DOI: 10.1002/chem.200700228

Tuning the Electronic Properties of N-Heterocyclic Carbenes

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Abstract: The electron-donating properties of N-heterocyclic carbenes ([N,N′-bis(2,6-dimethylphenyl)imidazol]-2-ylidene and the respective dihydro ligands) with 4,4′-R-substituted aryl rings (4,4′-R = NEt_2, $OC_{12}H_{25}$, Me, H, Br, S(4-tolyl), SO(4-tolyl), SO_2(4-tolyl)) were studied. Twelve new N-heterocyclic carbene (NHC) ligands were synthesized as well as the respective iridium complexes [IrCl(cod)(NHC)] and [IrCl$(CO)_2$(NHC)]. Cyclic voltammetry ($\Delta E_{1/2}$) and IR ($\tilde{\nu}$(CO)) can be used to measure the electron-donating properties of the carbene ligands. Modifying the 4-positions with electron-withdrawing substituents (4-R = $-SO_2Ar$, $\Delta E_{1/2} = +0.92$ V) results in NHC ligands with virtually the same electron-donating capacity as a trialkylphosphine in [IrCl(cod)(PCy_3)] ($\Delta E_{1/2} = +0.95$ V), while [IrCl(cod)(NHC)] complexes with 4-R = NEt_2 ($\Delta E_{1/2} = +0.59$ V) show drastically more cathodic redox potentials and significantly enhanced donating properties.

Keywords: IR spectroscopy · iridium · N-heterocyclic carbenes · redox chemistry

Introduction

Control over the electronic and steric properties of ligands is of critical importance for the optimization of the catalytic activity of transition-metal-based complexes.[1] Subtle variations of steric bulk and electron density at the active site may have drastic effects on the catalytic efficiency.[2–6] Consequently, the quantification of the steric and electronic effects of ligands,[7–10] such as through the classic approach by Tolman,[11] is essential.

N-Heterocyclic carbenes (NHCs) are rivaling the leading status of phosphines as ligands in homogeneous catalysis.[6,12–18] Thus the fine-tuning of NHC ligands is of prime importance for the design of tailored catalysts with optimized activities, most of this work has concentrated on the steric effects of NHC ligands, while the construction of a series of electronically variable NHC ligands with invariant bulk has been neglected.[19–21] Nonetheless, numerous studies have been devoted to determining the electron donating properties of NHC ligands; this is most often done by studying the $\tilde{\nu}$(CO) of [Ni$(CO)_3$(NHC)] or [MCl(CO)(NHC)] (M = Rh, Ir) complexes,[22–29] photoelectron spectroscopy,[30] or by determining the pK_a values.[31,32] A complaint has been that the TEP (TEP = Tolman electronic parameter) of the most common NHC ligands fall within a 3 cm^{-1} range, which is much smaller than the 12 cm^{-1} observed for typical phosphines.[33] While the differences between different types of NHC ligands can be much larger, this goes along with significant variation in space requirements; for a given steric profile, the electronic variability is only small.[34,35]

For the present work, we wanted to modify in a systematic manner two of the most commonly applied NHC ligands (N,N′-bis(2,6-dimethylphenyl)imidazol)-2-ylidene and N,N′-bis(2,6-dimethylphenyl)-4,5-dihydroimidazol)-2-ylidene), to allow the systematic tuning of the electron density of a metal bonded to NHC ligands. We wish to report here on the synthesis of twelve new NHC ligands, which have the same core structure and differ only with respect to electron-releasing capacity. To demonstrate this we have synthesized 28 different Ir complexes, all of which were studied by means of cyclic voltammetry ($\Delta E_{1/2}$) and IR spectroscopy (ν(CO)).

Results and Discussion

Synthesis of ligands and metal complexes: The respective imidazolium and imidazolinium salts were synthesized by following modified procedures from Arduengo and Noels.[36,37] These procedures are ideally suited to obtain the protonated NHC ligands with a variety of 4-R groups (Table 1). In order to cover a large range of electronic ef-

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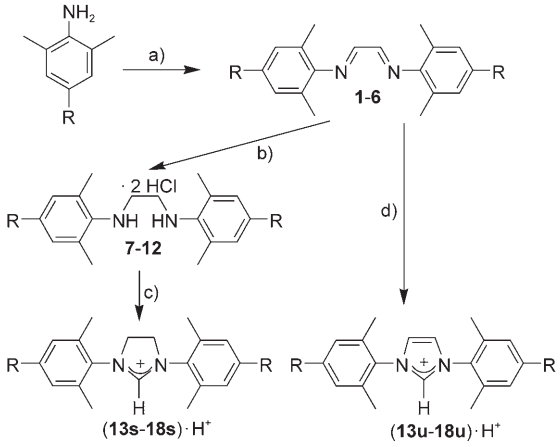
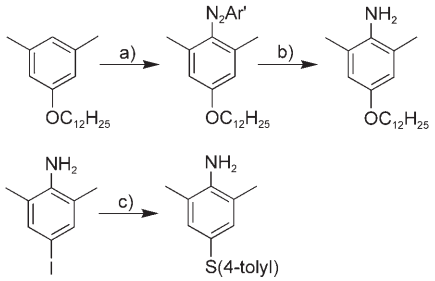
Table 1. Synthesis of imidazolium and imidazolinium salts with variable groups R (Ar = 4-tolyl).[a]



R	Products (yield [%])			
NEt_2	**1** (84)	**7** (99)	**13u**·H^+ (62)	**13s**·H^+ (93)
$OC_{12}H_{25}$	**2** (48)	**8** (61)	**14u**·H^+ (62)	**14s**·H^+ (54)
Me	**3**	**9**	**15u**·H^+	**15s**·H^+
H	**4**	**10**	**16u**·H^+	**16s**·H^+
Br	**5** (82)	**11** (57)	**17u**·H^+ (79)	**17s**·H^+ (74)
SAr	**6** (99)	**12** (76)	**18u**·H^+ (55)	**18s**·H^+ (19)

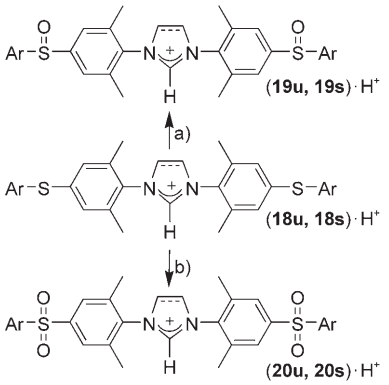
[a] Reagents and conditions: a) glyoxal, EtOH, HCOOH, RT; b) $LiAlH_4$, THF, RT, HCl/H_2O; c) $HC(OEt)_3$, HCOOH, 120 °C; d) $(CH_2O)_n$, HCl/dioxane, RT.

fects we planned on synthesizing the respective heterocycles with several electronically diverse groups at the 4-position (R = NEt_2, $OC_{12}H_{25}$, Me, H, S(4-tolyl), Br, CF_3, NO_2), which requires the respective 2,6-dimethylanilines with different 4-R groups. As two of the anilines (4-$OC_{12}H_{25}$, S(4-tolyl)) were not known, they had to be synthesized (Scheme 1). To



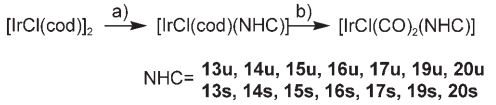
Scheme 1. Synthesis of the new anilines. a) AcOH, 2,4-$(NO_2)_2C_6H_3N_2^+$ Cl^-, 0 °C; b) H_2, Pd/C, THF/MeOH; c) 1,4-$C_6H_4(CH_3)(SH)$, *i*PrOH, HOC_2H_4OH, CuI, K_2CO_3, 80 °C.

obtain the NHC ligands, the anilines were reacted with glyoxal to form the corresponding diimines. We found that this procedure works well for all anilines, except for those with strongly electron-withdrawing groups (4-R = CF_3, NO_2). For the other anilines, the normal sequence of diimine formation (products **1**–**6**) and ring closure leads to the respective imidazolium salts (**13u**·H^+–**18u**·H^+) with a Cl^- counter ion. The sequence of diimine formation and $LiAlH_4$ reduction of the imines results in the formation of the related diamines (**7**–**12**) and ring closure leads to the analogous imidazolinium salts (**13s**·H^+–**18s**·H^+) with a Cl^- counter ion. Prior to our work, only the imidazolium and imidazolinium salts with 4-R = Me (**15u**·H^+, **15s**·H^+) or H (**16u**·H^+, **16s**·H^+) were known.[37] Despite the failure of the diimine formation with electron-deficient anilines, it was possible to synthesize four NHC precursors with strongly electron-withdrawing groups by oxidation of sulfur in the −SAr-substituted salts **18u**·H^+ and **18s**·H^+. The two substituted heterocycles were treated with stoichiometric amounts of H_2O_2 to allow the oxidation to the sulfoxides **19u**·H^+ and **19s**·H^+. The respective sulfones **20u**·H^+ and **20s**·H^+ were obtained by treatment of **18u**·H^+ and **18s**·H^+ with a large excess of H_2O_2 (Scheme 2).



Scheme 2. Synthesis of electron-deficient NHC·HCl (Ar = 4-tolyl). a) AcOH, 2.0 equiv H_2O_2 30%, RT; b) AcOH, 18.0 equiv H_2O_2 30%, RT (----- denotes either a single or a double bond).

Ir complexes of the type [IrCl(cod)(NHC)] were prepared in the reaction of $[IrCl(cod)]_2$ with the respective free carbene (Scheme 3) according to a general procedure by Herrmann.[38] Bubbling of CO through solutions of these complexes generated the respective $[IrCl(CO)_2(NHC)]$ complexes in virtually quantitative conversions.[38]



Scheme 3. Synthesis of the Ir complexes. a) THF, KO*t*Bu, azolium salt, RT; b) CH_2Cl_2, CO, RT, quantitative conversions.

IR spectroscopy of NHC–iridium complexes: The determination of $\tilde{\nu}$(CO) in metal complexes is a useful and widely applied method for the evaluation of the electron-donating properties of ligands attached to a metal center.[22] We studied the $\tilde{\nu}$(CO) of the two series of $[IrCl(CO)_2(NHC)]$ complexes (Table 2), which are nearly the same for the saturated

Table 2. $\tilde{\nu}$(CO) of the [IrCl(CO)$_2$(NHC)] complexes. (TEP = 0.722-($\tilde{\nu}_{av}$(CO) + 593 cm^{-1}) (Ar = 4-tolyl).

	unsaturated			saturated		
R =	NHC	$\tilde{\nu}$ [cm^{-1}]	TEP [cm^{-1}]	NHC	$\tilde{\nu}$ [cm^{-1}]	TEP [cm^{-1}]
NEt_2	**13u**	1978/ 2064	2052.2	**13s**	1979/ 2065	2052.9
Me	**15u**	1980/ 2066	2053.6	**15s**	1981/ 2068	2054.7
H	**16u**	1981/ 2067	2054.3	**16s**	1981/ 2069	2055.1
Br	**17u**	1982/ 2069	2055.4	**17s**	1984/ 2071	2056.9
SOAr	**19u**	1984/ 2073	2057.6	**19s**	1985/ 2073	2057.9
SO_2Ar	**20u**	1985/ 2074	2058.6	**20s**	1986/ 2075	2059.0
[IrCl(CO)$_2$(PCy$_3$)]		1985/ 2074	2058.6			

Table 3. Redox potentials of the [IrCl(cod)(NHC)] complexes in CH_2Cl_2 (scan rate 100 mV s^{-1}) (Ar = 4-tolyl). ΔE is the difference of the respective anodic and cathodic peak potentials (0.1 M NBu_4PF_6 referenced vs $FcMe_8$ $E_{1/2} = -0.010$ V).

[IrCl(cod)(NHC)]	unsaturated			saturated		
R =	NHC	$E_{1/2}$ [V]	ΔE [mV]	NHC	$E_{1/2}$ [V]	ΔE [mV]
NEt_2	**13u**	0.648	80	**13s**	0.591	68
$OC_{12}H_{25}$	**14u**	0.761	80	**14s**	0.730	86
Me	**15u**	0.765	80	**15s**	0.735	76
H	**16u**	0.786	78	**16s**	0.759	77
Br	**17u**	0.862	78	**17s**	0.838	82
SOAr	**19u**	0.870	72	**19s**	0.846	86
SO_2Ar	**20u**	0.920	80	**20s**	0.910	76
[IrCl(cod)(PCy$_3$)]		0.948	94			

and the unsaturated complexes, but the saturated NHC complexes appear to show marginally higher TEP values. It is interesting that the TEP of [IrCl(cod)(NHC)] (NHC = **20u**) (2059 cm^{-1}) and of [IrCl(cod)(PCy$_3$)] (2059 cm^{-1})[39] display the same values. The obvious conclusion is that the PCy_3 ligand has almost the same electron-donating capacity as the $-SO_2Ar$-substituted NHC ligand **20u**.

Electrochemistry of NHC–iridium complexes: Alternatively, the determination of the redox potentials of metal complexes may serve as a precise measure for the electron-donating properties of the NHC ligand. The electrochemical properties of Ru and Fe metal complexes of N-heterocyclic carbenes have been probed previously and were found to be sensitive to changes of the substituents at the ligands.[40] Demonceau, Noels et al. determined the redox potentials of a few NHC–Ru complexes, which were shown to be correlated with the catalytic activity of the respective NHC–Ru complexes in the atom transfer radical (ATR) polymerization.[41,42] Electrochemical data of Grubbs II and Grubbs–Hoveyda complexes with variable NHC ligands have been reported by us.[43,44]

We first studied complexes of the type [IrCl(CO)$_2$(NHC)] as such complexes were available from the IR studies. However, the electrochemistry of [IrCl(CO)$_2$(NHC)] is irreversible. This is probably due to the loss of CO ligands following the oxidation of the Ir^{I} center. Fortunately, the related [IrCl(cod)(NHC)], from which the respective carbonyl complexes are synthesized, are characterized by a reversible electrochemistry. The redox potential for the various unsaturated [IrCl(cod)(NHC)] complexes range between 0.648–0.920 V for NHC = **13u**–**17u**, **19u**, and **20u** and for the saturated [IrCl(cod)(NHC)] complexes (NHC = **13s**–**17s**, **19s**, and **20s**) between 0.591–0.910 V (Table 3). On comparing various Ir complexes, the redox potentials of complexes with the saturated NHC are consistently lower by between 10–57 mV. Thus we conclude that saturated NHC ligands are better electron donors than the related unsaturated ones, even though the differences appear to be small. Considering the more electron-donating character of sp^3 versus sp^2-carbon atoms in the saturated versus the unsaturated NHC ligands, this trend is reasonable. Nonetheless, it is surprising that a small change in the remote groups, 4-R, effect large changes in the redox potentials, while the effect of two sp^3 versus two sp^2-carbon atoms is rather small. To illustrate this point: the replacement of a 4-CH_3 group by a 4-H changes the redox potential of the Ir complexes by 21–24 mV, while the difference between the respective saturated and unsaturated complexes is roughly the same at 24–27 mV. It is hard to see why the transfer of electron density over three bonds should be less efficient than that over seven bonds. Furthermore the six- and five-membered rings are orthogonal, which can hardly promote the transfer of electronic information.

The validity of the data can be shown by the excellent correlation of the redox potentials determined by us for the saturated and the unsaturated Ir complexes with the respective Hammett parameters[45] which produce excellent linear fits ($R^2 > 0.98$ for both types of complexes, Figure 1).[46]

To place the donating properties of NHC ligands on the electrochemical scale in a more general context we have determined the redox potential of the phosphine complex [IrCl(cod)(PCy$_3$)]. At 0.948 V, this value is very close to that

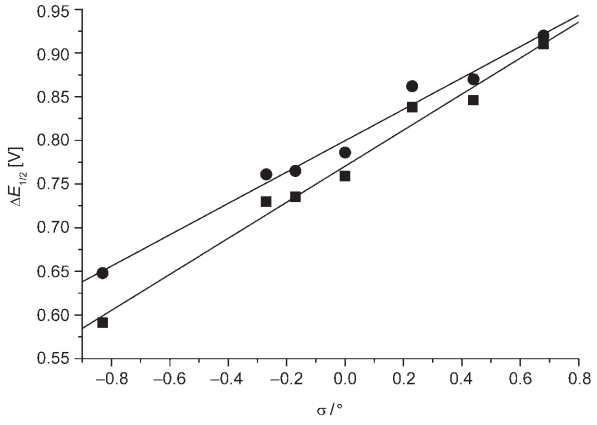


Figure 1. Correlation of Hammett parameters and redox potentials of [(IrCl(cod)NHC)] (NHC = **13u**–**20u** and **13s**–**20s**); ■ = saturated, ● = unsaturated.

of the SO_2Ar-substituted NHC complex **20u**. We thus (again) conclude that the electron-donating properties of SO_2Ar-substituted NHC ligands are almost the same as that of an electron-rich trialkylphosphine, such as PCy_3. Thus it is possible to close the gap between the electron-donating NHC ligands and phosphines.

On comparing the two different techniques for the determination of the electron donating properties, cyclic voltammetry seems to be the superior approach. For the complexes studied here, the difference between the most and the least electron-donating NHC ligand is 319 mV, which is more than 60 times higher than the precision with which a redox potential can be determined (approximately ± 5 mV). With the same series of complexes, the TEP based on the $\tilde{\nu}$(CO) differs only by 6 cm^{-1}, which is only twelve times the 0.5 cm^{-1} precision of the routine IR experiment, which is limited by the bandwidth of the respective absorptions and the spectrometer resolution. The advantage of the electrochemical method is not unexpected as the determination of a physical property of a metal center, which is directly bonded to the NHC ligand, should result in a higher dispersion than a method which probes the C–O vibration of a carbonyl ligand more remote from the NHC. Furthermore, the small modifications in the 4-R positions reported here extend the range of electronic diversity within a given series of NHC ligands to almost 7 cm^{-1}, bringing it much closer to the diversity reported for phosphines.

Crystal structure determinations of [IrCl(cod)(NHC)] (NHC = 13s and 16s): To learn whether changes in the electronic situation at the ligands have an effect on the NHC–metal interactions we have determined the crystal structures of two [IrCl(cod)(NHC)] complexes (Table 4, Figure 2) with 4-R = $-NEt_2$ and 4-R = H. The Ir–C52 (C in NHC) distances in both crystal structures are identical within estimated standard deviation (NHC **13s**: 205.0(4) and NHC **16s**: 205.7(10) pm). The bond lengths around Ir observed in [IrCl(cod)(**13s**)] and [IrCl(cod)(**16s**)] are similar to those in related [IrCl(cod)(NHC)] complexes, which typically range between 203–208 pm in monodentate,[22,26] abnormal,[27] bidentate,[23] or tripodal[47] NHC ligands. The small variance in the bond length between rather different NHC ligands underlines the weak influence of electronic and steric properties of the NHC ligand on the structures of such metal complexes.

The only significant deviation of the two structures concerns the orientation of the two pairs of mesityl flaps. In the crystal of [IrCl(cod)(**16s**)], the two ring units are more inclined towards Ir than in [IrCl(cod)(**13s**)]. This is apparent by comparing the average of the two pairs of distances Ir-C13/C23, which are 527 pm in R = H (NHC: **16s**) and 574 pm in R = NEt_2 (NHC: **13s**). It cannot be excluded that this is the result of different electronic interactions. However, we believe this to be caused by different packing forces in the crystals of [IrCl(cod)(**13s**)] and [IrCl(cod)(**16s**)]. The high flexibility of these NHC segments is also obvious from several crystal structures of Grubbs–Hoveyda-type complexes recently reported by Grela et al.;[48] a comparison of three closely related complexes shows the mesityl units to be the flexible section of the NHC ligands.

Table 4. Crystal data and structure refinement of [IrCl(cod)(**13u**)] and [IrCl(cod)(**16u**)].

	[IrCl(cod)(**13s**)]	[IrCl(cod)(**16s**)]
empirical formula	$C_{35}H_{52}ClIrN_4$	$C_{27}H_{34}ClIrN_2$
F_w	756.5	614.25
T [K]	153	153
crystal system	monoclinic	triclinic
space group	$P2_1/a$	$P\bar{1}$
unit cell dimensions [pm]		
a	1432.6	861.4
b	1421.6	876.8
c	1715.2	1696.2
α, β, γ [°]	90, 109.97, 90	91.26, 96.71, 107.50
V [Å^3]	3283.1	1211.1
Z	4	2
ρ_{calcd} [Mg m^{-3}]	1.53	1.684
μ [mm^{-1}]	4.178	5.639
F(000)	1536	608
crystal size [mm^3]	0.15 × 0.14 × 0.084	0.11 × 0.10 × 0.06
Θ range [°]	3.8–29.55	2.42–29.55
index ranges	$-19 \le h \le 19$	$-11 \le h \le 11$
	$-19 \le k \le 19$	$-11 \le k \le 11$
	$-23 \le l \le 23$	$-23 \le l \le 23$
reflections collected	58945	6569
independent reflections	9056	6569
absorption correction	numerical	numerical
data/restraints/parameters	6759/0/365	6569/0/273
final R indices [$I > 2\sigma(I)$], all data		
R_1	0.0451, 0.0752	0.0487, 0.1359
wR_2	0.0692, 0.0750,	0.0803, 0.1126
largest diff. peak/hole [eÅ^3]	1.16, −3.0 (near Ir)	1.21, −2.03 (near Ir)

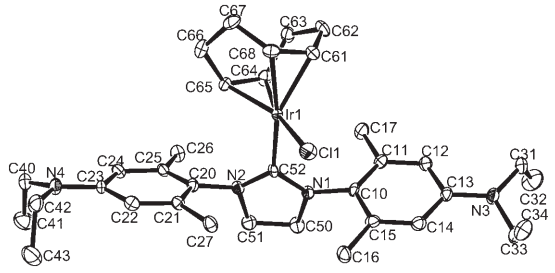


Figure 2. X-ray crystal structure of [IrCl(cod)(**13s**)] (ellipsoids with 50% probability).

Conclusions

The variation of the 4-R groups in N-arylated NHC ligands allows the systematic tuning of the electron-donating properties of the respective ligands, which can thus be adapted to the specific needs of metal complexes. Specifically, we have demonstrated that NHC ligands with strong electron-withdrawing substituents (SO_2Ar) have virtually the same electron-donating properties as PCy_3, while a modified

ligand with similar bulk and $-NEt_2$ substituents is an electron-rich carbene. We have used two different methods (cyclic voltammetry and IR spectroscopy) to probe the electronic properties of NHC ligands, observing either the redox potential of [IrCl(cod)(NHC)] complexes or the $\tilde{\nu}$(CO) in [IrCl(CO)$_2$(NHC)] complexes. We consider the use of [IrCl(cod)(NHC)] complexes in conjunction with cyclic voltammetry as the superior technique for the determination of the electron-donating properties of NHC ligands. The electrochemical response is more precise, in that the dispersion of the physical property studied is much larger with respect to the resolution of the respective physical technique. On the other hand, both approaches (IR, CV) can be easily combined as the [IrCl(CO)$_2$(NHC)] complex required for the IR method is synthesized from the respective [IrCl(cod)(NHC)] complexes.

Experimental Section

General experimental: All chemicals were purchased as reagent grade from commercial suppliers and used without further purification, unless otherwise noted. THF was distilled over potassium and benzophenone under an argon atmosphere. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on Bruker DRX 500 at 500, 125.75, and 202.46 MHz, respectively, or on Bruker DRX 300 at 300 or 75.07 MHz. The chemical shifts are given in parts per million (ppm) on the delta scale (δ) and are referenced to tetramethylsilane (^{1}H, ^{13}C NMR = 0 ppm; ^{31}P NMR used 65% aq. H_3PO_4 = 0 ppm). Abbreviations for NMR data: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, brs = broad singlet, and arom. = aromatic protons. IR spectra of the metal carbonyls were recorded on a Perkin–Elmer 1600 IR spectrometer in $CHCl_2$ solution as 100×10^{-6} m films between KBr plates. TLC was performed by using silica gel 60 F254 (0.2 mm) on aluminum plates. For preparative chromatography, E. Merck silica gel 60 (0.063–0.20 mesh) was used. The following compounds were prepared according to literature procedures: 2,6-dimethyl-4-bromoaniline as described for the 2,6-diisopropyl derivative,[49] 2,6-dimethyl-4-diethylaminoaniline,[50] 2,4,6-trimethylphenylimidazolium chloride and 2,4,6-trimethylimidazolinium chloride,[37] and [IrCl(cod)]$_2$.[51]

X-ray crystal structure determination:

Data collection: Data were recorded on a Stoe IPDS II diffractometer by using monochromated $Mo_{K\alpha}$ radiation.

Structure refinement: The structures were solved by using SHELXS-86[52] and were refined anisotropically on F^2 by using SHELXL-97.[53] Hydrogen atoms were refined by using a riding model. X-ray crystal data were processed by using the WINGX shell and ORTEP-3.[54] CCDC-636094 and -636095 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.

Synthesis of the anilines

2,6-Dimethyl-4-dodecyloxyaniline: NaOH (8.0 g, 0.2 mol, 1.5 equiv) was dissolved in water (100 mL), 3,5-dimethylphenol (16.2 g, 133 mmol, 1.0 equiv) was added and the mixture was stirred for 0.5 h. A solution of dodecylbromide (24.6 mL, 133 mmol, 1.0 equiv) in ethanol (100 mL) was added and the reaction mixture stirred at 100 °C for 14 h. After cooling to room temperature, the product was extracted with diethyl ether (3 × 100 mL). The combined organic layers were dried over $MgSO_4$ and the solvent was evaporated in vacuo. Yield: 16.1 g (41%) of 3,5-dimethyl-dodecyloxybenzene. The crude product was dissolved in glacial acetic acid (500 mL). The solution was cooled to 0 °C and 2,4-dinitrophenyldiazonium chloride solution, prepared from 2,4-dinitroaniline (15.28 g, 83.4 mmol, 1.5 equiv) and $NaNO_2$ (5.76 g, 83.4 mmol, 1.5 equiv), in aqueous HCl (5 M, 100 mL) was added. The reaction mixture was stirred for 14 h at room temperature. After this time, The red azo dye was filtrated, redissolved in $CHCl_3$ (250 mL), and washed with saturated $NaHCO_3$ solution. The organic layer was dried over $MgSO_4$ and the solvent was evaporated in vacuo. A sample of the azo dye (7.0 g, 14.5 mmol) was dissolved in THF/EtOH (8:1, 200 mL) and hydrogenated by using Pd on Charcoal (10 wt%, 10 mol% Pd, 1.53 g, 1.4 mmol, $p(H_2)$ = 5 bar). After 5 h, the reaction mixture was filtered over Celite and the solvent evaporated in vacuo. Purification by column chromatography (silica gel, cyclohexane/ethyl acetate 2:1) gave 2.39 g (54%) of 2,6-dimethyl-4-dodecyloxyaniline. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, 3H; CH_3), 1.20–1.50 (m, 18H; CH_2), 1.72 (m, 2H; CH_2), 2.16 (s, 6H; CH_3), ca. 3.10–3.50 (brs, 2H; NH_2), 3.86 (t, 2H; OCH_2), 6.55 ppm (s, 2H; arom.); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 13.1, 16.9, 21.7, 25.1, 28.3–28.7, 30.9, 67.6, 113.8, 122.1, 135.2, 150.6 ppm.

2,6-Dimethyl-4-(*p*-tolylthio)aniline: Following a general procedure by Kwong and Buchwald,[55] 2,6-dimethyl-4-iodoaniline (3.00 g, 12.1 mmol, 1.0 equiv), CuI (120 mg, 0.63 mmol, 5 mol%), and K_2CO_3 (3.31 g, 24.0 mmol, 2.0 equiv) were weighed into a Schlenk flask under an atmosphere of Ar. Isopropanol (12 mL, techn. grade), ethyleneglycol (1.3 mL), and 4-methylthiophenol (2.8 mL, 24.2 mmol, 2.0 equiv) were added. The reaction mixture was stirred at 80 °C for 4 d, then poured into water (50 mL), and extracted with diethyl ether (3 × 50 mL). The combined organic layers were dried over $MgSO_4$ and the solvent was evaporated in vacuo. Purification by column chromatography (silica gel; cyclohexane/ethyl acetate 5:1) gave 2,6-dimethyl-4-(*p*-tolylthio)aniline (2.56 g; 88%) as a brown solid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.14 (s, 6H; CH_3), 2.27 (s, 3H; CH_3), 3.64 (s, 2H; NH_2), 7.01 (m, 2H; arom. CH), 7.06 (m, 2H; arom. CH), 7.10 ppm (m, 2H; arom. CH); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 17.5, 20.9, 120.4, 122.6, 128.0, 128.3, 129.6, 134.3, 136.1, 142.6 ppm.

General procedure for the synthesis of diimines: The corresponding aniline (2.0–2.5 equiv) was dissolved in EtOH (2 mL mmol^{-1}) and then treated with aqueous glyoxal solution (40% wt, 1.0 equiv) and three drops of formic acid. The reaction mixture was stirred overnight. The yellow solid was filtered off, washed with cold MeOH, and dried in vacuo. The volume of the mother liquor was halved and the remaining solution kept at 4 °C overnight for a second batch of product.

***N*,*N*′-Bis(2,6-dimethyl-4-diethylaminophenyl)ethylenediimine (1)**: Starting materials used were 2,6-dimethyl-4-(diethylamino)aniline (21.85 g, 85 mmol, 2.5 equiv) and glyoxal (3.9 mL, 34 mmol, 1.0 equiv). Yield: 11.65 g (84%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.17 (t, 12H; CH_2CH_3), 2.23 (s, 12H; CH_3), 3.34 (q, 8H; CH_2CH_3). 6.43 (s, 4H; arom.), 8.11 ppm (s, 2H; CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 12.8, 19.4, 44.3, 112.0, 129.4, 139.8, 145.4, 162.2 ppm.

***N*,*N*′-Bis(2,6-dimethyl-4-dodecyloxyphenyl)ethylenediimine (2)**: Starting materials used were 2,6-dimethyl-4-dodecyloxyaniline (2.39, 7.8 mmol, 2.0 equiv) and glyoxal (0.45 mL, 3.9 mmol, 1.0 equiv). Yield: 1.18 g (48%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (t, 6H; CH_3), 1.20–1.47 (m, 36H; CH_2), 1.76 (m, 4H; CH_2), 2.19 (s, 12H; CH_3), 3.93 (t, 4H; OCH_2), 6.64 (s, 4H; arom.), 8.09 ppm (s, 2H; CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.1, 18.7, 22.7, 26.1, 29.4, 29.4, 29.6, 29.7, 29.7, 31.9, 68.1, 114.2, 128.6, 143.2, 156.3, 163.4 ppm.

***N*,*N*′-Bis(2,6-dimethyl-4-bromophenyl)ethylenediimine (5)**: Starting materials used were 2,6-dimethyl-4-bromoaniline (5.0 g, 17.8 mmol, 2.0 equiv) and glyoxal (1.02 mL, 8.9 mmol, 1.0 equiv). Yield: 3.08 g (82%); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.15 (s, 12H; CH_3), 7.16 (s, 4H; arom.), 8.07 ppm (s, 2H; CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.2, 117.9, 128.8, 131.1, 148.8, 163.7 ppm.

***N*,*N*′-Bis(2,6-dimethyl-4-tolylthiophenyl)ethylenediimine (6)**: Starting materials used were 2,6-dimethylamino-4-(*p*-tolylthio)aniline (2.56 g, 10.5 mmol, 2.0 equiv) and glyoxal (0.6 mL, 5.25 mmol, 1.0 equiv). Yield: 2.65 g (99%); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.12 (s, 12H; CH_3), 2.34 (s, 6H; CH_3), 7.08 (s, 4H; arom. CH), 7.13 (dd, 4H; arom. CH), 7.27 (dd, 4H; arom. CH), 8.09 ppm (s, 2H; CH=N); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 18.2, 21.8, 127.7, 129.9, 130.8, 131.1, 131.8, 132.5, 137.0, 148.9, 163.4 ppm.

General procedure for the synthesis of diamines: The corresponding ethylenediimine (1.0 equiv) was placed in a Schlenk flask and dissolved in anhydrous THF (10 mL mmol^{-1}) under an atmosphere of Ar. The solution was cooled to 0 °C and $LiAlH_4$ pellets (2.0 equiv) were added. The

reaction mixture was stirred overnight at room temperature and then poured carefully into an excess of an ice/concentrated HCl mixture.

Workup A: The white precipitate was collected by filtration, washed with cold water, and dried in vacuo.

Workup B: The reaction mixture was basified by using NaOH and extracted with diethyl ether (3×250 mL). The combined organic layers were dried over $MgSO_4$ and the solvent was evaporated in vacuo.

***N,N′*-Bis(2,6-dimethyl-4-diethylaminophenyl)ethylenediamine (7)**: Starting materials used were *N,N′*-bis(2,6-dimethyl-4-diethylaminophenyl)-ethylenediimine (10.82 g, 26.6 mmol, 1.0 equiv) and $LiAlH_4$ (2.0 g, 53.2 mmol, 2.0 equiv). Workup procedure B was followed. Yield: 10.9 g (99%); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.00$ (t, 12H; CH_2CH_3), 2.21 (s, 12H; $ArCH_3$), 2.98 (s, 2H; NH_2), 3.17 (q, 8H; CH_2CH_3), 6.32 ppm (s, 4H; arom.); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 12.8$, 19.2, 44.7, 50.0, 113.5, 132.0, 135.9, 143.9 ppm.

***N,N′*-Bis(2,6-dimethyl-4-dodecyloxyphenyl)ethylenediamine (8)**: Starting materials used were *N,N′*-bis(2,6-dimethyl-4-dodecyloxyphenyl)ethylenediimine (1.18 g, 1.9 mmol, 1.0 equiv) and $LiAlH_4$ (141 mg, 3.7 mmol, 2.0 equiv). Workup procedure B was followed. Yield: 0.74 g (61%); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.88$ (t, 6H; CH_3), 1.20–1.50 (m, 36H; CH_2), 1.60–1.70 (m, 4H; CH_2), 2.29 (s, 12H; CH_3), ca. 2.70–3.30 (br s, 2H; NH), 3.08 (s, 4H; NCH_2), 3.88 (t, 4H; OCH_2), 6.58 ppm (s, 4H; arom.); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 14.1$, 18.6, 22.7, 26.1, 29.4, 29.4, 29.6, 29.6, 29.7, 31.9, 49.6, 68.1, 114.7, 131.8, 139.0, 154.5 ppm.

***N,N′*-Bis(2,6-dimethyl-4-bromophenyl)ethylenediamine dihydrochloride (11)**: Staring materials used were *N,N′*-bis(2,6-dimethyl-4-bromophenyl)ethylenediimine (4.22 g, 10 mmol, 1.0 equiv) and $LiAlH_4$ (760 mg, 20 mmol, 2.0 equiv). Workup procedure A was followed. Yield: 2.84 g (57%); ^{1}H NMR (300 MHz, [D_6]DMSO): $\delta = 2.37$ (s, 12H; CH_3), 3.52 (s, 4H; CH_2), 7.23 ppm (s, 4H; arom.), NH_2 was not observed; ^{13}C NMR (75 MHz, [D_6]DMSO): $\delta = 18.1$, 46.3, 118.6, 129.9, 132.1 137.1 ppm.

***N,N′*-Bis(2,6-dimethyl-4-tolylthiophenyl)ethylenediamine dihydrochloride (12)**: Starting materials used were *N,N′*-bis(2,6-dimethyl-4-tolylthiophenyl)-ethylenediimine (15.0 g, 29.5 mmol, 1.0 equiv) and $LiAlH_4$ (2.24 g, 59.0 mmol, 2.0 equiv). Workup procedure A was followed. Yield: 13.3 g (76%); ^{1}H NMR ([D_6]DMSO, 300 MHz): $\delta = 2.29$ (s, 12H; CH_3), 2.34 (s, 6H; CH_3), 3.51 (s, 4H; CH_2), 5.92 (br s, 4H; NH_2), 7.00 (s, 4H; arom. CH), 7.18–7.23 ppm (m, 8H; arom. CH); ^{13}C NMR ([D_6]DMSO, 75 MHz): $\delta = 23.5$, 25.9, 51.7, 135.5, 136.0, 136.5, 137.5, 142.5 ppm.

General procedure for the synthesis of imidazolium chlorides (13u–18u)·H$^+$: The corresponding diimine (1.0 equiv) was dissolved in anhydrous THF (10 mL mmol^{-1}) under an atmosphere of Ar. A solution of paraformaldehyde (1.25–1.40 equiv) in HCl in dioxane (4M, 1.5 equiv) was prepared and added to the diimine solution at 0°C by syringe. The reaction mixture was stirred at room temperature for 4 h, the white precipitate was filtrated, washed with diethyl ether, and dried in vacuo.

***N,N′*-Bis(2,6-dimethyl-4-diethylaminophenyl)imidazolium chloride (13u·H$^+$)**: Starting materials used were *N,N′*-bis(2,6-dimethyl-4-diethylaminophenyl)ethylenediimine (1.95 g, 4.8 mmol, 1.0 equiv), paraformaldehyde (205 mg, 6.84 mmol, 1.4 equiv), HCl in dioxane (4M, 1.8 mL, 7.11 mmol, 1.5 equiv). Yield: 1.35 g (62%); ^{1}H NMR (300 MHz, [D_6]DMSO): $\delta = 1.10$ (t, 12H; CH_2CH_3), 2.06 (s, 12H; CH_3), 3.38 (q, 8H; CH_2CH_3), 6.56 (s, 4H; arom. H), 8.14 (s, 2H; HC=CH), 9.57 ppm (s, 1H; CH); ^{13}C NMR ([D_6]DMSO, 75 MHz): $\delta = 12.4$, 17.4, 43.7, 110.5, 121.3, 125.2, 134.9, 139.2, 148.3 ppm.

***N,N′*-Bis(2,6-dimethyl-4-dodecyloxyphenyl)imidazolium chloride (14u·H$^+$)**: Starting materials used were *N,N′*-bis(2,6-dimethyl-4-dodecyloxyphenyl)-ethylenediimine (650 mg, 1.03 mmol, 1.0 equiv), paraformaldehyde (38.5 mg, 1.28 mmol, 1.25 equiv) and HCl in dioxane (4M, 0.385 mL, 1.5 equiv). Yield: 435 mg (62%); ^{1}H NMR (300 MHz, [D_6]DMSO): $\delta =$ 0.85 (t, 6H; alkyl-CH_3), 1.20–1.40 (m, 36H; CH_2), 1.60–1.80 (m, 4H; CH_2), 2.11 (s, 12H; CH_3), 4.02 (t, 4H; OCH_2), 6.93 (s, 4H; arom. H), 8.24 (s, 2H; HC=CH), 9.69 ppm (s, 1H; CH); ^{13}C NMR ([D_6]DMSO, 75 MHz): $\delta = 13.9$, 17.4, 22.1, 25.4, 28.5, 28.7, 29.0, 31.3, 67.9, 114.3, 125.0, 126.1, 136.0, 139.0, 159.7 ppm.

***N,N′*-Bis(2,6-dimethyl-4-bromophenyl)imidazolium chloride (17u·H$^+$)**: Starting materials used were *N,N′*-bis(2,6-dimethyl-4-bromophenyl)ethylenediimine (420 mg, 1.0 mmol, 1.0 equiv), paraformaldehyde (38 mg, 1.25 mmol, 1.25 equiv) and HCl in dioxane (4M, 0.38 mL, 1.5 mmol, 1.5 equiv). Yield: 370 mg (79%); ^{1}H NMR ([D_6]DMSO, 500 MHz): $\delta =$ 1.97 (s, 12H; CH_3), 7.49 (d, 4H; arom. H), 8.15 (s, 2H; HC=CH), 9.65 ppm (s, 1H; CH); ^{13}C NMR ([D_6]DMSO, 126 MHz): $\delta = 17.1$, 124.2, 125.0, 131.8, 133.1, 137.8, 139.1 ppm.

***N,N′*-Bis(2,6-dimethyl-4-tolylthiophenyl)imidazolium chloride (18u·H$^+$)**: Starting materials used were *N,N′*-bis(2,6-dimethyl-4-tolylthiophenyl)ethylenediimine (1.21 g, 2.33 mmol, 1.0 equiv), paraformaldehyde (87 mg, 2.9 mmol, 1.25 equiv), and HCl in dioxane (4M, 0.76 mL, 3.0 mmol, 1.3 equiv). Yield: 714 mg (55%); ^{1}H NMR ([D_6]DMSO, 300 MHz): $\delta =$ 2.14 (s, 12H; CH_3), 2.34 (s, 6H; CH_3), 7.14 (s, 4H; arom. CH), 7.29 (d, 4H; arom. CH), 7.41 (d, 4H; arom. CH), 8.30 (d, 2H, ^4J(H,H) = 1.6 Hz; CH=N), 9.81 (t, 1H, ^4J(H,H) = 1.6 Hz; imidazolium H); ^{13}C NMR ([D_6]DMSO, 75 MHz): $\delta = 17.0$, 20.7, 124.7, 127.7, 128.2, 130.6, 131.4, 133.5, 135.7, 137.3, 138.7, 140.5 ppm.

General procedure for the synthesis of imidazolinium chlorides (13s–18s)·H$^+$

Procedure A: The corresponding diamine (1.0 equiv) and NH_4Cl (1.0 equiv) were suspended in $HC(OEt)_3$ (3.0 equiv) and 3 drops of formic acid were added. The reaction mixture was stirred at 120°C for 4 h and then poured into water (500 mL). The aqueous phase was washed with diethyl ether (2×300 mL) and extracted with CH_2Cl_2 (3× 300 mL). The combined organic layers were dried over $MgSO_4$ and the solvent was evaporated in vacuo.

Procedure B: The corresponding diamine dihydrochloride was suspended in $HC(OEt)_3$ (5 mL mmol^{-1}), 3 drops of formic acid were added and the reaction mixture was stirred at 120°C overnight. The white precipitate was filtered off, washed several times with diethyl ether and dried in vacuo.

***N,N′*-Bis(2,6-dimethyl-4-diethylaminophenyl)imidazolinium chloride (13s·H$^+$)**: Procedure A was followed and the starting materials used were *N,N′*-bis(2,6-dimethyl-4-diethylaminophenyl)ethylenediamine (10.8 g, 26.3 mmol, 1.0 equiv), NH_4Cl (1.40 g, 26.3 mmol, 1.0 equiv), and $HC(OEt)_3$ (13.1 mL, 78.8 mmol, 3.0 equiv). Yield: 11.2 g (93%); ^{1}H NMR (300 MHz, [D_6]DMSO): $\delta = 1.05$ (t, 6H; CH_3), 2.29 (s, 12H; CH_3), 3.33 (q, 8H; CH_2), 4.33 (s, 4H; CH_2), 6.46 (s, 4H; arom. H), 8.87 ppm (s, 1H; CH); ^{13}C NMR ([D_6]DMSO, 75 MHz): $\delta = 12.4$, 17.8, 43.6, 51.2, 110.7, 121.1, 136.0, 147.7, 160.8 ppm.

***N,N′*-Bis(2,6-dimethyl-4-dodecyloxyphenyl)imidazolinium chloride (14s·H$^+$)**: Procedure A was followed and the starting materials used were *N,N′*-bis(2,6-dimethyl-4-dodecyloxyphenyl)ethylenediamine (864 mg, 1.36 mmol, 1.0 equiv), NH_4Cl (73 mg, 1.36 mmol, 1.0 equiv), and $HC(OEt)_3$ (0.677 mL, 4.07 mmol, 3.0 equiv). Yield: 500 mg (54%); ^{1}H NMR (300 MHz, [D_6]DMSO): $\delta = 0.84$ (t, 6H; CH_3), 1.10–1.50 (m, 36H; CH_2), 1.60–1.81 (m, 4H; CH_2), 2.34 (s, 12H; CH_3), 3.96 (t, 4H; OCH_2), 4.41 (s, 4H; NCH_2CH_2N), 6.81 (s, 4H; arom.), 9.02 ppm (s, 1H; CH); ^{13}C NMR ([D_6]DMSO, 75 MHz): $\delta = 13.9$, 17.5, 22.1, 25.4, 28.5, 28.7, 29.0, 31.3, 51.1, 67.7, 114.4, 126.1, 137.1, 159.1, 160.7 ppm.

***N,N′*-Bis(2,6-dimethyl-4-bromophenyl)imidazolinium chloride (17s·H$^+$)**: Procedure B was followed and *N,N′*-bis(2,6-dimethyl-4-bromophenyl)-ethylenediamine dihydrochloride (2.50 g, 5.0 mmol) was used. Yield: 1.75 g (74%); ^{1}H NMR ([D_6]DMSO, 300 MHz): $\delta = 2.34$ (s, 12H; CH_3), 4.48 (s, 4H; CH_2), 7.54 (s, 4H; arom.), 9.11 ppm (s, 1H; CH); ^{13}C NMR ([D_6]DMSO, 126 MHz): $\delta = 17.0$, 50.8, 122.9, 131.4, 132.7, 138.5, 160.4 ppm.

***N,N′*-Bis(2,6-dimethyl-4-tolylthiophenyl)imidazolinium chloride (18s·H$^+$)**: Procedure B was followed and *N,N′*-bis(2,6-dimethyl-4-tolylthiophenyl)-ethylenediamine dihydrochloride (9.20 g, 15.8 mmol) was used. Yield: 1.6 g (19%); ^{1}H NMR ([D_6]DMSO, 300 MHz): $\delta = 2.30$ (s, 12H; CH_3), 2.37 (s, 6H; CH_3), 4.45 (s, 4H; CH_2), 7.02 (s, 4H; arom. CH), 7.26 (d, 4H; arom. CH), 7.36 (d, 4H; arom. CH), 9.13 ppm (s, 1H; imidazolinium H); ^{13}C NMR ([D_6]DMSO, 75 MHz): $\delta = 17.3$, 20.7, 50.8, 128.1, 128.6, 130.5, 131.6, 133.2, 136.9, 138.6, 139.2, 160.4 ppm.

Oxidation of *N,N′*-bis(2,6-dimethyl-4-tolylthiophenyl)azolium salts: *N,N′*-Bis(2,6-dimethyl-4-tolylsulfinylphenyl)imidazolium chloride (**19u**·H$^+$) (500 mg, 0.894 mmol, 1.0 equiv) was dissolved in glacial acetic acid

(8 mL). H_2O_2 (30%, 157 μL, 1.788 mmol, 2.0 equiv) was added and the reaction mixture was stirred overnight at room temperature. The volatiles were evaporated and the residue was dried in vacuo. Yield: 507 mg (96%); ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 2.18 (s, 12H; CH_3), 2.33 (s, 6H; CH_3), 7.37 (d, 4H; arom.), 7.68 (d, 4H; arom.), 7.74 (s, 4H; arom.), 8.33 (s, 2H; NCHCHN), 9.75 ppm (s, 1H; CH); ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 17.2, 20.8, 123.7, 124.2, 124.4, 130.2, 135.0, 136.6, 138.7, 141.6, 142.2, 148.8 ppm.

***N,N′*-Bis(2,6-dimethyl-4-tolylsulfinylphenyl)imidazolinium chloride (19s·H$^+$)**: *N,N′*-Bis(2,6-dimethyl-4-tolylthiophenyl)imidazolium chloride (293 mg, 0.524 mmol, 1.0 equiv) was dissolved in glacial acetic acid (10 mL). H_2O_2 (30%, 110 μL, 1.074 mmol, 2.0 equiv) was added and the reaction mixture was stirred overnight at room temperature. The volatiles were evaporated and the residue dried in vacuo. Yield: 312 mg (99%); ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 2.30 (s, 12H; CH_3), 2.33 (s, 6H; CH_3), 4.44 (s, 4H; NCH_2CH_2N), 7.05 (s, 4H; arom.), 7.26 (d, 4H; arom.), 7.35 (d, 4H; arom.), 9.07 ppm (s, 1H; CH); ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 17.3, 20.7, 50.8, 124.2, 128.1, 128.6, 130.5, 131.6, 13.2, 136.9, 138.6, 139.2 ppm.

***N,N′*-Bis(2,6-dimethyl-4-tolylsulfonylphenyl)imidazolium chloride (20u·H$^+$)**: *N,N′*-Bis(2,6-dimethyl-4-tolylthiophenyl)imidazolium chloride (1.00 mg, 1.79 mmol, 1.0 equiv) was dissolved in glacial acetic acid (40 mL). H_2O_2 (30%, 3.2 mL, 31.4 mmol, 17.6 equiv) was added and the reaction mixture was stirred for 2 d at room temperature. The volatiles were evaporated and the residue dried in vacuo. Yield: 1.11 g (99%); ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 2.22 (s, 12H; CH_3), 2.38 (s, 6H; CH_3), 7.46 (d, 4H; arom.), 7.92 (d, 4H; arom.), 8.01 (s, 4H; arom. CH), 8.36 (d, 2H; NCHCHN), 9.88 ppm (t, 1H; CH); ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 17.2, 21.0, 124.3, 127.3, 127.7, 130.3, 137.1, 137.2, 137.5, 138.7, 143.4, 144.9 ppm.

***N,N′*-Bis(2,6-dimethyl-4-tolylsulfonylphenyl)imidazolinium chloride (20s·H$^+$)**: *N,N′*-Bis(2,6-dimethyl-4-tolylthiophenyl)imidazolinium chloride (1.00 mg, 1.79 mmol, 1.0 equiv) was dissolved in glacial acetic acid (40 mL). H_2O_2 (30%, 3.2 mL, 31.4 mmol, 17.6 equiv) was added and the reaction mixture was stirred for 2 d at room temperature. The volatiles were evaporated and the residue dried in vacuo. Yield: 1.11 g (99%); ^{1}H NMR ([D$_6$]DMSO, 300 MHz): δ = 2.36 (s, 6H; CH_3), 2.45 (s, 12H; CH_3), 4.50 (s, 4H; NCH_2CH_2N), 7.43 (d, 4H; arom.), 7.86–7.89 (m, 8H; arom.), 9.14 ppm (s, 1H; CH); ^{13}C NMR ([D$_6$]DMSO, 75 MHz): δ = 17.5, 21.2, 50.7, 127.3, 127.6, 130.3, 137.4, 137.7, 138.3, 142.5, 144.7, 160.3 ppm.

General procedure for the synthesis of [IrCl(cod)(NHC)] complexes: [Ir(μ-Cl)(cod)]$_2$ (1.0 equiv) and KO*t*Bu (2.0 equiv) were placed in a Schlenk tube, dissolved in THF (5 mL) under an atmosphere of Ar and stirred for 10 min at room temperature. To this mixture was added the corresponding azolium salt (1.8 equiv). The reaction mixture was stirred for 2 h at room temperature and the solvent was evaporated in vacuo.

Workup A: The residue was dissolved in diethyl ether and purified by column chromatography using diethyl ether as an eluent. The product was obtained as a yellow powder.

Workup B: The residue was washed with diethyl ether (3 mL), dissolved in CH_2Cl_2, and filtrated over Celite. The solvent was evaporated in vacuo leaving a yellow powder.

[IrCl(cod)(13s)]: Starting materials used were [Ir(μ-Cl)(cod)]$_2$ (50 mg, 0.075 mmol, 1.0 equiv), KO*t*Bu (17 mg, 0.15 mmol, 2.0 equiv), and *N,N′*-bis(2,6-dimethyl-4-diethylaminophenyl)imidazolinium chloride (62 mg, 0.135 mmol, 1.8 equiv). Workup procedure A was followed. Yield: 78 mg (76%); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.14–1.28 (m, 4H; cod CH_2), 1.14–1.19 (m, 12H; CH_3), 1.61–1.66 (m, 4H; cod CH_2), 2.32 (s, 6H; CH_3), 2.53 (s, 6H; CH_3), 3.17 (m, 2H; cod CH), 3.30–3.41 (q, 8H; NCH_2), 3.87 (s, 4H; NCH_2CH_2N), 4.06 (m, 2H; cod CH), 6.40 (d, 2H; arom.), 6.43 ppm (d, 2H; arom.); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 11.6, 18.2, 19.4, 27.7, 32.5, 43.4, 50.0, 51.2, 81.2, 109.6, 111.0, 126.6, 135.0, 137.9, 146.1, 207.0 ppm.

[IrCl(cod)(13u)]: Starting materials used were [Ir(μ-Cl)(cod)]$_2$ (50 mg, 0.075 mmol, 1.0 equiv), KO*t*Bu (17 mg, 0.15 mmol, 2.0 equiv) and *N,N′*-bis(2,6-dimethyl-4-diethylaminophenyl)imidazolium chloride (61 mg, 0.135 mmol, 1.8 equiv). Workup procedure A was followed. Yield: 70 mg (69%); ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.17–1.35 (m, 4H; cod CH_2), 1.20 (t, 12H; CH_3), 1.66–1.76 (m, 4H; cod CH_2), 2.11 (s, 6H; CH_3), 2.34 (s, 6H; CH_3), 3.08 (m, 2H; cod CH), 3.32–3.44 (m, 8H; NCH_2), 4.12 (m, 2H; cod CH), 6.42 (s, 2H; arom.), 6.46 (s, 2H; arom.), 6.92 ppm (s, 2H; NCHCHN); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 11.6, 17.8, 19.3, 28.0, 32.6, 43.4, 50.0, 80.2, 109.1, 110.6, 122.6, 126.5, 134.3, 137.0, 146.6, 180.7 ppm.

[IrCl(cod)(14s)]: Starting materials used were [Ir(μ-Cl)(cod)]$_2$ (18 mg, 0.027 mmol, 1.0 equiv), KO*t*Bu (6.1 mg, 0.054 mmol, 2.0 equiv), and *N,N′*-bis(2,6-dimethyl-4-dodecyloxyphenyl)imidazolinium chloride (34 mg, 0.049 mmol, 1.8 equiv). Workup procedure A was followed. Yield: 30 mg (61%); ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 0.88 (t, 6H; CH_3), 1.24–1.36 (m, 36H; CH_2), 1.44–1.46 (m, 4H; cod CH_2), 1.64–1.65 (m, 4H; CH_2), 1.76–1.79 (m, 4H; cod CH_2), 2.34 (s, 6H; CH_3), 2.55 (s, 6H; CH_3), 3.08–3.09 (m, 2H; cod CH), 3.88 (s, 4H; NCH_2CH_2N), 3.94–3.98 (t, 4H; OCH_2), 4.11 (m, 2H; cod CH), 6.66 (d, 2H; arom.), 6.68 ppm (d, 2H; arom.); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 13.1, 17.7, 19.3, 21.7, 25.0, 27.7, 28.3, 28.3, 28.4, 28.6, 28.6, 28.6, 28.7, 30.9, 32.5, 50.3, 50.9, 67.0, 82.6, 112.8, 113.1, 130.7, 135.7, 138.6, 157.3, 207.0 ppm.

[IrCl(cod)(14u)]: Starting materials used were [Ir(μ-Cl)(cod)]$_2$ (25 mg, 0.037 mmol, 1.0 equiv), KO*t*Bu (8.3 mg, 0.074 mmol, 2.0 equiv), and *N,N′*-bis(2,6-dimethyl-4-dodecyloxyphenyl)imidazolium chloride (46 mg, 0.067 mmol, 1.8 equiv). Workup procedure A was followed. Yield: 40 mg (61%); ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 0.88 (t, 6H; CH_3), 1.25–1.37 (m, 36H; CH_2), 1.45–1.50 (m, 4H; cod CH_2), 1.64–1.76 (m, 4H; CH_2), 1.77–1.83 (m, 4H; cod CH_2), 2.15 (s, 6H; CH_3), 2.36 (s, 6H; CH_3), 2.97 (m, 2H; cod CH), 3.97–4.01 (m, 2H; cod CH), 4.16 (t, 4H; OCH_2), 6.69 (s, 2H; arom.), 6.71 (s, 2H; arom.), 7.26 ppm (s, 2H; NCHCHN); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 13.1, 17.5, 19.1, 21.7, 25.0, 25.9, 28.0, 28.3, 28.3, 28.4, 28.6, 28.6, 28.7, 30.9, 32.6, 50.3, 67.1, 81.5, 112.5, 112.9, 122.5, 130.5, 134.9, 137.9, 157.9, 180.5 ppm.

[IrCl(cod)(15s)]: Starting materials used were [Ir(μ-Cl)(cod)]$_2$ (50 mg, 0.075 mmol, 1.0 equiv), KO*t*Bu (17 mg, 0.15 mmol, 2.0 equiv), and *N,N′*-bis(2,4,6-trimethylphenyl)imidazolinium chloride (46 mg, 0.135 mmol, 1.8 equiv). Workup procedure A was followed. Yield: 62 mg (72%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.18–1.34 (m, 4H; cod CH_2), 1.59–1.62 (m, 4H; cod CH_2), 2.31 (s, 6H; CH_3), 2.34 (s, 6H; CH_3), 2.55 (s, 6H; CH_3), 3.07 (m, 2H; cod CH), 3.90 (s, 4H; NCH_2CH_2N), 4.09 (m, 2H; cod CH), 6.94 (s, 2H; arom.), 6.97 ppm (s, 2H; arom.); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 17.4, 18.8, 20.0, 27.6, 32.4, 50.4, 50.8, 82.7, 127.3, 128.8, 134.2, 135.2, 136.7, 137.0, 206.3 ppm.

[IrCl(cod)(15u)]: Starting materials used were [Ir(μ-Cl)(cod)]$_2$ (50 mg, 0.075 mmol, 1.0 equiv), KO*t*Bu (17 mg, 0.15 mmol, 2.0 equiv), and *N,N′*-bis(2,4,6-trimethylphenyl)imidazolium chloride (46 mg, 0.135 mmol, 1.8 equiv). Workup procedure A was followed. Yield: 80 mg (93%); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.18–1.34 (m, 4H; cod CH_2), 1.61–1.70 (m, 4H; cod CH_2), 2.16 (s, 6H; CH_3), 2.36 (s, 6H; CH_3), 2.36 (s, 6H; CH_3), 2.97 (m, 2H; cod CH), 4.15 (m, 2H; cod CH), 6.95 (s, 2H; NCHCHN), 6.98 (s, 2H; arom.), 7.04 ppm (s, 2H; arom.); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 17.2, 18.6, 20.1, 27.9, 32.5, 50.4, 81.5, 122.3, 127.1, 128.5, 133.4, 135.1, 136.3, 137.6, 179.8 ppm.

[IrCl(cod)(16s)]: Starting materials used were [Ir(μ-Cl)(cod)]$_2$ (50 mg, 0.075 mmol, 1.0 equiv), KO*t*Bu (17 mg, 0.15 mmol, 2.0 equiv), and *N,N′*-bis(2,6-dimethylphenyl)imidazolinium chloride (43 mg, 0.135 mmol, 1.8 equiv). Workup procedure A was followed. Yield: 75 mg (90%); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.18–1.33 (m, 4H; cod CH_2), 1.54–1.63 (m, 4H; cod CH_2), 2.40 (s, 6H; CH_3), 2.59 (s, 6H; CH_3), 3.05 (m, 2H; cod CH), 3.94 (s, 4H; NCH_2CH_2N), 4.09 (m, 2H; cod CH), 7.23 (s, 6H; arom.), 7.25 ppm (s, 6H; arom.); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 17.6, 19.0, 27.6, 32.4, 50.5, 50.6, 83.1, 126.7, 127.2, 128.1, 134.6, 137.5, 137.6, 206.2 ppm.

[IrCl(cod)(16u)]: Starting materials used were [Ir(μ-Cl)(cod)]$_2$ (50 mg, 0.075 mmol, 1.0 equiv), KO*t*Bu (17 mg, 0.15 mmol, 2.0 equiv), and *N,N′*-bis(2,6-dimethylphenyl)imidazolium chloride (42 mg, 0.135 mmol, 1.8 equiv). Workup procedure A was followed. Yield: 69 mg (82%); ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.23–1.27 (m, 2H; cod CH_2), 1.32–1.35 (m, 2H; cod CH_2), 1.63–1.70 (m, 4H; cod CH_2), 2.21 (s, 6H; CH_3), 2.40 (s, 6H; CH_3), 2.95 (m, 2H; cod CH), 4.15 (m, 2H; cod CH), 7.00 (s, 2H; NCHCHN), 7.18 (m, 6H; arom.), 7.31 ppm (s, 6H; arom.); ^{13}C NMR

($CDCl_3$, 125 MHz): $\delta = 17.3$, 18.8, 27.9, 32.5, 50.5, 81.9, 122.2, 126.5, 127.8, 127.9, 133.8, 136.8, 137.4, 179.6 ppm.

[IrCl(cod)(17s)]: Starting materials used were $[Ir(\mu\text{-}Cl)(cod)]_2$ (50 mg, 0.075 mmol, 1.0 equiv), KO*t*Bu (17 mg, 0.15 mmol, 2.0 equiv), and *N*,*N*′-bis(2,6-dimethyl-4-bromophenyl)imidazolinium chloride (91 mg, 0.135 mmol, 1.8 equiv). Workup procedure A was followed. Yield: 71 mg (68%); ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 1.18$–1.43 (m, 4H; cod CH_2), 1.58–1.75 (m, 4H; cod CH_2), 2.35 (s, 6H; CH_3), 2.57 (s, 6H; CH_3), 2.98 (m, 2H; cod CH), 3.89 (s, 4H; NCH_2CH_2N), 4.20 (m, 2H; cod CH), 7.31 ppm (d, 4H; arom.); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 17.4$, 18.9, 27.6, 32.4, 50.5, 50.8, 84.4, 120.8, 129.6, 130.9, 136.6, 136.7, 139.7 ppm, Ir–C could not be observed.

[IrCl(cod)(17u)]: Starting materials used were $[Ir(\mu\text{-}Cl)(cod)]_2$ (50 mg, 0.075 mmol, 1.0 equiv), KO*t*Bu (17 mg, 0.15 mmol, 2.0 equiv), and *N*,*N*′-bis(2,6-dimethyl-4-bromophenyl)imidazolium chloride (90 mg, 0.135 mmol, 1.8 equiv). Workup procedure A was followed. Yield: 65 mg (63%); ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 1.18$–1.46 (m, 4H; cod CH_2), 1.63–1.85 (m, 4H; cod CH_2), 2.18 (s, 6H; CH_3), 2.37 (s, 6H; CH_3), 2.89 (m, 2H; cod CH), 4.25 (m, 2H; cod CH), 6.97 (s, 2H; NCHCHN), 7.26 (s, 2H; arom.), 7.35 ppm (s, 2H; arom.); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta =$ 17.2, 18.7, 27.9, 32.5, 50.7, 83.2, 121.7, 122.3, 129.4, 130.7,136.0, 136.4, 138.9, 180.2 ppm.

[IrCl(cod)(19s)]: Starting materials used were $[Ir(\mu\text{-}Cl)(cod)]_2$ (50 mg, 0.075 mmol, 1.0 equiv), KO*t*Bu (17 mg, 0.15 mmol, 2.0 equiv), and *N*,*N*′-bis(2,6-dimethyl-4-tolylsulfinylphenyl)imidazolinium chloride (79 mg, 0.135 mmol, 1.8 equiv). Workup procedure B was followed. Yield: 45 mg (40%); ^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 1.08$–1.44 (m, 8H; cod CH_2), 2.38 (m, 12H; CH_3), 2.58 (s, 6H; CH_3), 2.82–2.84 (m, 2H; cod CH), 3.96 (m, 4H; NCH_2CH_2N), 4.01–4.06 (m, 2H; cod CH), 7.24–7.27 (m, 5H; arom.), 7.37 (m, 1H; arom.), 7.34 (m, 1H; arom.), 7.52–7.56 ppm (s, 5H; arom.); ^{13}C NMR ($CDCl_3$, 125 MHz): $\delta = 18.7$, 19.8, 20.8, 27.8, 32.5, 51.7, 51.1, 85.7, 124.4, 124.9, 128.0, 128.5, 129.5, 137.1, 139.3, 141.1, 141.8, 144.6 ppm, Ir–C could not be observed.

[IrCl(cod)(19u)]: Starting materials used were $[Ir(\mu\text{-}Cl)(cod)]_2$ (50 mg, 0.075 mmol, 1.0 equiv), KO*t*Bu (17 mg, 0.15 mmol, 2.0 equiv), and *N*,*N*′-bis(2,6-dimethyl-4-tolylsulfinylphenyl)imidazolium chloride (79 mg, 0.135 mmol, 1.8 equiv). Workup procedure B was followed. Yield: 76 mg (63%); ^{1}H NMR (500 MHz): $\delta = 0.83$–0.89 (m, 2H; cod CH_2), 1.54 (m, 6H; cod-CH_2), 2.19 (m, 6H; CH_3), 2.36–2.39 (m, 12H; CH_3), 2.69–2.89 (m, 2H; cod CH), 4.01–4.07 (m, 2H; cod CH), 7.00–7.57 ppm (m, 14H; arom.); ^{13}C NMR ($CDCl_3$, 125 MHz): $\delta = 17.5$, 19.0, 20.4, 27.6, 32.3, 50.6, 83.1, 121.7, 122.3, 123.2, 124.1, 129.2, 131.4, 138.5, 139.2, 140.9, 141.4, 145.3, 180.1 ppm.

[IrCl(cod)(20s)]: Starting materials used were $[Ir(\mu\text{-}Cl)(cod)]_2$ (50 mg, 0.075 mmol, 1.0 equiv), KO*t*Bu (17 mg, 0.15 mmol, 2.0 equiv), and *N*,*N*′-bis(2,6-dimethyl-4-tosylphenyl)imidazolinium chloride (84 mg, 0.135 mmol, 1.8 equiv). Workup procedure B was followed. Yield: 110 mg (89%); ^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 1.06$–1.26 (m, 8H; cod CH_2), 2.39 (s, 6H; CH_3), 2.40 (s, 6H; CH_3), 2.60 (s, 6H; CH_3), 2.75 (m, 2H; cod CH), 3.94 (s, 4H; NCH_2CH_2N), 3.94–3.96 (m, 2H; cod CH), 7.30 (d, 4H; arom.), 7.68 (s, 2H; arom.), 7.72 (s, 2H; arom.), 7.81 ppm (d, 4H; arom.); ^{13}C NMR ($CDCl_3$, 125 MHz): $\delta = 19.2$, 20.6, 22.0, 28.6, 33.4, 51.5, 52.1, 91.3, 127.0, 128.0, 128.5, 130.3, 137.7, 139.0, 141.0, 141.6, 142.8, 144.6, 208.2 ppm.

[IrCl(cod)(20u)]: Starting materials used were $[Ir(\mu\text{-}Cl)(cod)]_2$ (50 mg, 0.075 mmol, 1.0 equiv), KO*t*Bu (17 mg, 0.15 mmol, 2.0 equiv), and *N*,*N*′-bis(2,6-dimethyl-4-tosylphenyl)imidazolium chloride (83 mg, 0.135 mmol, 1.8 equiv). Workup procedure B was followed. Yield: 115 mg (93%); ^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 1.06$–1.11 (m, 2H; cod CH_2), 1.16–1.30 (m, 4H; cod CH_2), 1.32–1.40 (m, 2H; cod CH_2), 2.20 (s, 6H; CH_3), 2.40 (s, 12H; CH_3), 2.67 (m, 2H; cod CH), 4.01 (m, 2H; cod CH), 7.01 (s, 2H; NCHCHN), 7.32 (d, 4H; arom.), 7.76 (s, 4H; arom.), 7.83 ppm (d, 4H; arom.); ^{13}C NMR ($CDCl_3$, 125 MHz): $\delta = 17.5$, 19.0, 20.6, 27.5, 32.1, 50.6, 83.7, 122.1, 125.4, 126.7, 126.9, 129.0, 135.6, 137.4, 138.8, 140.9, 141.2, 143.4, 180.2 ppm.

General procedure for the synthesis of $[IrCl(CO)_2(NHC)]$ complexes: The corresponding [IrCl(cod)(NHC)] complex was dissolved in CH_2Cl_2 (10 mL) and CO was bubbled through this solution for 15 min. The solvent was evaporated and the residue washed with pentane (10 mL) to obtain the products as yellow powders. The conversions for all reactions are quantitative, the lower isolated yields result from small losses (several mg) of material during workup.

[IrCl(CO)$_2$(13s)]: Complex [(**13s**)Ir(cod)Cl] (58 mg, 0.077 mmol) was used. Yield: 52 mg (95%); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.18$ (t, 12H; CH_3), 2.40 (s, 12H; Ar-CH_3), 3.35 (q, 8H; CH_2), 3.94 (s, 4H; CH_2CH_2), 6.38 ppm (s, 4H; ArH); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 12.8$, 19.3, 44.2, 52.3, 111.0, 125.8, 136.8, 147.6, 169.0, 180.9, 202.3 ppm; HRMS: *m*/*z*: calcd for $C_{29}H_{40}N_4O_2ClIr$: 704.2465; found: 704.24694.

[IrCl(CO)$_2$(13u)]: Complex [IrCl(cod)(**13u**)] (52 mg; 0.069 mmol) was used. Yield: 39 mg (80%); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.21$ (t, 12H; CH_3), 2.18 (s, 12H; Ar-CH_3), 3.38 (q, 8H; CH_2), 6.41 (s, 4H; ArH), 7.04 ppm (s, 2H; CHCH); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 12.7$, 19.1, 44.2, 110.6, 124.0, 126.0, 136.0, 148.0, 168.7, 176.8, 180.7 ppm; HRMS: *m*/*z*: calcd for $C_{29}H_{38}N_4O_2ClIr$: 702.2308; found: 702.22938.

[IrCl(CO)$_2$(15s)]: Complex [IrCl(cod)(**15s**)] (50 mg; 0.078 mmol) was used. Yield: 36 mg (78%); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.32$ (s, 6H; Ar-CH_3), 2.43 (s, 12H; Ar-CH_3), 4.00 (s, 4H; CH_2CH_2), 6.96 ppm (s, 4H; ArH); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 18.6$, 21.1, 51.8, 129.6, 134.7, 135.9, 138.7, 168.6, 180.2, 201.8 ppm; HRMS: *m*/*z*: calcd for $C_{23}H_{26}N_2O_2ClIr$: 590.1308; found: 590.12688.

[IrCl(CO)$_2$(15u)]: Complex [IrCl(cod)(**15u**)] (60 mg, 0.093 mmol) was used. Yield: 48 mg (87%); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.21$ (s, 12H; Ar-CH_3), 2.36 (s, 6H; Ar-CH_3), 7.01 (s, 4H; ArH), 7.10 ppm (s, 2H; CHCH); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 18.5$, 21.2, 123.6, 129.3, 134.8, 135.1, 139.5, 168.4, 176.1, 180.0 ppm; HRMS: *m*/*z*: calcd for $C_{23}H_{24}N_2O_2ClIr$: 588.1151; found: 588.11485.

[IrCl(CO)$_2$(16s)]: Complex [IrCl(cod)(**16s**)] (47 mg, 0.077 mmol) was used. Yield: 36 mg (83%); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.48$ (s, 12H; Ar-CH_3), 4.05 (s, 4H; CH_2CH_2), 7.15 (d, 4H; ArH), 7.25 ppm (t, 2H; ArH); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 18.8$, 51.6, 129.9, 129.1, 136.4, 137.1, 168.5, 180.0, 201.8 ppm; HRMS: *m*/*z*: calcd for $C_{21}H_{22}N_2O_2ClIr$: 562.0995; found: 562.09575.

[IrCl(CO)$_2$(16u)]: Complex [IrCl(cod)(**16u**)] (31 mg; 0.051 mmol) was used. Yield: 20 mg (69%); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.27$ (s, 12H; Ar-CH_3), 7.16 (s, 4H; ArH), 7.21 (d, 4H; ArH), 7.33 ppm (t, 2H; ArH); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 18.6$, 123.5, 129.6, 129.7, 135.6, 136.2, 168.3, 176.0, 179.8 ppm; HRMS: *m*/*z*: calcd for $C_{21}H_{20}N_2O_2ClIr$: 560.0838; found: 560.08177.

[IrCl(CO)$_2$(19s)]: Complex [IrCl(cod)(**19s**)] (40 mg; 0.05 mmol) was used. Yield: 37 mg (95%); ^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 2.39$ (s, 6H; CH_3), 2.46 (s, 6H; CH_3), 2.48 (s, 6H; CH_3), 4.01 (s, 4H; NCH_2CH_2N), 7.26 (s, 2H; arom.), 7.29 (d, 4H; arom.), 7.46 (s, 2H; arom.), 7.55 ppm (d, 4H; arom.); ^{13}C NMR ($CDCl_3$, 125 MHz): $\delta = 18.0$, 20.4, 27.0, 50.5, 123.9, 124.0, 124.3, 127.7, 128.8, 129.2, 129.3, 138.1, 141.0, 145.0, 167.2, 178.4, 201.1 ppm; HRMS: *m*/*z*: calcd for $C_{35}H_{34}N_2O_4ClIrS_2$: 838.1278; found: 838.12569.

[IrCl(CO)$_2$(19u)]: Complex [IrCl(cod)(**19u**)] (19 mg; 0.02 mmol) was used. Yield: 17 mg (93%); ^{1}H NMR (500 MHz): $\delta = 2.25$ (s, 6H; CH_3), 2.27 (s, 6H; CH_3), 2.40 (s, 6H; CH_3), 7.14 (s, 2H; NCHCHN), 7.31 (d, 4H; arom.), 7.38 (s, 2H; arom.), 7.52 (s, 2H; arom.), 7.57 ppm (d, 4H; arom.); ^{13}C NMR ($CDCl_3$, 125 MHz): $\delta = 17.9$, 20.5, 27.0, 122.5, 123.5, 123.7, 124.3, 127.7, 129.2, 136.2, 138.0, 140.9, 141.1, 146.0, 167.0, 175.2, 178.2 ppm; HRMS: *m*/*z*: calcd for $C_{35}H_{32}N_2O_4ClIrS_2$: 836.11216; found: 836.11202.

[IrCl(CO)$_2$(20s)]: Complex [IrCl(cod)(**20s**)] (23 mg; 0.03 mmol) was used. Yield: 22 mg (96%); ^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 2.43$ (s, 6H; CH_3), 2.48 (s, 12H; CH_3), 4.00 (s, 4H; NCH_2CH_2N), 7.25 (s, 2H; arom.), 7.34 (d, 4H; arom.), 7.72 (s, 2H; arom.), 7.81 ppm (d, 4H; arom.); ^{13}C NMR ($CDCl_3$, 125 MHz): $\delta = 19.0$, 21.6, 28.0, 51.4, 127.7, 127.9, 128.0, 128.7, 130.1, 138.0, 138.2, 140.9, 142.2, 144.6, 168.2, 179.3, 201.9 ppm; HRMS: *m*/*z*: calcd for $C_{35}H_{34}N_2O_6ClIrS_2$: 870.1176; found: 870.11335.

[IrCl(CO)$_2$(20u)]: Complex [IrCl(cod)(**20u**)] (51 mg; 0.06 mmol) was used. Yield: 51 mg (98%); ^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 2.27$ (s, 12H; CH_3), 2.44 (s, 6H; CH_3), 7.14 (s, 2H; NCHCHN), 7.36 (d, 4H; arom.), 7.75 (s, 4H; arom.), 7.87 ppm (d, 4H; arom.); ^{13}C NMR ($CDCl_3$,

125 MHz): $\delta = 17.2$, 17.8, 20.6, 122.6, 126.7, 127.0, 129.1, 136.4, 136.5, 136.6, 136.9, 139.7, 142.1, 143.7, 167.0, 175.0, 178.0 ppm; HRMS: m/z: calcd for $C_{35}H_{32}N_2O_6ClIrS_2$: 868.10199; found: 868.10494.

Acknowledgements

This work was supported by the DFG and the TU Darmstadt. We wish to thank Dr. K. Hofmann for the X-ray data collection.

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Received: February 7, 2007
Published online: June 25, 2007

