

DOI:10.1002/ejic.201400076

ChemPubSoc Europe

The Synthesis of Dimeric Re^I–Phenylenediimine Conjugates: Spectroscopic and Electrochemical Studies

Abed Hasheminasab,^[a] James T. Engle,^[a] Jacob Bass,^[b] Richard S. Herrick,^{*[b]} and Christopher J. Ziegler^{*[a]}

Dedicated to Professor Joe Templeton on the occasion of his 65th birthday

Keywords: Rhenium / Dimers / Bridging ligands / UV/Vis spectroscopy / Cyclic voltammetry

A series of dimeric Re^I(CO)₃ compounds have been prepared by means of a one-pot reaction of [Re(CO)₅X] (X = Cl, Br), pyridine-2-carboxyaldehyde, and *o*-, *m*-, or *p*-phenylenediamine. For the *m*- and *p*-substituted phenylenediamine reactions, phenyl-bridged bis(pyridine-2-carbaldimine) compounds of the formula [Re(CO)₃X]₂(μ -PPC) [**3**–**7**; X = Cl, Br; μ -PPC = *m*- or *p*-phenylene bis(pyridine-2-carbaldimine)] were produced, with *m*-phenylenediamine forming a mixture of isomers. For reactions with *o*-phenylenediamine, multiple products formed (compounds **8–11**), which ranged from the

Introduction

Over the past few decades, organometallic complexes of the general type $[\text{Re}(X)(\text{CO})_3(\text{diimine})]$ (X = Cl, Br) have received much attention owing to their potential use in photophysical applications as emission sensitizers, photosensitizers, photooxidants, photocatalysts, and electrocatalysts.^[1-6] These compounds have absorptions in the visible spectrum with long-lived excited states that frequently arise from metal-to-ligand charge transfer (MLCT) transitions. Interest in these compounds is driven by their attractive features, including a stable low-spin d⁶ rhenium metal center and the ability to tune their photophysical properties by varying the diimine ligand, the sixth ligand (such as the halide), and solvent.^[7,8]

The chemistry and properties of Re^I complexes containing bidentate heterocyclic diimine ligands, such as 2,2'-bipyridine, 1,10-phenanthroline, and their derivatives, have been extensively investigated.^[9–12] In addition to these traditional ligands, the chemistry of substituted 1,4-diazabutadi-

http://www.uakron.edu/chemistry/faculty-staff/ziegler.dot [b] Department of Chemistry, College of the Holy Cross, Department of Chemistry, College of the Holy Cross,

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201400076.

desired *o*-phenylene bis(pyridine-2-carbaldimine) adduct to 2-pyridylbenzimidazole and bridging dipyridinylquinoxaline complexes. An example of each complex was structurally elucidated by single-crystal X-ray methods. The dimeric *m*-and *p*-phenylene-bridged Re(CO)₃X compounds, including a sulfonate derivative designed to improve solubility, were investigated for possible photophysical applications through the use of UV/Vis spectroscopy and cyclic voltammetry; the study revealed coupling between the rhenium centers.

enes (DAB) has also gained significant attention.^[13–17] For several years, we have been investigating the syntheses of Re(CO)₃ compounds with DAB-type ligands by means of metal-mediated one-pot reactions that involve Schiff base condensation.^[18–20] Relative to traditional aromatic diimine ligands like bipyridine or phenanthroline, DAB complexes have lower π^* -orbital energies. Additionally, the absorption properties can be tuned by means of the ligand electronic structure to increase diffusion time and thus minimize hole– electron recombination, which is important for various photophysical applications.^[15,21–27]

We have recently started to investigate dimeric $\text{Re}(\text{CO})_3$ complexes as part of our research into the synthesis of peptide-based Re/Tc imaging agents. We found that $\text{Re}(\text{CO})_3$ dimers could be produced in one-pot reactions with amino acids or peptides.^[18,28] We found that pyridine-2-carboxyaldehyde, when treated with amino acids under one-pot conditions, resulted in dimers with chelating diamines (pyridine-2-carbaldimine; pyca) bound to the metal centers.^[18] These compounds exhibit MLCT transitions, and we hypothesized that similar synthetic methods could be used to generate binuclear $\text{Re}(\text{CO})_3$ compounds for photophysical applications.

There have been many examples of bridged $\text{Re}(\text{CO})_3$ complexes, and it has been shown that the identity of the bridging unit affects the degree of coupling between the two coordination complexes. Connick and co-workers published a study on binuclear $\text{Re}(\text{CO})_3$ compounds, in which the

 [[]a] Department of Chemistry, University of Akron, OH 44325-3601, USA
 E-mail: ziegler@uakron.edu

Box C, Worcester, MA 01610-2395, USA http://academics.holycross.edu/chemistry/faculty-staff/herrick





Figure 1. Compounds reported in this work.

bridging unit is a cyclophane linked to two chelating units constructed from pyridine-2-carbaldimines.^[29] These types of bridged complexes exhibit metal-metal interactions upon reduction, as demonstrated by cyclic voltammetry. Additionally, the bridging unit not only affects the MLCT interaction but also alters the metal-metal interactions and intramolecular electron transfer depending on the type, size, aromaticity, and conjugation of the bridge.[30-37] In addition, heterodentate bridging ligands have been found to be useful in designing binuclear and trinuclear complexes.^[38-40] Included in the study by Connick et al. was one complex in which two pyridine-2-carbaldimine Re-(CO)₃ centers are bridged by a para-substituted benzene ring.^[29] We hypothesized that the degree of coupling between Re(CO)₃ centers might depend on the position of substitution on the phenylene ring. Having experience with the preparation and characterization of d⁶ rhenium pyridine-2-carbaldimine compounds,^[18-20] we decided to explore this area further.

Herein, we report a series of binuclear Re^I complexes bridged by a phenylene bis(pyridine-2-carbaldimine) (PPC) ligand constructed from an *o*-, *m*-, or *p*-phenylenediamine and pyridine-2-carbaldehyde by using one-pot conditions (Figure 1). The *para*-substituted version of this ligand has been referred to as *p*-phenylenebis(picolinaldimine) by Connick and co-workers,^[29] and could alternatively be described as *p*-phenylenebis(2-pyridinylmethyleneamine). In our procedures, pyridine-2-carbaldehyde and phenylenediamines were mixed in the presence of [Re(CO)₅X] (X = Cl, Br) to form dimeric Schiff base complexes with bridging PPC ligands (compounds **3**–7). We also prepared com-

pound 5 with a pendant sulfonate that had enhanced solubility. As controls to better understand the effects of dimerization, we also generated monomeric compounds 1 and 2; to the best of our knowledge, 1 is a new compound, whereas 2 was previously synthesized.^[41–45] Additionally, the binuclear compound 3 has been previously generated but was not structurally elucidated.^[29] Analogous reactions with ophenylenediamine resulted in multiple compounds, including the desired o-PPC adduct (8) as well as 2-pyridylbenzimidazole (11), bridging dipyridinylquinoxaline (9), or benzimidazole (10) complexes. For the desired p- and m-PPC complexes, we recorded UV-visible absorption spectra and performed cyclic voltammetry experiments to confirm that the bridging phenylene unit does mediate coupling between the Re(CO)₃X coordination complexes. In the cyclic voltammetry experiments, we observed coupled two-electron redox behavior, and the reversibility was mediated by the identity of the halide.

Results and Discussion

Syntheses and Structures

As previously demonstrated in our work^[18–20] and in the work of Miguel et al.,^[46–48] chelating aldehydes readily react with primary amines in the presence of $[\text{Re}(\text{CO})_5\text{X}]$ to afford the corresponding Schiff base compounds (Scheme 2). For example, mononuclear Re^I complexes 1 and 2 were synthesized by using this method for use as controls in this study. Compound 2 has been previously generated,^[41–44] but we observed a new crystal form. Compound 1 has neither

2644



been synthesized nor structurally elucidated prior to this study, but similar compounds have been generated.^[13–17,44,49,50] In prior work, the Schiff bases were synthesized first, typically through mixing the aniline or phenylene diamine with pyridine-2-carbaldehyde in dry methanol for 20 min to afford a pale yellow solution that contained the Schiff base product. Generally, these Schiff bases are sensitive to hydrolysis, which makes them prone to degradation. We found that one-pot conditions that contained the phenylenediamine, [Re(CO)₅X], and pyridine-2-carbaldehyde produce the desired metal-bound Schiff base complexes in reasonable yields (Scheme 1). The reactions were readily monitored through the formation of a red solution owing to the formation of products with metal-to-ligand charge-transfer bands.



Scheme 1. Synthesis of monomeric complexes 1 and 2.

Compounds 1 and 2 were soluble in hot solvents such as methanol and THF. Crystals suitable for X-ray diffraction structural elucidation were collected through slow cooling and solvent evaporation. The structures of these compounds, shown in Figure 2, reveal the expected bidentate coordination mode of the pyridineimine and diazabutadiene ligands on 1 and 2, respectively, as well as the standard facial $\text{Re}(\text{CO})_3$ unit.

For the bridged *p*- and *m*-PPC compounds, we were able to isolate the corresponding dimeric adducts 3-7(Schemes 2 and 3). All four compounds showed limited solubility in most solvents, with the exception of the sulfonatemodified compound **5**, which exhibited increased solubility. We were able to structurally elucidate the *p*-phenylenediamine compound **5** and both *m*-phenylene compounds **6** and 7, but we were unable to isolate suitable crystals of **3** or **4**. The structures of **5**–7 are shown in Figures 3 and 4.

For compound 5, the structural features of the Re^I centers are in good agreement with previously elucidated Re(CO)₃(diimine) compounds and monomeric species such as $2^{[43-45]}$ Owing to the presence of the sulfonate group, free rotation of the adjacent C–N bond is hindered, but the opposite C–N bond [bound to the Re(1) center] is free to rotate. For compound 5, one can consider the formation of two possible isomers in the dimer structure, which results from the presence of chlorides either on the same side or on opposite sides of the phenylenediimine plane. However, in the ¹H NMR spectra of 3 and 4, we observed only one imine proton resonance, and in the elucidated structure of 5, we observed only one of the two isomers. It is important



Figure 2. The structures of monomeric complexes 1 and 2 with 35% thermal ellipsoids. Hydrogen atoms have been omitted for clarity.



Scheme 2. Synthesis of binuclear complexes **3**, **4**, **6**, and **7** from the reaction of pyca and *m*- or *p*-phenylenediamine.



Scheme 3. Synthesis of complex 5.



Figure 3. The structures of binuclear complex 7 with 35% thermal ellipsoids. Hydrogen atoms have been omitted for clarity. Compound **6** has an identical structure but shows some disorder along the Cl(2)–Re(2)–CO axis (see the Supporting Information).



Figure 4. The structure of sulfonate-modified binuclear complex **5** with 35% thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

to note that the appearance of one resonance in the NMR spectra might be due to the similarity in chemical shift for the imine proton in both isomers, and the observation of a single isomer in the crystal structure does not rule out the existence of the alternate isomer.

Compounds 6 and 7 also exhibit the expected structural features around the two rhenium atoms in these dimers. Isomerization is clearly observed in the NMR spectra and X-ray structures of 6 and 7, with the halides observed on both the same side and on opposite sides of the phenylenediimine plane (Figure 3). In the crystal structures, these two compounds exhibit a chiral twist around a C_2 axis that is coincident with that of the phenylenediimine unit. We observe both enantiomers in each crystal structure in addition to the two diastereomers that result from the orientation of the halide atoms. We believe that the two twist enantiomers might be able to interconvert through rotation about the C– N bonds of the phenylenediimine units.

The reactions of o-phenylenediamine with pyridine-2carbaldehyde and [Re(CO)₅X] did not exclusively produce

the desired dimeric compounds. Instead, we observed the formation of mixtures of different compounds, as shown by the reactions in Scheme 4. We were able to isolate crystals of four different products (Figure 5), but we were not able to successfully control these one-pot reactions to exclusively produce the desired dimeric compounds and we were not able to purify the compounds from these mixtures. Three of the four compounds were obtained from reactions with $[Re(CO)_5Cl]$ and one with $[Re(CO)_5Br]$. The primary product of these reactions is (2'-pyridyl)benzimidazole complexes of Re(CO)₃, such as compound 10. The formation of these compounds is not surprising, as o-phenylenediamine will react with pyridine-2-carbaldehyde to form the free (2'pyridyl)benzimidazole. Upon treating o-phenylenediamine with pyridine-2-carbaldehyde in the absence of metal, we never observed the formation of the desired free o-PPC ligand, in contrast to prior reports.^[51-53] We also observed a second (2'-pyridyl)benzimidazole complex that resulted from the addition of a second equivalent of pyridine-2carbaldehyde to the exterior nitrogen site on the ligand, compound 11. We did observe the formation of a small amount of the desired compound 8. However, we additionally observed that this compound could ring close to form a dimeric Re(CO)₃X compound with a bridging dipyridinylquinoxaline unit (9). Our observations on these compounds parallel those seen by Chattopadhyay and co-workers on a series of similar reactions with $[Ru(bpy)_2]$ (bpy = 2,2'bipyridyl) reagents.[54]



Scheme 4. Observed products from the reaction between pyca and *m*-phenylenediamine.

One characteristic resonance for these compounds is the imine-bound hydrogen atom, which appears in the deshielded region of $\delta = 9.0-9.5$ ppm. As discussed above, for



Figure 5. The structures of complexes **8**, **9**, **10**, and **11** with 35% thermal ellipsoids. Hydrogen atoms have been omitted for clarity. Compound **11** shows a half-occupied solvent water molecule hydrogen-bound to the free pyridine nitrogen atom.

compounds that exhibit isomerism, we can readily observe the presence of two structurally similar isomers in the NMR spectra. The IR spectra of compounds 1–7 show either two or three distinct carbonyl stretching frequencies between 2030 and 1860 cm⁻¹. The pseudo- $C_{3\nu}$ symmetry that results from a facial arrangement of carbonyls at the Re centers will produce stretches that correspond to the a_1 and e vibrational modes; however, deviations from $C_{3\nu}$ cause the e mode to split in some cases.

Re(CO)₃ diimine complexes with pendant aromatic rings show two types of electronic absorption in the UV-visible spectrum. First, there are higher-energy absorptions between 300 and 350 nm that comprise intraligand bands that could result from $\pi \rightarrow \pi^*$ transitions. These bands are not sensitive to solvent changes, which is indicative of $\pi \rightarrow \pi^*$ character. Additionally, there are lower-energy bands located between 400–450 nm that result from metal-to-ligand charge transfer (MLCT) transitions. These bands exhibit solvatochromism, and increasing the dielectric constant of the solvent will shift the position to the lower wavelengths. This solvatochromism was examined by Connick et al.^[29] in their previous report on **3**. Experiments that show the solvent dependency of these MLCT bands can be found in the Supporting Information. The electronic structure of the diimine does affect the magnitude of the extinction coefficient for these MLCT transitions, as can be seen between diazabutadiene compound 1 ($\varepsilon = 3.34 \times 10^3 \text{ m}^{-1} \text{ cm}^{-1}$) and pyca complex 2 ($\varepsilon = 5.55 \times 10^3 \text{ m}^{-1} \text{ cm}^{-1}$). The dimeric complexes exhibit more intense MLCT absorptions than the corresponding monomeric compounds, with the highest values for the *p*-phenylenediamine-bridged dimers (**3–5**) relative to the *m*-phenylenediamine variants (**6**, **7**).

Cyclic Voltammetry

The redox potentials for solutions of compounds 1–7 in dimethylformamide (DMF) were determined using 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as the electrolyte. Scan rates between 0.10 to 0.50 V s⁻¹ were examined, whereas the best sensitivity was observed at $10.0 \,\mu\text{AV}^{-1}$. Generally, Re^I–carbonyls show irreversible oxidations near approximately 1.5 V; however, the reduction potentials are readily observable and reversible in solution



in DMF. The cyclic voltammograms for the cathodic region for compounds 1-7 are shown in Figure 6, and Table 1 lists the observed reduction potentials along with other parameters. For the monomeric compounds 1 and 2, we observe very different reduction chemistry. Compound 1 shows multiple reductions and some irreversible behavior owing to the redox activity of the diazabutadiene unit.^[30-32] Compound 2 shows much cleaner redox behavior, with a single reduction that can be assigned to the rhenium pyridine imine complex. For the dimeric compounds 3-7, we observe two well-defined separated reversible reductions. For the pphenylenediamine-bridged compounds, the reductions are separated by 188 and 178 mV, respectively, for 3 and 4. We observe slightly smaller separations for 6 and 7 with values of 175 and 144 mV. Additionally, we observed differences in reversibility between the chloride analogues (3 and 6) and the corresponding bromide compounds (4 and 7). The chlorides show significantly greater reversibility than the bromides, as measured by the i_{pa}/i_{pc} for the two waves taken together. For the sulfate-modified complex 5, we observe only one reduction in contrast to the two redox events in compounds 3–7. The overall negative shift of the reduction, and the lack of a corresponding second wave, results from the presence of the anionic group in the bridging ligand.



Figure 6. Cyclic voltammograms of monomers and dimers in 0.1 m TBAPF_6/DMF at 0.25 V and 10.0 $\mu A V^{-1}$ sensitivity versus AgCl.

Table 1. Reduction potential data.

	$\frac{E_1^{0'} [V]}{(\Delta E_p [mV])}$	$E_2^{0'}$ [V] (ΔE_p [mV])	ΔE [mV]	$i_{\rm pa}/i_{\rm pc}$	K _c
2	-0.918(73)	_	_	0.92	_
3	-0.790(82)	-0.978(70)	188	0.92	1507
4	-0.768(61)	-0.946(70)	178	0.79	1021
5	-1.06(76)	-	_	0.93	_
6	-0.811(70)	-0.986(73)	175	0.89	909
7	-0.816(21)	-0.960(61)	144	0.72	272

For the four compounds that show two waves, we can calculate a conproportionation constant (K_c) ,^[55] which cor-

responds to the degree of coupling between the coordination complexes. These values, shown in Table 1, are much larger than the noninteracting statistical value of 4. Although the measurements of K_c using potentials have been shown to be unpredictable and dependent on the anion,^[56] we observe higher values than what is seen for the corresponding cyclophane compounds developed by Connick et al.,^[29] as would be expected for systems with direct π overlap. Additionally, we also see a slight increase when comparing the para- to the meta-substituted complexes, as would be expected from resonance arguments. Lastly, we do observe differences between the bromide and chloride variants as well, with the bromide analogues exhibiting smaller K_c values. This difference can be interpreted in two ways: Either the identity of the halide affects the coupling between the coordination complexes, or the anion has an effect on the reduction processes, as noted in other mixedvalence metal systems by D'Alessandro and Keene et al.^[56] However, the identity of the halide has a small effect overall, and might also influence the redox chemistry by means of kinetic processes.

Conclusion

We have investigated the synthesis of a series of phenylene-bridged dimer species that incorporate the $\text{Re}(\text{CO})_3 X$ unit (X = Cl, Br) by using one-pot methods for their synthesis. We are continuing our work in this area by investigating alternate bridging units as well as incorporating $\text{Re}(\text{CO})_3 X$ into phenylene-bridged polymeric systems.

Experimental Section

Materials and Methods: Reagents were purchased from Strem, Acros Organics, or Sigma–Aldrich and used as received without further purification. Syntheses were performed to limit exposure to air or water. For CV experiments, THF, acetonitrile (MeCN), DMF, DMSO, chloroform, dichloromethane, and benzene were dried and deoxygenated by alumina and copper columns in the Pure Solve solvent system (Innovative Technologies, Inc.); they were stored over molecular sieves. Sodium 2,5-diaminobenzenesulfonate was prepared by mixing an aqueous solution of 2,5-diaminobenzenesulfonic acid (1 equiv.) with sodium hydrogen carbonate (1 equiv.) for 1 h. The solvent water was then evaporated and a brown solid was dried under vacuum for two days.

NMR spectra were recorded with Varian Mercury 300 and 500 MHz instruments. Chemical shifts were reported with respect to residual solvent peaks as internal standard (¹H: [D₆]DMSO, $\delta = 2.50$ ppm; ¹³C: [D₆]DMSO, $\delta = 39.7$ ppm). Infrared spectra were collected with a Nexus 870 FTIR instrument. Electronic absorption spectra were recorded with a Hitachi U-2000 UV-visible spectro-photometer. Elemental analyses were performed by Atlantic Micro-lab of Norcross, GA. Mass spectrometric analyses were carried out at the Mass Spectrometry and Proteomics Facility at the Ohio State University in Columbus, OH or at The University of Akron in Akron, OH.

X-ray Data Collection and Structure Determination: X-ray intensity data for compounds 1, 2, 6, 7, 8, and 10 were measured at 100 K



	1	2	5	6
Empirical formula	C ₁₇ H ₁₂ ClN ₂ O ₃ Re	$C_{15}H_{10}CIN_2O_3Re$	NaC ₂₄ H ₁₃ Cl ₂ N ₄ O ₉ Re ₂ S	$C_{24}H_{14}Cl_2N_4O_6Re_2$
Formula weight	513.95	487.90	976.74	897.69
Crystal system	orthorhombic	triclinic	triclinic	monoclinic
Space group	Pnma	$P\overline{1}$	ΡĪ	$P2_1/c$
a [Å]	10.3518(17)	7.9120(19)	9.4398(3)	14.0136(14)
b [Å]	19.220(3)	7.9120(19)	12.4025(4)	11.8934(12)
c [Å]	8.2014(14)	16.322(4)	16.2635(6)	16.0657(16)
a [°]	90	99.325(4)	100.487(2)	90
β [°]	90	91.969(4)	99.660(2)	104.0500(10)
γ [°]	90	93.705(4)	102.676(2)	90
<i>V</i> [Å ³]	1631.8(5)	1529.5(6)	1783.30(10)	2597.6(5)
Ζ	4	4	2	4
$D_{\rm calcd.} [{\rm Mg}{\rm m}^{-3}]$	2.092	2.119	1.819	2.295
$\mu \text{ [mm^{-1}]}$	7.628	8.132	15.415	9.565
F(000)	976	920	832	1672
Reflections collected	12941	12772	20463	21944
Independent reflections	1936	6694	5458	5963
GoF on F^2	1.448	0.935	1.025	0.753
$R_1 \text{ [on } F_0^2, I > 2\sigma(I) \text{]}$	0.0309	0.0542	0.0296	0.0393
wR_2 [on F_o^2 , $I > 2\sigma(I)$]	0.0598	0.0993	0.0728	0.1018
R_1 (all data)	0.0415	0.1046	0.0332	0.0529
wR_2 (all data)	0.0624	0.1174	0.0746	0.1168

Table 2. Crystallographic data for 1-6.

Table 3. Crystallographic data for 7–11.

	7	8	9	10	11
Empirical formula	$C_{24}H_{14}Br_2N_4O_6Re_2$	C ₂₄ H ₁₄ Cl ₂ N ₄ O ₆ Re ₂	C ₂₄ H ₁₂ Cl ₂ N ₄ O ₆ Re ₂	C ₁₇ H ₁₅ ClN ₃ O ₄ ReS	C ₂₁ H ₁₄ BrN ₄ O _{3.5} Re
Formula weight	986.61	897.69	895.68	579.03	644.47
Crystal system	triclinic	orthorhombic	triclinic	orthorhombic	monoclinic
Space group	PĪ	Pbca	PĪ	Pbca	Cc
<i>a</i> [Å]	8.067(3)	17.991(4)	7.7720(3)	14.220(6)	21.9528(11)
<i>b</i> [Å]	12.008(5)	11.987(2)	11.8847(5)	10.837(5)	12.7721(7)
<i>c</i> [Å]	14.269(6)	23.220(5)	14.6527(6)	25.327(11)	8.7439(5)
a [°]	102.066(5)	90	70.690(2)	90	90
β [°]	91.049(5)	90	89.783(2)	90	109.201(3)
γ [°]	95.591(5)	90	79.473(2)	90	90
V [Å ³]	1344.2(9)	5007.4(18)	1253.46(9)	3903(3)	2315.3(2)
Ζ	2	8	2	8	4
$D_{\text{calcd.}} [\text{Mg}\text{m}^{-3}]$	2.438	2.382	2.373	1.967	1.849
$\mu [{ m mm}^{-1}]$	12.016	9.924	20.992	6.498	7.004
<i>F</i> (000)	908	3344	832	2216	1224
Reflections collected	11107	28686	13425	4334	9466
Indep. reflections	5796	4437	3787	4334	4303
GoF on F^2	0.969	0.887	0.913	1.952	0.992
$R_1 \text{ [on } F_0^2, I > 2\sigma(I) \text{]}$	0.0438	0.0384	0.0225	0.0729	0.0334
wR_2 [on F_0^2 , $I > 2\sigma(I)$]	0.0926	0.1096	0.0581	0.0998	0.0777
R_1 (all data)	0.0737	0.0596	0.0251	0.0879	0.0387
wR_2 (all data)	0.1079	0.1300	0.0605	0.1016	0.0801

with a CCD-based X-ray diffractometer system equipped with a Mo-target X-ray tube (Mo- K_{α} radiation, $\lambda = 0.71073$ Å) operated at 2000 W power. Data for **5**, **9**, and **11** were collected with a CCD-based diffractometer with dual Cu/Mo ImuS microfocus optics (Cu- K_{α} radiation, $\lambda = 1.54178$ Å). Crystals were mounted on a cryoloop using Paratone oil and placed under a steam of nitrogen at 100 K. The detector was placed at a distance of 5.009 cm from the crystal. Crystal data and structure refinement parameters are summarized in Tables 2 and 3.

CCDC-979430 (for 1), -979431 (for 2), -979432 (for 5), -979433 (for 6), -979434 (for 7), -979435 (for 8), -979436 (for 9), -979437 (for 10), and -979438 (for 11) contain 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.

Cyclic Voltammetry: Cyclic voltammograms were obtained with a standard three-electrode cell and a BAS 100B electrochemical analyzer from Bioanalytical Systems and were recorded at 298 K under the following conditions: 10^{-3} M samples in dried DMF in the presence of 0.1 M TBAPF₆ as a supporting electrolyte, Ag/Ag⁺ reference electrode, 0.79 mm² gold working electrode, and platinum wire auxiliary electrode. The working electrode was polished first with 3 µm fine diamond, then 0.05 µm alumina. The electrode was rinsed with ethanol and deionized water after each polishing and wiped with a Kimwipe. The nonaqueous Ag/Ag⁺ reference electrode was used to avoid an excess amount of junction potential and

2649



water contamination. It was prepared by soaking the silver wire in the degassed DMF solution of 0.01M AgClO₄/0.1M TBAPF₆. To compare with previous studies, the approximated formal potentials for reversible redox couples [$E^{o'} = (E_{\rm pc} + E_{\rm pa})/2$] were all referenced against Ag/AgCl. $\Delta E_{\rm p} = E_{\rm pa} - E_{\rm pc}$, $\Delta E = (E_1^{o'} - E_2^{o'})$, and peak currents were calculated by use of an extrapolated baseline current.^[57,58] Potentials were converted to Ag/AgCl reference electrode based on standard conversion factors reported by Amatore and Kochi et al. [Equation (1)]^[59,60] and compared with previous data reported by Connelly and Geiger.^[61] The linear dependence between the square root of the scan rate ($v^{1/2}$) and both the cathodic ($i_{\rm pc}$) and anodic ($i_{\rm pa}$) currents were examined between 0.1 to 0.7 V s⁻¹, and the formal potentials are independent of scan rate. At a 0.25 V s⁻¹ sweep rate, the Fc/Fc⁺ occurs at (0.414 ± 0.005) V ($\Delta E_{\rm p} = 83$ mV; $i_{\rm pa}/i_{\rm pc} = 0.99$).

$$E(\text{NHE}) = E(\text{SCE}) + 0.24 = E(\text{Ag/AgCl}) + 0.28 = E(\text{Ag/AgClO}_4) + 0.66$$
 (1)

[Re(CO)₃(dab-Ph)Cl] (1): Compounds similar to 1 have been prepared.^[13–17,44,62,63] Aniline (0.026 g, 0.282 mmol) was mixed with glyoxal (0.0081 g, 0.141 mmol) in methanol for 20 min. [Re-(CO)₅Cl] (0.050 g, 0.141 mmol) was added and the mixture was heated to reflux for 2 h. Compound 1 was obtained as a solid by evaporation of the reaction solvent, washed with diethyl ether, and dried. Crystals suitable for X-ray diffraction were also produced by slow evaporation of the reaction solvent, yield 62 mg (85%). ¹H NMR (300 MHz, [D₆]DMSO): δ = 9.00 (s, 2 H, N=CH), 7.58 (m, 10 H, H on phenyl) ppm. ¹³C NMR (75 MHz, [D₆]DMSO): δ = 185.3, 168.5, 150.7, 130.2, 130.1, 122.7 ppm. 197.2. C₁₇H₁₂ClN₂O₃Re (513.95): calcd. C 39.73, H 2.35, N 5.45; found C 39.71, H 2.22, N 5.61. IR (CO stretch): $\tilde{v} = 2019$, 1909 cm⁻¹. MS (ESI): calcd. for $ReC_{17}H_{12}N_2O_3CINa [M + Na^+]$: 536.99; found 536.98. UV/Vis (acetone): λ_{max} (ϵ , M^{-1} cm⁻¹) = 360 (8.3 × 10³), 474 nm (3.34×10^3) .

[Re(CO)₃(pyca-Ph)Cl] (2): This previously reported compound^[43–45] can be prepared by using one-pot conditions. Aniline (0.0131 g, 0.141 mmol) was mixed with pyridine-2-carboxyaldehyde (0.0151 g, 0.141 mmol) in methanol for 20 min. [Re(CO)₅Cl] (0.050 g, 0.141 mmol) was then added and the mixture was heated to reflux for 4 h. The solution was evaporated slowly to afford light red crystals, which were suitable for X-ray diffraction. We obtained a crystal structure of **2** in a new crystal form, yield 55 mg (80%). UV/Vis (acetone): λ_{max} (ε , M^{-1} cm⁻¹) = 393 (5.55 × 10³), 414 nm (5.00 × 10³).

Syntheses of $[Re(CO)_3X(p-PPC)Re(CO)_3X]$ (3, X = Cl; 4, X = Br): The procedure for the synthesis of 3 is representative of both compounds.

Compound 3: [Re(CO)₅Cl] (0.050 g, 0.141 mmol), *p*-phenylenediamine (0.00762 g, 0.0704 mmol), and pyridine-2-carbaldehyde (0.0151 g, 0.141 mmol) were heated to reflux in methanol (25 mL) for 4 h. The resultant solid product was filtered and washed with diethyl ether for characterization, yield 54 mg (84%). ¹H NMR (300 MHz, [D₆]DMSO): $\delta = 9.47$ (s, 2 H, N=CH), 9.10 (d, J =5.1 Hz, 2 H, H on py), 8.40 (d, J = 4.2 Hz, 4 H, H on py), 7.88 (dd, J = 3.0 Hz, 2 H, on py), 7.79 (s, 4 H, on phenyl) ppm. ¹³C NMR (75 MHz, [D₆]DMSO): $\delta = 197.5$, 196.8, 187.4, 170.8, 154.9, 153.1, 150.4, 140.6, 130.7, 130.1, 123.5 ppm. C₂₄H₁₄Cl₂N₄O₆Re₂ (897.70): calcd. C 32.11, H 1.57, N 6.24; found C 32.34, H 1.73, N 6.32. IR (CO stretch): $\tilde{v} = 2016$, 1886 cm⁻¹. MS (ESI): calcd. for Re₂C₂₄H₁₄O₆N₄Cl₂Na [M + Na⁺]: 920.93; found 920.94. UV/Vis (DMF): λ_{max} (ε , m⁻¹cm⁻¹) = 341 (1.80 × 10⁴), 390 nm (8.93 × 10³). **Compound 4:** Yield 97 mg (78%). ¹H NMR (300 MHz, [D₆]-DMSO): δ = 9.44 (s, 2 H, N=CH), 9.13 (d, *J* = 3.0 Hz, 2 H, H on py), 8.40 (m, *J* = 7.2 Hz, 4 H, H on py), 7.87 (m, 2 H, on py), 7.80 (d, *J* = 0.9 Hz, 4 H, on phenyl) ppm. ¹³C NMR (75 MHz, [D₆]-DMSO): δ = 197.5, 196.9, 187.2, 171.3, 155.4, 153.8, 151.1, 151.1, 141.0, 131.3, 130.4, 124.0 ppm. C₂₄H₁₄Br₂N₄O₆Re₂ (986.61): calcd. C 29.21, H 1.43, N 5.67; found C 30.02, H 1.35, N 5.80. IR (CO stretch): \hat{v} = 2016, 1894 cm⁻¹. MS (ESI): calcd. for C₂₄H₁₄N₄O₆-Re₂Br₂Na [M + Na⁺]: 1008.82; found 1008.82. UV/Vis (DMF): λ_{max} (ϵ , M⁻¹ cm⁻¹) = 342 (1.61 × 10⁴), 412 nm (6.81 × 10³).

Synthesis of [Re(CO)₃Cl(p-PPC-SO₃Na)Re(CO)₃Cl] (5): Sodium 2,5-diaminobenzenesulfonate (DABS) was prepared by dissolving 2,5-diaminobenzenesulfonic acid in deionized water and adjusting the pH of the solution to 7.0-7.5 by adding small portions of a sodium hydrogen carbonate solution. The solution was heated, then water was removed to yield a brown solid, which was dried at 90 °C under vacuum overnight. DABS (0.0300 g, 142 mmol) was then dissolved in a 10 mL mixture of MeOH/2-propanol (1:3) and stirred for 10 min. Pyridine-2-carbaldehyde (0.0302 g, 0.282 mmol) was added to the mixture while stirring. Then, [Re(CO)₅Cl] (0.100 g, 0.282 mmol) was added and the mixture heated to reflux for 8 h. The solvent was then removed by rotary evaporation. CH₂Cl₂ was added to the solid, and the mixture was filtered. The red solid was dried under vacuum. Crystals suitable for X-ray diffraction were obtained by slow evaporation of a methanol solution, yield 40.0 mg (59%). ¹H NMR (500 MHz, [D₆]DMSO): $\delta = 9.48$ (2 H, N=CH), 9.08 (d, J = 4.0 Hz, 2 H, H on py), 8.43-8.37 (m, 4 H, H on py), 8.06 (s, 1 H, on phenyl), 7.95 (d, J = 8.5 Hz, 1 H on phenyl), 7.86 (s, 2 H on py), 7.74 (d, J = 8.5 Hz, 1 H on phenyl) ppm. ¹³C NMR (75 MHz [D₆]DMSO): δ = 198.4, 198.0, 196.9, 187.9, 187.2, 173.7, 171.4, 155.5, 155.3, 153.5, 149.2, 147.5, 141.1, 140.9, 140.8, 131.2, 130.9, 130.5, 130.4, 125.5, 124.1, 122.0 ppm. C₂₄H₁₃Cl₂N₄NaO₉Re₂S (999.74): calcd. C 28.83, H 1.31, N 5.60; found C 30.71, H 1.87, N 5.63. IR (CO stretch): v = 2022, 1894 cm⁻¹. MS (ESI): calcd. for Re₂C₂₄H₁₃O₉N₄SCl₂ [M - Na⁻]: 976.88; found 976.55. UV/Vis (THF): λ_{max} (ϵ , M^{-1} cm⁻¹) = 317 (8.93 × 10³), 435 nm (1.26×10^{4}) .

Syntheses of $[Re(CO)_3X(m-PPC)Re(CO)_3X]$ (6, X = Cl; 7, X = Br): The procedure for the synthesis of 6 is representative of both compounds.

Compound 6: [Re(CO)₅Cl] (0.050 g, 0.141 mmol), *m*-phenylenediamine (0.00762 g, 0.0704 mmol), and pyridine-2-carbaldehyde (0.0151 g, 0.141 mmol) were mixed in methanol and heated to reflux for 4 h. The solution was evaporated slowly to yield crystals, which were washed with diethyl ether and hexane, yield 33.3 mg (53%). ¹H NMR (300 MHz, [D₆]DMSO): δ = 9.44 (2 H, N=CH), 9.10 (d, *J* = 5.1 Hz, 2 H, H on py), 8.40 (d, *J* = 6.0 Hz, 4 H, H on py), 7.88 (m, 2 H, on py), 7.81–7.66 (two sets of m, 4 H on phenyl) ppm. ¹³C NMR (75 MHz [D₆]DMSO): δ = 197.5, 196.8, 187.1, 170.9, 154.8, 153.2, 151.0, 140.6, 130.9, 130.2, 122.8, 116.3, 116.0 ppm. C₂₄H₁₄Cl₂N₄O₆Re₂ (897.70): calcd. C 32.11, H 1.57, N 6.24; found C 32.29, H 1.48, N 6.54. IR (CO stretch): \tilde{v} = 2022, 1903, 1879 cm⁻¹. MS (ESI): calcd. for Re₂C₂₄H₁₄O₆N₄Cl₂Na [M + Na⁺]: 920.93; found 920.93. UV/Vis (DMF): λ_{max} (ε , m⁻¹ cm⁻¹) = 300 (2.89 × 10⁴), 410 nm (8.64 × 10³).

Compound 7: Yield 64.2 mg (51%). ¹H NMR (300 MHz, [D₆]-DMSO): $\delta = 9.42$ (s, 2 H, N=CH), 9.13 (d, J = 5.4 Hz, 2 H, H on py), 8.40 (m, 4 H, H on py), 7.86 (m, 2 H, on py), 7.83–7.71 (m, 4 H on phenyl) ppm. ¹³C NMR (75 MHz, [D₆]DMSO): $\delta = 197.5$, 196.8, 187.0, 171.3, 155.2, 153.9, 151.5, 141.0, 131.4, 131.3, 130.5, 123.3, 117.1 ppm. C₂₄H₁₄Br₂N₄O₆Re₂ (986.61): calcd. C 29.11, H 1.43, N 5.67; found C 29.82, H 1.33, N 5.89. IR (CO stretch): $\tilde{v} =$



2020, 1910 cm⁻¹. MS (ESI): calcd. for $C_{24}H_{14}N_4O_6Re_2Br_2Na$ [M + Na⁺]: 1008.82; found 1008.82. UV/Vis (DMF): λ_{max} (ϵ , M^{-1} cm⁻¹) = 303 (2.17 × 10⁴), 420 nm (6.38 × 10³).

Syntheses of 8–11: Attempts to generate the *ortho*-substituted phenylenebis(pyridine-2-carbaldimine) $\text{Re}(\text{CO})_3 \text{X}$ dimers resulted in complex mixtures of products that were not readily separable. [$\text{Re}(\text{CO})_5\text{CI}$] or [$\text{Re}(\text{CO})_5\text{Br}$] (0.050 g, 0.141 mmol), *o*-phenylenediamine (0.00762 g, 0.0704 mmol), and pyridine-2-carbaldehyde (0.0151 g, 0.141 mmol) were mixed in methanol and heated to reflux for 4 h. The solution was evaporated slowly to yield a mixture of solid and crystalline materials, which were washed with diethyl ether and hexane. Four different types of crystals suitable for X-ray diffraction were isolated from the product mixtures. Compounds **8–10** were obtained from the [$\text{Re}(\text{CO})_5\text{CI}$] reaction, whereas a crystal of compound **11** was selected from the [$\text{Re}(\text{CO})_5\text{Br}$] reaction.

Supporting Information (see footnote on the first page of this article): NMR and UV/Vis absorption spectroscopy on compounds 1–7.

Acknowledgments

R. S. H. would like to thank the Petroleum Research Fund (grant number 51085-UR3) for financial support of this research. C. J. Z. would like to acknowledge the University of Akron for support of this work as well as and the National Science Foundation (NSF) (grant CHE-9977144) for funds used to purchase the diffractometer used in this work.

- [1] R. Lin, T. F. Guarr, Inorg. Chim. Acta 1994, 226, 79-90.
- [2] W. B. Connick, A. J. Di Bilio, M. G. Hill, J. R. Winkler, H. B. Gray, *Inorg. Chim. Acta* **1995**, 240, 169–173.
- [3] R. J. Lin, K. S. Lin, I. J. Chang, *Inorg. Chim. Acta* 1996, 242, 179–183.
- [4] F. P. A. Johnson, M. W. George, F. Hartl, J. J. Turner, Organometallics 1996, 15, 3374–3387.
- [5] P. Christensen, A. Hamnett, A. V. G. Muir, J. A. Timney, J. Chem. Soc., Dalton Trans. 1992, 9, 1455–1463.
- [6] T. R. O'Toole, B. P. Sullivan, M. R. M. Bruce, L. D. Margerum, R. W. Murray, T. J. Meyer, *J. Electroanal. Chem.* 1989, 259, 217–239.
- [7] D. J. Stufkens, Comments Inorg. Chem. 1992, 13, 359–385.
- [8] K. S. Schanze, D. B. MacQueen, T. A. Perkins, L. A. Cabana,
- Coord. Chem. Rev. **1993**, 122, 63–89. [9] M. Wrighton, D. L. Morse, J. Am. Chem. Soc. **1974**, 96, 998–
- 1003. [10] J. C. Luong, L. Nadjo, M. S. Wrighton, J. Am. Chem. Soc.
- **1978**, 100, 5790–5795. [11] D. J. Stufkens, A. Vlcek Jr., Coord. Chem. Rev. **1998**, 177, 127–
- 179.
- [12] L. Wallace, D. P. Rillema, Inorg. Chem. 1993, 32, 3836–3843.
- [13] A. Juris, S. Campagna, I. Bidd, J. M. Lehn, R. Ziessel, *Inorg. Chem.* 1988, 27, 4007–4011.
- [14] B. D. Rossenaar, C. J. Kleverlaan, M. C. E. van de Ven, D. J. Stufkens, A. Oskam, J. Fraanje, K. Goubitz, J. Organomet. Chem. 1995, 493, 153–162.
- [15] S. Das, I. Chakraborty, A. Chakravorty, *Inorg. Chem.* 2003, 42, 6545–6555.
- [16] L. S. M. Lam, W. K. Chan, ChemPhysChem 2001, 4, 252-256.
- [17] L. S. M. Lam, W. K. Chan, A. B. Djurisic, E. H. Li, Chem. Phys. Lett. 2002, 362, 130–134.
- [18] H. Qayyum, R. S. Herrick, C. J. Ziegler, *Dalton Trans.* 2011, 40, 7442–7445.
- [19] K. Chanawanno, J. T. Engle, K. X. Le, R. S. Herrick, C. J. Ziegler, *Dalton Trans.* 2013, 42, 13679–13684.

- [20] R. Costa, K. Chanawanno, J. T. Engle, B. Baroody, R. S. Herrick, C. J. Ziegler, J. Organomet. Chem. 2013, 734, 25–31.
- [21] B. D. Rossenaar, D. J. Stufkens, A. Vlcek Jr, *Inorg. Chem.* 1996, 35, 2902–2909.
- [22] L. H. Staal, A. Oskama, K. Vrieze, J. Organomet. Chem. 1979, 170, 235–245.
- [23] B. D. Rossenaar, D. J. Stufkens, A. Vlcek Jr, *Inorg. Chim. Acta* 1996, 247, 247–255.
- [24] B. D. Rossenaar, C. J. Kleverlaan, M. C. E. van de Ven, D. J. Stufkens, A. Vlcek Jr, *Chem. Eur. J.* **1996**, *2*, 228–237.
- [25] G. J. Stor, D. J. Stufkens, A. Oskam, *Inorg. Chem.* 1992, 31, 1319–1320.
- [26] B. D. Rossenaar, M. W. George, F. P. A. Johnson, D. J. Stufkens, J. J. Turner, A. Vlcek Jr, J. Am. Chem. Soc. 1995, 117, 11582–11583.
- [27] C. J. Kleverlaan, D. M. Martino, H. van Willigen, D. J. Stufkens, A. Oskam, J. Phys. Chem. 1996, 100, 18607–18611.
- [28] R. S. Herrick, C. J. Ziegler, K. L. Kennedy, C. Luu, J. T. Engle, *Eur. J. Inorg. Chem.* 2013, 8, 1265–1268.
- [29] P. J. Ball, T. R. Shtoyko, J. A. K. Bauer, W. J. Oldham, W. B. Connick, *Inorg. Chem.* 2004, 43, 622–632.
- [30] G. J. Stor, F. Hartl, J. W. M. Van Outersterp, D. J. Stufkens, Organometallics 1995, 14, 1115–1131.
- [31] B. D. Rossenaar, F. Hartl, D. J. Stufkens, *Inorg. Chem.* 1996, 35, 6194–6203.
- [32] J. W. M. Van Outersterp, F. Hartl, D. J. Stufken, Organometallics 1995, 14, 3303–3310.
- [33] S. V. Wallendael, R. J. Shaver, D. P. Rillema, B. J. Yoblinski, M. Stathis, T. F. Guard, *Inorg. Chem.* **1990**, *29*, 1761–1767.
- [34] A. Vogler, J. Kisslinger, Inorg. Chim. Acta 1986, 115, 193-196.
- [35] C. Bruckmeier, M. W. Lehenmeier, R. Reithmeier, B. Rieger, J. Herranzb, C. Kavaklib, *Dalton Trans.* 2012, 41, 5026–5037.
- [36] B. J. Yoblinski, M. Stathis, T. F. Guarr, *Inorg. Chem.* **1992**, *31*, 5–10.
- [37] M. Panigati, M. Mauro, D. Donghi, P. Mercandelli, P. Mussini, L. D. Cola, G. D. Alfonso, *Coord. Chem. Rev.* 2012, 256, 1621– 1643.
- [38] G. Pereiras-Gabian, E. M. Vazquez-Lopez, U. Abram, Z. Anorg. Allg. Chem. 2004, 630, 1665–1670.
- [39] R. Carballo, J. S. Casas, E. Garcia-Martinez, G. Pereiras-Gabian, A. Sanchez, U. Abram, E. M. Vazquez-Lopez, *CrystEngComm* **2005**, *7*, 113–120.
- [40] J. A. Cabeza, A. Llamazares, V. Riera, R. Trivedi, Organometallics 1998, 17, 5580–5585.
- [41] R. N. Dominey, B. Hauser, J. Hubbard, J. Dunham, *Inorg. Chem.* 1991, 30, 4754–4758.
- [42] V. Wing-Wah Yam, K. Man-Chung Wong, V. Wing-Man Lee, K. Kam-Wing Lo, K. K. Cheung, *Organometallics* 1995, 14, 4034–4038.
- [43] W. Wang, B. Spingler, R. Alberto, *Inorg. Chim. Acta* 2003, 355, 386–393.
- [44] N. M. Shavaleev, Z. R. Bell, G. Accorsi, M. D. Ward, *Inorg. Chim. Acta* 2003, 351, 159–166.
- [45] W. Liu, K. Heinze, Dalton Trans. 2010, 39, 9554-9564.
- [46] C. M. Alvarez, R. Garcia-Rodriguez, D. Miguel, J. Organomet. Chem. 2007, 692, 5717–5726.
- [47] C. M. Alvarez, R. Garcia-Rodriguez, D. Miguel, *Dalton Trans.* 2007, 32, 3546–3554.
- [48] C. M. Alvarez, R. Garcia-Rodriguez, D. Miguel, *Inorg. Chem.* 2012, 51, 2984–2996.
- [49] L. S. M. Lam, S. H. Chan, W. K. Khan, Macromol. Rapid Commun. 2000, 21, 1081.
- [50] S. H. Chan, L. S. M. Lam, C. W. Tse, K. Y. K. Man, W. T. Wong, A. B. Djurisi, W. K. Chan, *Macromolecules* 2003, *36*, 5482–5490.
- [51] A. Garoufis, S. Kasselouri, C. A. Mitsopoulou, J. Sletten, C. Papadimitriou, N. Hadjiliadis, *Polyhedron* 1999, 18, 39–47.
- [52] M. Tsiouri, J. C. Plakatouras, A. Garoufis, V. Nastopoulos, N. Hadjiliadis, *Inorg. Chem. Commun.* 2002, 5, 844–847.



- [53] M. Shakir, M. Azam, Y. Azim, S. Parveen, A. U. Khan, *Polyhedron* 2007, 26, 5513–5518.
- [54] D. Mishra, S. Naskar, R. J. Butcher, S. K. Chattopadhyay, *Inorg. Chim. Acta* 2005, 358, 3115–3121.
- [55] D. E. Richardson, H. Taube, Inorg. Chem. 1981, 20, 1278–1285.
- [56] D. M. D. Alessandro, F. R. Keene, *Dalton Trans.* 2004, 23, 3950–3954.
- [57] P. T. Kissinger, W. R. Heineman, J. Chem. Educ. 1983, 60, 702-706.
- [58] A. D. Le, L. Yuz, J. Electrochem. Soc. 2011, 158, F10-F14.
- [59] J. O. Howell, J. M. Goncalves, C. Amatore, L. Klasinc, R. M. Wightman, J. K. Kochi, J. Am. Chem. Soc. 1984, 106, 3968– 3976.
- [60] C. Amatore, C. Lefrou, J. Electroanal. Chem. 1992, 325, 239– 246.
- [61] N. G. Connelly, W. E. Geiger, Chem. Rev. 1996, 96, 877-9110.
- [62] L. S. M. Lam, S. H. Chan, W. K. Khan, Macromol. Rapid Commun. 2000, 21, 1081–1085.
- [63] S. H. Chan, L. S. M. Lam, C. W. Tse, K. Y. K. Man, W. T. Wong, A. B. Djurisic, W. K. Chan, *Macromolecules* 2003, 36, 5482–5490.

Received: January 21, 2014 Published Online: April 30, 2014