -30 °C.

Table 3. Selected EPR Spectroelectrochemical Data of Reduced Species[a]

species	g_{iso} (293 K)	g_{av} (LT) ^{b}	g_1 (LT)	g_2 (LT)	g_3 (LT)	Δg (LT)^c
(Bu$_3$terpy)$^{\cdot-}$	2.0029					
(terpy)$^{\cdot-}$	2.0039					
(Tolterpy)$^{\cdot-}$	2.0030					
[(terpy)Ni(Mes)]$^{\cdot}$	2.0006	2.0006	2.009	2.002	1.991	0.018
[(Clterpy)Ni(Xyl)]$^{\cdot}$	2.0025	2.0027	2.009	2.004	1.995	0.014
[(Tolterpy)Ni(Xyl)]$^{\cdot}$	2.0005	2.0005	2.008	2.002	1.991	0.017
[(Tolterpy)Ni(Mes)]$^{\cdot}$	2.0004	2.0004	2.007	2.003	1.991	0.016
[(Bu$_3$terpy)Ni(Xyl)]$^{\cdot}$	2.0006	2.0007	2.008	2.003	1.991	0.017

^{a} Generated by in situ electrolysis in THF/0.1 M ^{n}Bu$_4$NPF$_6$ at ambient temperatures, measured at 293 or 110 K (LT). ^{b} $g_{av} = (g_1 + g_2 + g_3)/3$. ^{c} $\Delta g = g_1 - g_3$. Reduction of Clterpy under the same conditions leads to the observation of the (terpy)$^{\cdot-}$ radical.

ligands and complexes is essentially constant by about 0.55 V ($E_{Red1} - E_{Red2}$). The same (constant) differences have been observed for other transition metal complexes of terpy ligands,[14,21−24] and we conclude that the two reversible reductions in the nickel complexes occur essentially terpy-centered (π^* orbitals). The positive shift of the potentials is probably caused by metal−ligand orbital interactions. Indeed, contributions by admixed nickel orbitals to the terpy π^* lowest unoccupied molecular orbital (LUMO) cannot be ruled out on the basis of electrochemical results, but have to be established from spectroscopic studies of the reduced species. It can also be noted that the influence of the R' substituents on the terpy ligand is not very large, but the observed trends correspond to the expected character of the substituents. Lowest reduction potentials are thus found for R' = ^{t}Bu, while the highest values were obtained for R' = Cl.

Spectroelectrochemistry (UV/vis/NIR and EPR) of the Reduced States. To probe for the character of the reduced states, selected samples were submitted to spectroelectrochemical experiments.[16]

As an example Figure 3 shows the absorption spectra of [(terpy)Ni(Mes)]Br in DMF/^{n}Bu$_4$NPF$_6$ solution taken in situ during cathodic electrolysis. Figure 4 shows representative EPR spectra of reduced radical complexes [(R'terpy)Ni(Mes)]$^{\cdot}$ and free ligands generated by in situ electrolysis; Tables 2 and 3 summarize the obtained data.

Upon the first reduction of the complexes [(R'terpy)-Ni(aryl)]$^+$ several long-wavelength, partly structured absorptions appear in the spectra in the NIR and visible region (Table 2). Furthermore strong bands at around 390 nm were observed, replacing or obscuring the charge transfer absorptions at 428 nm and the intraligand bands at 267 nm. The second reduction leads to spectra which are characterized by two partly structured long-wavelength bands (in the NIR) and a broad and intense band system in the visible. The reverse processes lead in all cases back to the spectra of the starting complexes (more than 95% recovered) assessing thus the complete reversibility of the reductions. Gray et al. have reported dimerization equilibria occurring in the same experiments for [(terpy)PtCl]$^+$ which complicated the spectral assignment.[14] For our nickel derivative we can rule out such phenomena, which is probably due to the mesityl co-ligand shielding the metal center. We can thus ascribe all the bands to the singly or doubly reduced species [(R'terpy)Ni(aryl)]$^{\cdot}$ and [(R'terpy)Ni(aryl)]$^-$, respectively. The two extremely long-wavelength bands are due to intra ligand transitions, since they occur also in the spectra of the reduced free ligand terpy,[22] as well as in the radical complexes [(terpy)Pt(R)]$^{\cdot}$ (R = Cl or Me)[14,23] or [(terpy)ZnCl$_2$]$^{\cdot}$.[14] An interesting feature is the characteristically structured band system observed at 570 nm for [(terpy)Ni(aryl)], which is highly sensitive to both substitution on the 4' position and to the nature of the coordinated metal. In our systems this band is visible for R' = H or ^{t}Bu, while for R' = Tol or Cl it is absent or obscured by other bands. For

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[(terpy)PtCl]$^{\cdot}$ a corresponding band at 543 nm is observed,[14] whereas for [(terpy)ZnCl$_2$]$^{\cdot-}$ and for the free ligand terpy no such bands were found, indicating that a mixed intraligand/metal-to-ligand charge transfer transition might be responsible for this band.

In view of the potential lability of the Clterpy ligand (see Electrochemistry) were examined the spectra of the mono- and doubly reduced complexes containing the Clterpy ligand very carefully for evidence for a Cl-cleavage and the expected in situ formation of terpy complexes. Since the spectra obtained for the Clterpy nickel complexes differ markedly from those of the corresponding terpy complexes (see Table 2) we can, from our experiments rule out an appreciable formation of the latter during out experiments. Additionally we performed experiments at −30 °C and obtained qualitatively identical spectra.

The EPR spectra of the reduced terpy ligands all exhibit unresolved (no hyper-fine splitting) narrow (line width about 5 G) lines centered at around $g = 2.0029$, very close to the value of the "free electron" ($g = 2.0023$) [see, for example, Figure 4]. For the Clterpy ligand we obtained a signal at $g = 2.0038$, which clearly corresponds to the dehalogenated species (terpy)$^{\cdot-}$ in agreement with our further findings. For the reduced complexes at ambient temperature far broader (line width about 40 G), but also unresolved lines were observed with slightly lower g values, except for the 4′-Cl derivative. For this complex the g value is markedly higher but still lies in the typical range expected for largely ligand-centered radicals. It is important to note, that even prolonged electrolysis of this complex does not lead to dehalogenation and formation of the terpy-containing complex species. This can be clearly ruled out from the very different g values of the two species. Thus the reduced Clterpy complex [(Clterpy)Ni(Xyl)]$^{\cdot}$ is stable under the chosen conditions.

At 110 K anisotropic spectra of rhombic symmetry were found. The averaged g value (g_{av}) coincides with the g_{iso} value obtained at ambient temperature, proving that the same species are measured. The g anisotropy Δg of all the four complex radicals is rather small. The values around 0.016 are very similar the g-anisotropy of the low-temperature EPR signal of [(bpy)Ni(Mes)$_2$]$^{\cdot-}$ ($\Delta g = 0.018$ with a g_{av} of 2.0047).[12] The values reported by Vicic for [(terpy)Ni(Me)]$^{\cdot}$ were $\Delta g = 0.057$ and $g_{iso} = 2.021$.[6a]

Thus, the organic co-ligand (methyl or aryl) seems to play a marked role in the distribution of the unpaired electron since both the shape of the EPR spectra and the g anisotropy as well as the isotropic g value shift markedly going from the methyl derivative to the aryl complexes. Within the series of our complexes we can state, that the influence of the R′ substituents on the character of the reduced states is small, with the exception of the 4′-Cl derivative. This is not unexpected since the 4,4′ and 4″ position of terpy is not very susceptible to electronic influence by substituents.[6a]

For the Pt(II) complex [(terpy)PtCl]$^{\cdot}$ a Δg of 0.101 has been reported ($g_{iso} = 1.98$).[14] However, in view of the intrinsically higher spin−orbit coupling for the heavier element Pt(II) [$\zeta_{Pt(II)} \approx 5000$ cm^{-1}, $\zeta_{Pd(II)} = 1460$ cm^{-1}, $\zeta_{Ni(II)} = 630$ cm^{-1}][25] both values yield strong evidence that the admixture of metal orbitals is rather small and that the SOMO is mainly terpy-centered, although from the occurrence of broad lines for the nickel complexes and rhombic spectra in glassy frozen solution we can conclude that it has marked contributions of nickel orbitals.

Conclusion

The results from the electrochemical and spectroelectrochemical studies on a series of terpy-containing organonickel complexes [(R′terpy)Ni(aryl)]X (R′terpy = derivatives of 2,2′;6′,2″-terpyridine; aryl = 2,6-dimethylphenyl = Xyl or 2,4,6-trimethylphenyl = Mes; X = Br or PF$_6$) clearly point to mainly terpy ligand-centered reductions for the nickel complexes with only marginal metal contributions. The variation of the R′ substituents on the terpy ligands yielded only marked alteration of electrochemical and spectroscopic properties for the 4′-Clterpy derivative. The description of the reduced complexes should mainly consider a singly or doubly reduced terpy ligand and Ni(II) [(R′terpy)$^{n-}$Ni(II)-(aryl)]$^{-(n-1)}$, with no evidence for a Ni(I) description. Furthermore, we can confirm that the reduced species studied are relatively stable, at least under the conditions of the spectroelectrochemical experiments (2−30 min). This includes the Clterpy derivatives, in which the ligand is largely stabilized by the coordination to nickel, while the free ligand Clterpy readily disintegrates upon electrochemical reduction yielding terpy.

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