Angewandte Chemie

DOI: 10.1002/anie.200705781

Actinide Complexes

Mixed Valency in a Uranium Multimetallic Complex**

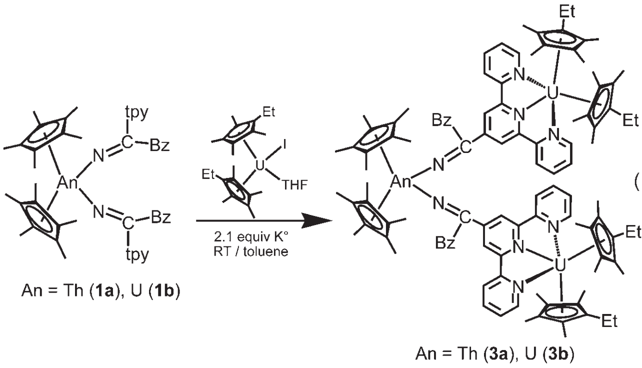
Eric J. Schelter, Ruilian Wu, Brian L. Scott, Joe D. Thompson, David E. Morris, and Jaqueline L. Kiplinger**

The electronic structures of early actinide (Th–Pu) compounds present unique challenges to study because of their very large spin–orbit coupling and appreciable 5f/6d metal–ligand orbital overlap. In fact, it is the interplay of (non)-participating 5f/6d orbitals in bonding that is the primary factor responsible for the unusual properties of Pu metal, which lies at the interface of localized and delocalized (electronically itinerant) behavior in the actinides,[1] and for the emergence of diverse magnetic and conducting phases in early actinide intermetallics.[2]

Recent studies have shown that multimetallic molecular systems may serve as models for understanding electronic structures in complex actinide materials,[3] wherein 5f/6d electrons can span the continuum from corelike and nonbonding to delocalized with appreciable covalent character. Although mixed valency and the corresponding electrochemical, spectroscopic, and magnetic signatures for classical Robin–Day delocalization are well established for multimetallic transition-metal complexes,[4] they are essentially unknown for the actinides.[5]

We previously described the synthesis of $[\mathrm{Cp^*_2An\{N{=}C(Bz)(tpy)\}_2}]$ (An = Th (**1a**), U (**1b**); Bz = $\mathrm{CH_2Ph}$; tpy = 2,2′:6′,2′′-terpyridine; $\mathrm{Cp^* = C_5Me_5}$).[3b] Reaction of **1a**,**b** with the $\mathrm{Yb^{II}}$ precursor $[\mathrm{Cp^*_2Yb(OEt_2)}]$ leads to the formation of the mixed-metal complexes $[\mathrm{Cp^*_2An\{N{=}C(Bz)(tpy\text{-}YbCp^*_2)\}_2}]$ (An = Th (**2a**), U (**2b**)). As these complexes showed the first distinctive signs of 5f–4f metal–metal magnetic and electrochemical communication, we were compelled to prepare the all-actinide analogues in this structural motif. Herein, we report mixed-valent homo- and hetero-trimetallic actinide complexes that show intriguing signs of Robin–Day delocalization.

In the absence of a readily available divalent uranium synthon, we discovered that addition of a slight excess of potassium and two equivalents $[\mathrm{Cp^{\ddagger}_2UI(thf)}]$ ($\mathrm{Cp^{\ddagger} = C_5Me_4Et}$)[6] to **1a**,**b** produced the actinide multimetallic complexes **3a**,**b** [Eq. (1)] in good yields.



(1)

Figure 1 displays the X-ray crystal structure of **3b**, which reveals that the products are consistent with the formulation $[\mathrm{Cp^*_2An\{N{=}C(Bz)(tpy\text{-}An'Cp^{\ddagger}_2)\}_2}]$ (An = $\mathrm{Th^{IV}}$, An′ = $\mathrm{U^{III}}$ (**3a**); An = $\mathrm{U^{IV}}$, An′ = $\mathrm{U^{III}}$ (**3b**)).[6] Comparison of the bond lengths in **3a** and **3b** shows that the structures are very similar. The $\mathrm{An{-}N_{ketimide}}$ bond lengths in **3a** (2.239(5) and 2.247(5) Å) and **3b** (2.162(6) and 2.159(6) Å) are consistent with reported values for other Th/U ketimide complexes.[5a,b,7] Differences in these bond lengths between the $\mathrm{Th^{IV}/U^{IV}}$ congeners are attributed to the approximately 0.05 Å larger ionic radius for the $\mathrm{Th^{IV}}$ ion.[8] The external $\mathrm{U^{III}{-}N_{tpy}}$ bond lengths in **3a**,**b** are identical and range from 2.442(5) to 2.486 Å, while the internal $\mathrm{U^{III}{-}N_{tpy}}$ bond lengths are 2.323(5) and 2.339(5) Å in **3a** and 2.351(5) and 2.352(5) Å in **3b**.

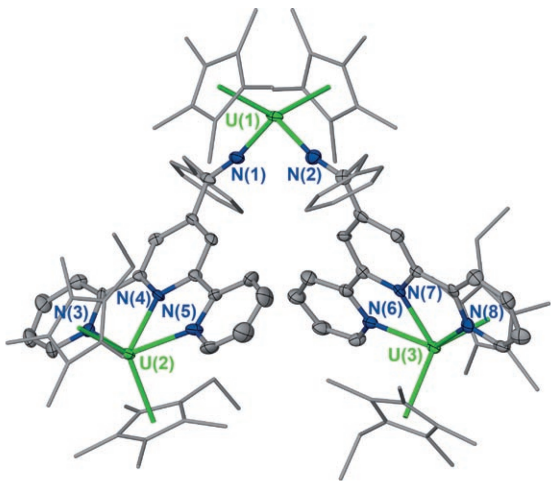


Figure 1. Molecular structure of **3b** with ellipsoids shown at the 50% probability level. A thermal ellipsoid plot of **3a** is provided in the Supporting Information.

---

[*] Dr. E. J. Schelter, Dr. R. Wu, Dr. B. L. Scott, Dr. J. D. Thompson,
Dr. D. E. Morris, Dr. J. L. Kiplinger
Los Alamos National Laboratory
MS J514, Los Alamos, NM 87545 (USA)
Fax: (+1) 505-667-9905
E-mail: demorris@lanl.gov
kiplinger@lanl.gov

[**] For financial support of this work, we acknowledge LANL (Frederick Reines & Director's Postdoctoral Fellowships to E.J.S.), the LANL LDRD Program, and the Division of Chemical Sciences, Office of Basic Energy Sciences, Heavy Element Chemistry program.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

The complex [$Cp^{+}_2U(tpy)$] (**4**) was prepared in a manner similar to that reported for [$Cp^*_2U(tpy)$] for use in elucidation of electrochemical data for **3a**,**b** (see below).[9] Both **4** and [$Cp^*_2U(tpy)$] consist of formal U^{III} ions coordinated by $tpy^{\bullet-}$ ligands. The external U^{III}–N_{tpy} bond lengths in **3a**,**b** are about 0.02 Å longer than those in **4** and [$Cp^*_2U(tpy)$], while the internal bond lengths are slightly shorter (0.03 Å), accounting for standard deviations.

Studies of the magnetic properties of **3a**,**b** were undertaken to detect the presence of a magnetically coupled ground state in **3b**. The structural data afford assignment of the localized valence states, formally $5f^3$ U^{III} ions coordinated by singly reduced terpyridyl–ketimide moieties that contain an unpaired electron and are linked to the An^{IV} metal center through the ketimide group. Figure 2 shows magnetic data for complexes **3a**,**b**. The high-temperature χT product for **3a** attains a value of 2.34 emu K mol^{-1} at 300 K. This result is about twice the reported value for [$Cp^*_2U(tpy)$] of 1.1 emu K mol^{-1} assuming noninteracting U^{III} and $tpy^{\bullet-}$ spin centers at this temperature.[9] The χT product for **3b** is 3.74 emu K mol^{-1} at 300 K, a difference of 1.40 emu K mol^{-1} from that of **3a**, in agreement with the presence of the additional $5f^2$ U^{IV} spin center. The value of 1.40 emu K mol^{-1} for the U^{IV} ion is close to the reported value for **1b** (1.25 emu K mol^{-1})[5b] and to values known for the U^{IV} ion.[5a,10]

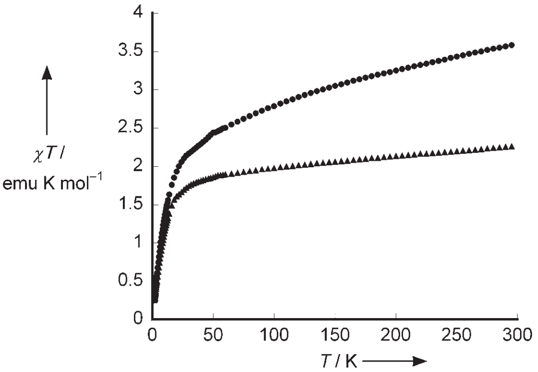


Figure 2. Temperature-dependent χT products of **3a** (bottom data set) and **3b** (top data set).

The χT products for both **3a** and **3b** decrease gradually with temperature down to 50 K, where both decrease sharply. These decreases in the χT vs. T plot are due to ligand field effects of the ions, which lift the degeneracy of their nominal $^3H_4$ (for U^{IV}) and $^4I_{9/2}$ (for U^{III}) terms, quenching their orbital angular momenta. As these ligand field effects comprise the primary temperature dependences of the χT products of these complexes, detection of perturbation of their susceptibilities from magnetic coupling interactions is not possible. We and others have employed subtraction techniques using diamagnetic analogues to elucidate signatures of magnetic coupling in f-element complexes.[5b,11] However, the number of spin centers, complexity of the system, and a shortage of suitable analogues to accurately reproduce the ligand field effects in this case preclude reliable detection of magnetic coupling in **3b** using this method.

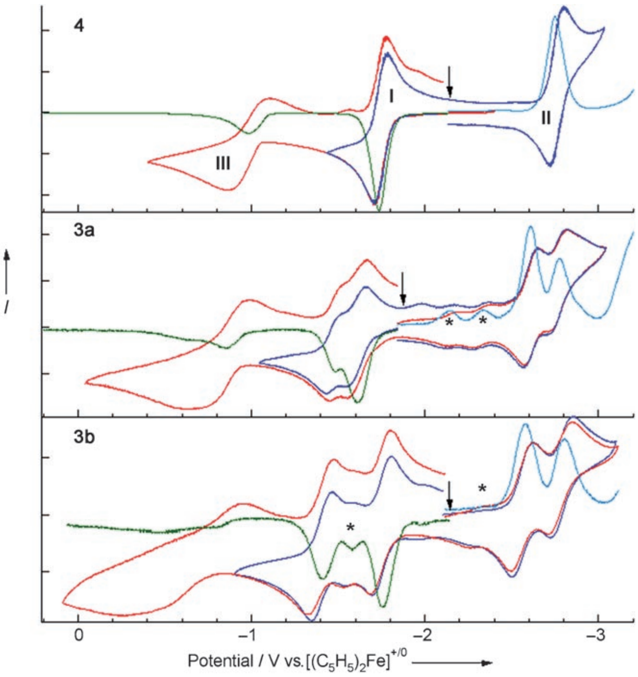


Figure 3. Cyclic (200 mV s^{-1}; red and blue traces) and square-wave (pulse height 10 mV, frequency 60 Hz; green and light blue traces) voltammograms in 0.1 M [Bu_4N][$B(C_6F_5)_4$]/THF. Current is shown in arbitrary units. Vertical arrows indicate rest potentials for each system. Waves associated with impurities and/or decomposition products are denoted with asterisks. Waves I–III are described in the text.

Table 1: Data from cyclic and square-wave voltammetry experiments.[a]

Cmpd	U^{IV}/U^{III}	$tpy^0/tpy^{\bullet-}$	$tpy^{\bullet-}/tpy^{2-}$
4	−0.98	−1.74	−2.75
3a	−0.70, −0.86	−1.47, −1.61	−2.61, −2.78
3b	−0.48, −0.79	−1.41, −1.76	−2.58, −2.80
1a	n.a.	−2.42, −2.63	n.o.
1b	−2.42	−2.25, −2.53	n.o.
free tpy		−2.66	n.o.

[a] Potentials are $E_{1/2}$ values in V vs. [$(C_5H_5)_2Fe$]$^{+/0}$ derived from peaks in SWV scans. For quasi-reversible U^{IV}/U^{III} couples, SWV peaks are only approximate indicators of $E_{1/2}$ values; see reference [12]. n.a. = not applicable. n.o. = not observed under these experimental conditions.

The clearest evidence for electronic interactions between the metal centers in these complexes comes from the electrochemical data (Figure 3 and Table 1). For **4**, wave I is ascribed to oxidation of $tpy^{\bullet-}$ to the neutral ligand, wave II to reduction of $tpy^{\bullet-}$ to the ligand dianion (tpy^{2-}), and wave III to oxidation of the metal center (U^{IV}/U^{III}). These assignments are based on comparison of data for the ytterbocene complex [$Cp^*_2Yb(tpy)$] and free tpy ligand, and on the observed electron-transfer kinetic behavior consistent with our observations for other f-element metallocenes that the rates for the metal-based oxidation are generally slower than for the ligand-based processes that exhibit nearly reversible electron-transfer behavior.[12] Square-wave voltammetry (SWV) data were collected to assist in resolving closely spaced waves, but these data for **4** provide a vivid illustration that the SWV peaks for quasi-reversible processes (e.g., the U^{IV}/U^{III} wave) are diminished in peak current, broadened, and are less symmetric relative to peaks for reversible processes (e.g., the tpy-based waves) as noted previously.[13] The positive shift of the tpy-based redox couples in the complex relative to that of the free ligand (Table 1) is consistent with behavior observed in other transition-metal and f-element complexes and results from stabilization of the ligand π^* orbitals from chelation to the metal center. Much more notable is the approximate 1–1.5 V positive shift of the U^{IV}/U^{III} couple relative to its potential in tetravalent $[Cp^*_2UL_2]$ complexes (L = halide, alkyl, ketimide).[12a] This remarkable stabilization of the trivalent oxidation state in **4** can be attributed to U→tpy π backbonding as noted in other low-valent uranium complexes.[14]

For **3a** and **3b**, each of the three redox processes identified in Figure 3 for **4** splits into two discrete components. For two equivalent but noninteracting redox centers, the two voltammetric waves should be unresolvable (ca. 36 mV theoretical separation[15]) even by SWV. In **3a**,**b** significant splittings between each pair of waves are seen (Table 1), demonstrating electronic communication between these centers. Notably, the splittings are larger in all cases for the U^{IV} bridge than for the Th^{IV} bridge. This observation was noted previously for precursors **1a**,**b** (Table 1) and ascribed to the enhanced ability of the U^{IV} bridge with its occupied valence orbitals to induce stronger coupling between the peripheral tpy moieties. The interaction must occur through the central metal bridge; otherwise the result would be the same for both Th and U systems. Redox activity was also anticipated for the U^{IV} center in **3b**, comparable to that reported previously for **1b**.[3b] No distinct waves attributable to either oxidation or reduction of this center were identified. We believe this is a result of substantial perturbations to the redox energetics of the U^{IV} ketimide arising from the π^*-electron density on the tpy ligands.

UV/Vis/NIR absorption data[6] for **3a**,**b** and **4** provide no additional insight into interactions among the metal centers in these complexes because the spectra are dominated over the entire energy range by intense, broad, vibronically structured bands localized on the tpy radicals that have been assigned to allowed π–π^* and π^*–π^* transitions. In particular, no f–f bands for either U^{III} or U^{IV} or potential intervalence charge-transfer bands between these centers are resolved, presumably because of the much lower oscillator strengths anticipated for such transitions.

We have developed a general procedure for the synthesis of a set of mixed-valent $An^{IV}U^{III}_2$ complexes (An = Th, U) and determined that their valences are best described as "trapped". Conclusions regarding the true magnetic ground state of **3b** remain elusive because of the usual obfuscation of evidence for magnetic coupling in the susceptibility by ligand field signatures of the uranium ions, but the possibility of a magnetically coupled ground state in these complexes cannot be discounted. Similarly, electronic absorption signatures of delocalization (e.g., U^{III}–U^{IV} intervalence transitions) are obscured by intense π–π^* transitions localized on the reduced tpy groups. Magnetic circular dichroism experiments are currently planned to elucidate the presence of such transitions in **3b**.

Experimental Section

All manipulations were performed in either a recirculating Vacuum Atmospheres (Model HE-553-2 with a MO-40-2 Dri-Train or NEXUS with a 40CFM Dual Purifier NI-Train) drybox (N_2), or by using standard Schlenk line techniques.

3a: Potassium mirror (0.034 g, 0.87 mmol, 2.1 equiv) was prepared on the bottom of a 125-mL side-arm flask, and toluene (30 mL) was added. With stirring, **1a** (0.50 g, 0.42 mmol) and $[Cp^+_2U(I)(thf)]$ (0.64 g, 0.87 mmol, 2.1 equiv) were added simultaneously, producing a dark green solution that was stirred at room temperature for 48 h. Over this time the reaction mixture became dark blue in color and a solid precipitated from the solution. The solution was filtered through a celite-padded coarse frit, and the filtrate was collected and concentrated to 5 mL under reduced pressure. Solid **3a** was precipitated from the toluene solution with addition of $(Me_3Si)_2O$ (50 mL). Crystalline, analytically pure **3a** was obtained from saturated solutions of $(Me_3Si)_2O$/toluene (10:1 v/v) set at room temperature for three days. Yield: 0.59 g, 0.24 mmol (62%). ^1H NMR ($[D_8]$toluene, 100°C): $\delta = 17.88$ (brs, 12H, $C_5Me_4(CH_2CH_3)$), 12.22 (brs, 24H, $C_5(CH_3)_2(CH_3)_2Et$), 11.47 (brs, 24H, $C_5(CH_3)_2(CH_3)_2Et$), 4.54 (brs, 2H, *p*-H in Bz), 3.84 (brs, 4H, ArH), 2.93 (brs, 8H, $C_5Me_4(CH_2CH_3)$), 0.64 (brs, 4H, CH_2Ph), −0.23 (s, 30H, $C_5(CH_3)_5$), −2.15 (brs, 4H, ArH), −3.04 (brs, 4H, ArH), −16.84 (brs, 4H, ArH), −19.38 (brs, 8H, ArH), −24.05 ppm (brs, 4H, ArH). Elemental analysis (%) calcd for $C_{110}H_{131}N_8U_2Th\cdot 2(C_6H_{18}OSi_2)$ (2596.37 $g\,mol^{-1}$): C 56.40, H 6.48, N 4.31; found: C 56.67, H 6.55, N 4.36.

3b: The synthesis of **3b** is analogous to that of **3a**. Yield: 0.638 g, 0.258 mmol (60%). ^1H NMR ($[D_8]$toluene, 90°C): $\delta = 18.02$ (brs, 12H, $C_5Me_4(CH_2CH_3)$), 12.75 (brs, 24H, $C_5(CH_3)_2(CH_3)_2Et$), 11.97 (brs, 24H, $C_5(CH_3)_2(CH_3)_2Et$), 4.93 (brs, 2H, *p*-H in Bz), 4.13 (brs, 4H, ArH), 3.60 (brs, 8H, $C_5Me_4(CH_2CH_3)$), 1.20 (brs, 4H, CH_2Ph), −4.25 (s, 30H, $C_5(CH_3)_5$), −23.75 (brs, 4H, ArH), −87.09 ppm (brs, 4H, ArH), additional tpy-H resonances were not observed. Elemental analysis (%) calcd for $C_{110}H_{131}N_8U_3$ (2279.36 $g\,mol^{-1}$): C 57.96, H 5.79, N 4.92; found: C 57.95, H 5.69, N 5.14.

Received: December 12, 2007

Keywords: actinides · electrochemistry · magnetic properties · mixed-valent compounds · uranium

---

[1] D. L. Clark, S. S. Hecker, G. D. Jarvinen, M. P. Neu in *The Chemistry of the Actinide and Transactinide Elements*, *Vol. 2* (Eds: L. R. Morss, N. M. Edelstein, J. Fuger), Springer, Dordrecht, **2006**, pp. 813–1264.

[2] a) J. D. Thompson, T. Park, N. J. Curro, F. Ronning, R. Movshovich, E. D. Bauer, J. L. Sarrao, *J. Magn. Magn. Mater.* **2007**, *310*, 532–535; b) N. J. Curro, T. Caldwell, E. D. Bauer, L. A. Morales, M. J. Graf, Y. Bang, A. V. Balatsky, J. D. Thompson, J. L. Sarrao, *Nature* **2005**, *434*, 622–625.

[3] a) E. J. Schelter, P. Yang, B. L. Scott, J. D. Thompson, R. L. Martin, P. J. Hay, D. E. Morris, J. L. Kiplinger, *Inorg. Chem.* **2007**, *46*, 7477–7488; b) E. J. Schelter, J. M. Veauthier, J. D. Thompson, B. L. Scott, K. D. John, D. E. Morris, J. L. Kiplinger, *J. Am. Chem. Soc.* **2006**, *128*, 2198–2199; c) J. L. Kiplinger, J. A. Pool, E. J. Schelter, J. D. Thompson, B. L. Scott, D. E. Morris, *Angew. Chem.* **2006**, *118*, 2090–2095; *Angew. Chem. Int. Ed.* **2006**, *45*, 2036–2041.

[4] P. N. Schatz in *Inorganic Electronic Structure and Spectroscopy, Vol. 2* (Eds: E. I. Solomon, A. P. B. Lever), Wiley, New York, **1999**, pp. 175–226.

[5] a) P. B. Duval, C. J. Burns, W. E. Buschmann, D. L. Clark, D. E. Morris, B. L. Scott, *Inorg. Chem.* **2001**, *40*, 5491–5496; b) G. Nocton, F. Burdet, J. Pecaut, M. Mazzanti, *Angew. Chem.* **2007**, *119*, 7718–7722; *Angew. Chem. Int. Ed.* **2007**, *46*, 7574–7578; c) C. P. Larch, F. G. N. Cloke, P. B. Hitchcock, *Chem. Commun.* **2008**, 82–84.

[6] See the Supporting Information for synthesis and characterization details.

[7] a) E. J. Schelter, P. Yang, B. L. Scott, R. E. Da Re, K. C. Jantunen, R. L. Martin, P. J. Hay, D. E. Morris, J. L. Kiplinger, *J. Am. Chem. Soc.* **2007**, *129*, 5139–5152; b) K. C. Jantunen, C. J. Burns, I. Castro-Rodriguez, R. E. Da Re, J. T. Golden, D. E. Morris, B. L. Scott, F. L. Taw, J. L. Kiplinger, *Organometallics* **2004**, *23*, 4682–4692.

[8] R. D. Shannon, *Acta Crystallogr. Sect. A* **1976**, *32*, 751–767.

[9] T. Mehdoui, J. C. Berthet, P. Thuery, L. Salmon, E. Riviere, M. Ephritikhine, *Chem. Eur. J.* **2005**, *11*, 6994–7006.

[10] a) E. A. Boudreaux, L. N. Mulay, *Theory and Applications of Molecular Paramagnetism*, Wiley, New York, **1976**; b) J. Grunzweig-Genossar, M. Kuznietz, F. Friedman, *Phys. Rev.* **1968**, *173*, 562–573; c) P. Gans, J. Marriage, *J. Chem. Soc. Dalton Trans.* **1972**, 46; d) D. G. Karraker, J. A. Stone, *Inorg. Chem.* **1972**, *11*, 1742–1746; e) L. Salmon, P. Thuery, E. Riviere, S. Miyamoto, T. Yamato, M. Ephritikhine, *New J. Chem.* **2006**, *30*, 1220–1227; f) I. Castro-Rodriguez, K. Meyer, *Chem. Commun.* **2006**, 1353–1368.

[11] a) J.-P. Costes, F. Dahan, A. Dupuis, J. P. Laurent, *Chem. Eur. J.* **1998**, *4*, 1616–1620; b) L. Salmon, P. Thuery, E. Riviere, J. J. Girerd, M. Ephritikhine, *Dalton Trans.* **2003**, 2872–2880; c) J. P. Sutter, M. L. Kahn, *Magnetism: Molecules to Materials V*, Wiley-VCH, Weinheim, **2005**, pp. 161–187; d) S. A. Kozimor, B. M. Bartlett, J. D. Rinehart, J. R. Long, *J. Am. Chem. Soc.* **2007**, *129*, 10672–10674.

[12] a) D. E. Morris, R. E. Da Re, K. C. Jantunen, I. Castro-Rodriguez, J. L. Kiplinger, *Organometallics* **2004**, *23*, 5142–5153; b) C. R. Graves, B. L. Scott, D. E. Morris, J. L. Kiplinger, *J. Am. Chem. Soc.* **2007**, *129*, 11914–11915.

[13] a) J. J. O'Dea, J. Osteryoung, R. A. Osteryoung, *Anal. Chem.* **1981**, *53*, 695–701; b) M. J. Nuwer, J. J. O'Dea, J. Osteryoung, *Anal. Chim. Acta* **1991**, *251*, 13–25.

[14] a) P. Roussel, W. Errington, N. Kaltsoyannis, P. Scott, *J. Organomet. Chem.* **2001**, *635*, 69–74; b) M. Mazzanti, R. Wietzke, J. Pecaut, J. M. Latour, P. Maldivi, M. Remy, *Inorg. Chem.* **2002**, *41*, 2389–2399; c) T. Mehdoui, J. C. Berthet, P. Thuery, M. Ephritikhine, *Dalton Trans.* **2005**, 1263–1272.

[15] A. J. Bard, L. R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, 2nd ed., Wiley, New York, **2001**, p. 246.