Thiazole-Annelated Imidazolium Salts: A New Architecture for N-Heterocyclic Carbenes

Claudia Lohre, Roland Fröhlich, Frank Glorius*

Institute of Organic Chemistry, Westfälische Wilhelms-Universität Münster, Corrensstraße 40, 48149 Münster, Germany
Fax +49(251)8333202; E-mail: glorius@uni-muenster.de

Received 5 May 2008

Dedicated to Professor Reinhard W. Hoffmann on the occasion of his 75th birthday

Abstract: A short synthesis of thiazole-annelated imidazolium salts is presented. Deprotonation of these salts allowed the formation of new N-heterocyclic carbenes (NHCs) and the investigation of their respective electronic properties, which were determined by X-ray crystal structure analysis and IR spectroscopy of the corresponding iridium carbonyl complexes. Finally, the ability of these NHCs to form the corresponding palladium complexes was demonstrated.

Key words: N-heterocyclic carbene (NHC), imidazolium salt, thiazole, NHC–metal complex

The development of N-heterocyclic carbenes (NHCs) and their application in transition-metal catalysis, organocatalysis and other areas of chemistry has already been a tremendous success story.[1,2,3] Many favorable characteristics render NHCs to be attractive ligands for catalysis.[1] First of all, they are electron-rich donor ligands and generally form intriguingly stable complexes with many metals. In addition, most NHCs successfully employed in catalysis can be considered to be sterically demanding. Moreover, the shape of NHCs differs from other ligands, and monodentate NHCs can easily influence the metal's coordination sphere. Interestingly, it has been found that the steric demand of NHCs can more easily be tuned than their electronic character.[1b]

Arguably, 1,3-disubstituted imidazolylidenes IMes, IiPr and their saturated analogues are the most commonly applied NHCs in transition-metal catalysis (Figure 1). Still, in many cases, other NHCs are optimal and the design and synthesis of NHCs with new electronic and steric properties is highly desirable and should lead to an increasing number of applications in catalysis.[4] Recently, we and others designed a class of annelated NHCs **1** and we successfully applied them in Suzuki–Miyaura cross-coupling reactions.[5,6] As a result of the bicyclic structure of **1**, the R^2 substituent is placed in close proximity to a carbene-bound metal, thus allowing significant shielding of the metal (Figure 1). Using the same substituents (R^1, R^2 = Mes), the steric demand is estimated to be significantly larger compared to IMes.

Based on the different geometry of five-membered compared to six-membered rings, the steric demand of carbenes **2** should lie between those of monocyclic NHCs like IMes and imidazo[1,5-a]pyridine-3-ylidenes (**1**).

To the best of our knowledge, fully unsaturated five-ring annelated NHCs (**2**) have not previously been made. In this communication, we report the first synthesis and investigation of NHCs of type **2** with X = S.

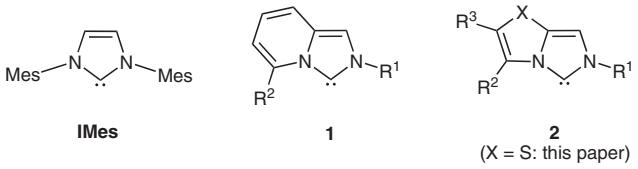


Figure 1 Structural comparison of monocyclic NHC IMes and bicyclic annelated NHCs **1** and **2**

We selected the thiazole-annelated system (X = S), since sulphur has been shown to exhibit interesting carbene stabilizing properties in thiazolium salt derived NHCs.[2] Thus, the symmetrical imidazolium salt **6** was selected as the initial target. Our synthetic endeavour commenced with the synthesis of bisthiazole **5**, easily available by reaction of dithiooxalamide (**3**) and α-bromopinacolone (**4**) in refluxing ethanol (Scheme 1).[7] However, treatment of **5** under conditions developed for the formation of imidazolium salts from bisimines or bioxazolines failed to provide any significant amounts of **6**. Interestingly, *N*,*O*-acetal **7** formed in high yield and was unequivocally characterized by single-crystal X-ray structural analysis (Figure 2).[8] Unfortunately, **7** could not be transformed into the desired imidazolium salt **6** by either heating in tetrahydrofuran

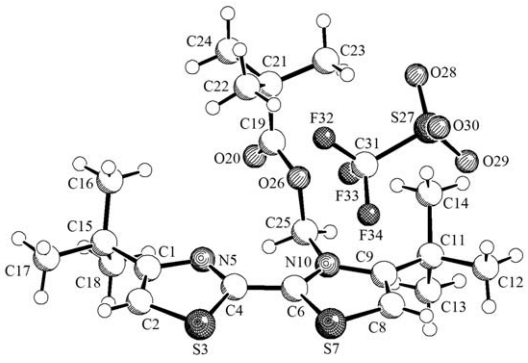
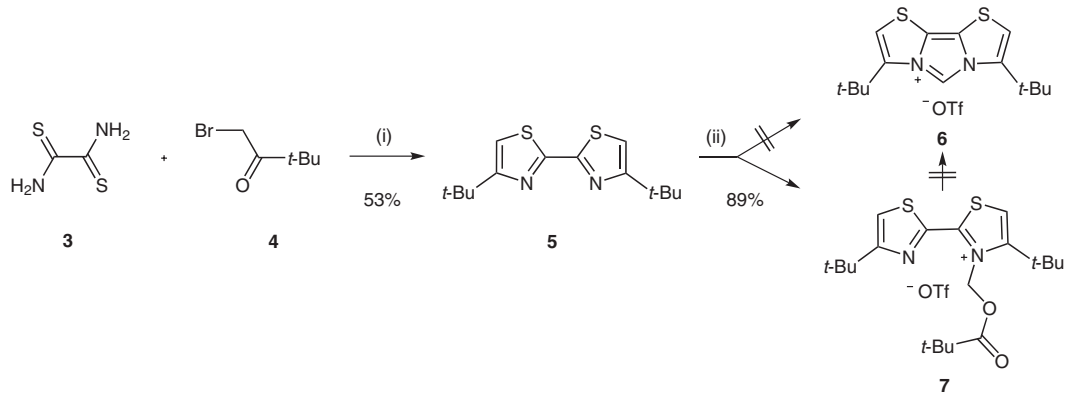


Figure 2 Structure of **7** obtained by X-ray crystal structure analysis[8]

SYNTHESIS 2008, No. 14, pp 2221–2228
Advanced online publication: 18.06.2008
DOI: 10.1055/s-2008-1067147; Art ID: C02008SS

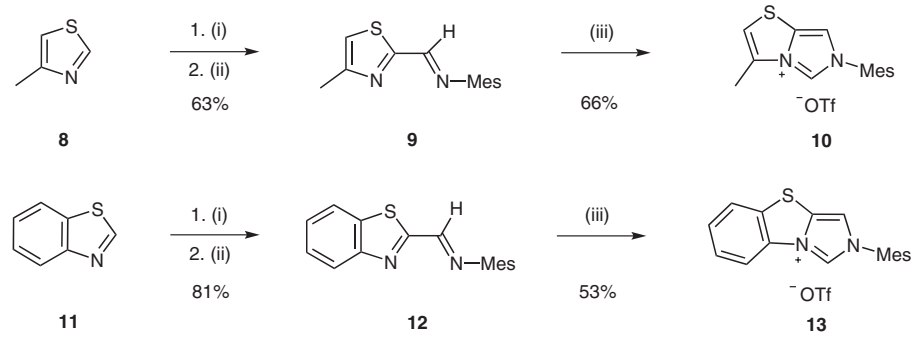


Scheme 1 *Reagents and conditions*: (i) EtOH, reflux, 4 h; (ii) AgOTf, chloromethyl pivalate, CH_2Cl_2, 40 °C, 16 h.

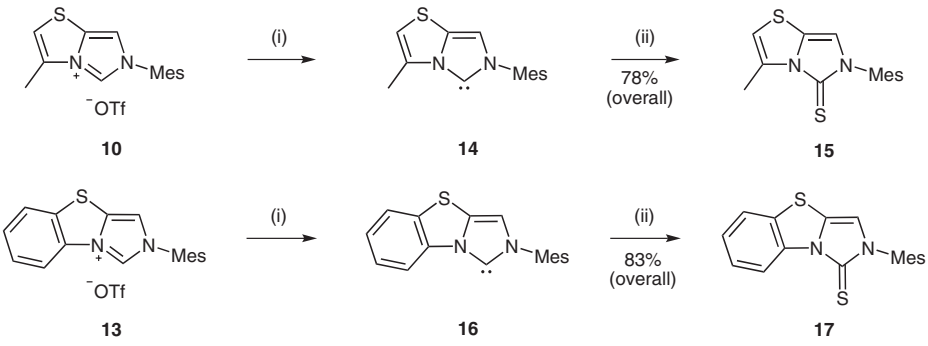
(80 °C) or dioxane (120 °C). In addition, activation of the pivalate leaving group by the Lewis acid $BF_3{\cdot}OEt_2$ or by the nucleophilic catalyst 4-(*N*,*N*-dimethylamino)pyridine (DMAP) was unsuccessful (Scheme 1).

Since the corresponding cyclization of bisimines to imidazolium salts proceeds smoothly, the cyclization of the mixed imine thiazoles **9** and **12** was then investigated (Scheme 2). Selective deprotonation of 4-methylthiazole (**8**) and benzothiazole (**11**) at the 2-position, was followed by formylation with *N*,*N*-dimethylformamide (DMF) and subsequent imine formation by heating the aldehydes in the presence of mesityl amine. Employing a recently developed protocol[4c] resulted in the formation of the desired cyclized imidazolium salts. Namely, chloromethyl pivalate and AgOTf were stirred in dichloromethane at ambient temperature for 45 minutes with the exclusion of light and, subsequently, the AgCl precipitate was allowed to settle. The supernatant was then added to the bisimine and the solution was stirred at 40 °C in the dark. Imidazolium salts **10** and **13** were thus obtained in good overall yields. It has already been noted that the counterion of imidazolium salts has a dramatic influence on the solubility.[1,4] Thus, despite the ionic character of the triflate products, purification by chromatography was the method of choice. The structure of the imidazolium salts was unequivocally established by X-ray structural analysis of single crystals (Figure 3).

With these imidazolium salts in hand, the formation of the corresponding carbenes and their properties was investigated. First of all, the imidazolium triflates **10** and **13** were stirred in tetrahydrofuran with potassium *tert*-butoxide for five minutes, after which time elemental sulphur was add-



Scheme 2 *Reagents and conditions*: (i) *n*-BuLi, Et_2O, –78 °C, 1 h; DMF, 0–20 °C, 3 h; (ii) 2,4,6-trimethylaniline, EtOH, reflux, 3 h; (iii) AgOTf, chloromethyl pivalate, CH_2Cl_2, r.t.; 40 °C, 16 h.



Scheme 3 *Reagents and conditions*: (i) *t*-BuOK, THF, r.t., 5 min; (ii) S_8, r.t., 12 h.

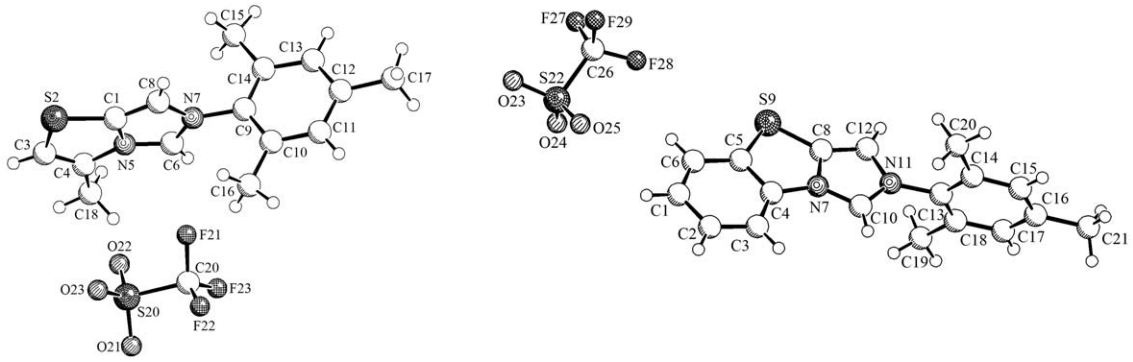


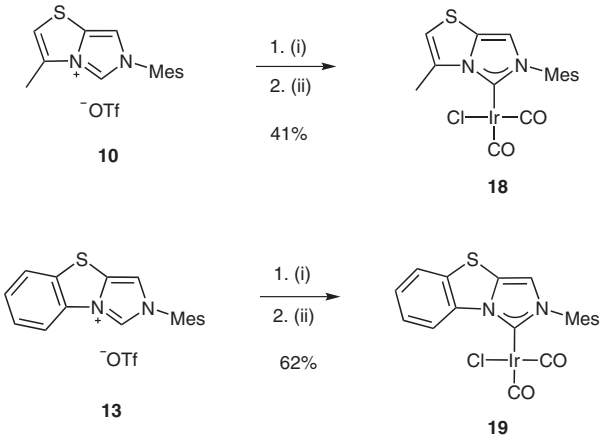
Figure 3 Structures of **10** and **13** obtained by X-ray crystal structure analysis.[8] Selected bond lengths (Å) and angles (°): **10**: N5–C4, 1.406(4); C4–C3, 1.339(5); C3–S2, 1.733(4); S2–C1, 1.729(3); C1–N5, 1.378(4); N5–C6, 1.341(4); C6–N7, 1.325(4); N7–C8, 1.384(4); C8–C1, 1.357(4); N7–C6–N5, 106.8(3); C6–N5–C1, 109.4(2); C6–N7–C8, 110.8(3); **13**: C1–C2, 1.389(8); C2–C3, 1.374(7); C3–C4, 1.380(7); C4–C5, 1.392(7); C5–C6, 1.394(7); C6–C1, 1.360(8); N7–C4, 1.410(5); C4–C5, 1.392(7); C5–S9, 1.745(5); S9–C8, 1.727(5); C8–N7, 1.390(6); C8–C12, 1.348(7); C12–N11, 1.379(6); N11–C10, 1.333(5); C10–N7, 1.336(5); N7–C10–N11, 107.3(4); C10–N7–C8, 109.4(4); C10–N11–C12, 109.7(4).

ed. The resulting formation of thiones **15** and **17** in good yields was a strong indication that the NHCs had formed in situ (Scheme 3).[9] More information on the free carbenes was obtained by conducting the deprotonation in an NMR tube with perdeuterated tetrahydrofuran as the solvent. Although the ^{1}H and ^{13}C NMR spectra of NHCs provide some information on the characteristics, these data did not allow a direct correlation with the electronic properties of these carbenes. The signal of the carbene carbon was found at $\delta = 207.50$ ppm and at $\delta = 202.32$ ppm, for **14** and **16**, respectively. It is interesting to note that the corresponding ^{13}C NMR chemical shifts of most other NHCs occur at lower field.[6]

Many different methods for the determination of the electronic properties of NHC ligands in transition-metal complexes have been applied.[10] The most widely accepted methodology, however, is the IR-spectroscopic analysis of the CO stretching frequencies of $(L)Ni(CO)_3$, $(L)Rh(CO)_2Cl$, $(L)Ir(CO)_2Cl$ or related complexes.[11,12] σ-Donor ligands (L) lead to an increased electron-density on the metal center that causes stronger back-bonding from the transition-metal to the π* of the CO-ligands and, thus, a weakening of the CO bond, which is detectable by IR-spectroscopy. However, care has to be taken in the comparison, since not only have different transition metals been used, but also different vibrational frequencies were taken into account (frequency of the *trans*-CO ligand vs. averaged frequency of all CO ligands).[12] Since an extensive range of reference data exists for $(NHC)Ir(CO)_2Cl$ complexes,[7,11d] the corresponding iridium complexes of carbenes **14** and **16** were therefore prepared.

The imidazolium salts **10** and **13** were deprotonated with potassium *tert*-butoxide and the generated carbenes were transferred to $[Ir(COD)Cl]_2$ to give air-stable intermediates. The COD/CO-ligand exchange was realized by bubbling a slow stream of carbon monoxide through a solution of the COD complex in dichloromethane at 0 °C, resulting in the formation of dicarbonyl complexes **18** and **19**, respectively (Scheme 4). It is important to note that for reasons of comparability, the IR spectra (and thus the ν_{CO}) have to be measured in solution (Table 1). Comparison of the obtained data suggests that carbene **14**, exhibiting lower ν_{CO} and a lower ν_{CO}^{av}, is slightly more electron-rich than benzannulated carbene **16**. Interestingly, **14** and the well known IMes exhibit similar electronic properties. Based on work by Nolan, the ν_{CO}^{av} can be correlated with Tolman's electronic parameter {TEP; TEP $(cm^{-1}) = 0.847x + 336$ [$x = \nu_{CO}^{av}(cm^{-1})$]} (Table 1), in order to obtain a convenient and comparable measure for the ligands' electronic character.[11d]

As expected, the single-crystal X-ray structure of complex **18** (Figure 4) reveals a square-planar coordination geometry of the iridium. Comparison of the two iridium–CO bond lengths reveals that the Ir–C bond *trans* to the NHC is significantly longer compared to the one *cis* to the NHC. The bond length of the iridium–NHC bond [2.075(4) Å] corresponds to those known in the literature.



Scheme 4 *Reagents and conditions*: (i) *t*-BuOK, THF, $[Ir(COD)Cl]_2$, r.t., 16 h; (ii) CO, CH_2Cl_2, 0 °C.

The importance of palladium-NHC complexes in catalysis has been amply demonstrated.[1b] Thus, we explored the ability of the new NHC **14** to form a stable palladium complex. We decided to synthesize a palladium–PEPPSI

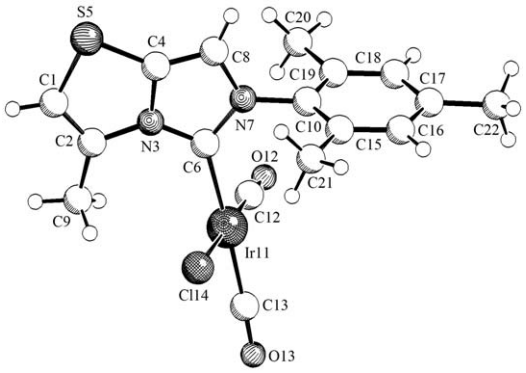


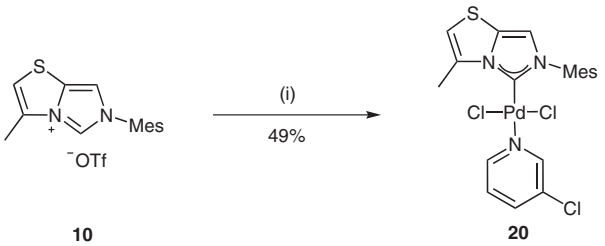
Figure 4 Structure of **18** obtained by X-ray crystal structure analysis.[8] Selected bond lengths (Å) and angles (°): C1–C2, 1.345(6); C1–S5, 1.749(5); S5–C4, 1.739(5); C4–N3, 1.391(5); N3–C2, 1.411(5); C4–C8, 1.352(7); C8–N7, 1.390(6); N7–C6, 1.360(5); C6–N3, 1.367(6); Ir–C12 (*cis* to NHC), 1.855(6); Ir–C13 (*trans* to NHC), 1.880(5); Ir–Cl14, 2.3479(13); Ir–C6, 2.075(4); C6–Ir–C13, 174.6(2); C6–Ir–C12, 92.60(19); C6–Ir–Cl14, 87.19(12).

Table 1 IR Data of Complexes **18** and **19** and the Corresponding IMes Complex Obtained by Measurement in Dichloromethane Solution

Complex	ν_{CO} (cm^{-1})	ν_{CO} (cm^{-1})	ν_{CO}^{av} (cm^{-1})	TEP[a] (cm^{-1})
18	2065.8	1982.3	2024.1	2050.4
19	2069.0	1985.9	2027.4	2053.2
IMes	2066.4	1979.8	2023.1	2049.6[b]

[a] TEP value calculated by linear regression on the basis of the $Ir(CO)_2Cl(NHC)$ complexes.[11d]
[b] The real TEP value derived from $Ni(CO)_3$IMes was found to be 2050.7.[3b]

complex (PEPPSI = Pyridine-Enhanced Precatalyst Preparation, Stabilization and Initiation), since PEPPSI complexes are known to be good precatalysts that easily enter the catalytic cycle.[13] Heating the imidazolium salt **10** in the presence of $PdCl_2$ and K_2CO_3 in neat 3-chloropyridine gave access to the desired complex **20** (Scheme 5). Single crystals were grown and the identity of **20** was unequivocally determined by X-ray structural analysis (Figure 5). In the structure obtained, the palladium exhibits a square-planar geometry and the resulting coordination plane of the palladium is virtually orthogonal to the plane of the NHC bicycle. The palladium–carbene bond length [1.962(2) Å] has a value typical for palladium–NHC complexes.



10 20

Scheme 5 *Reagents and conditions*: (i) K_2CO_3, $PdCl_2$, 3-chloropyridine, 80 °C, 16 h.

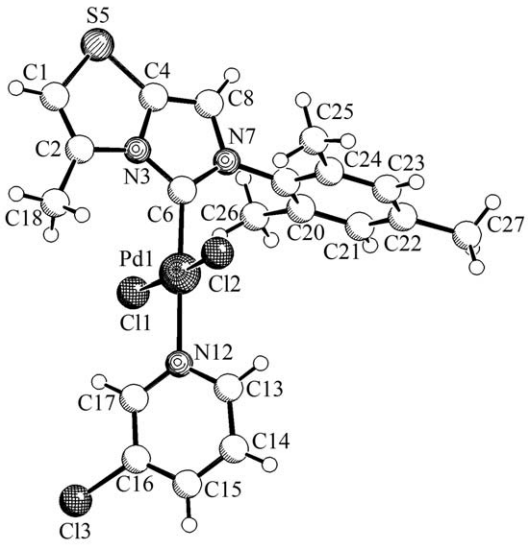


Figure 5 Structure of **20** obtained by X-ray crystal structure analysis.[8] Selected bond lengths (Å) and angles (°) for molecule A: C4–S5, 1.740(6); S5–C1, 1.736(7); C1–C2, 1.336(9); C2–N3, 1.413(8); N3–C6, 1.360(8); C6–N7, 1.354(8); N7–C8, 1.407(7); C8–C4, 1.330(9); C4–N3, 1.397(8); C6–Pd, 1.962(2); Pd–Cl1, 2.307(2); Pd–N12, 2.103(5); C6–Pd–N12, 177.5(3); C6–Pd–Cl1, 87.5(2).

In conclusion, a new class of thiazole-annelated NHCs was synthesized in a few steps and their electronic properties were characterized by several methods. For the first time, NHCs with a fully conjugated bicyclic [3.3.0] backbone have been prepared. The catalytic properties of these NHCs in organocatalysis and transition-metal catalysis are under investigation and will be reported in due course.

All commercially available compounds were used as received and all reactions were conducted in dried glassware equipped with a magnetic stirring bar under an atmosphere of argon. Solvents were distilled or dried prior to use over the indicated drying agents: CH_2Cl_2 (CaH), THF (sodium/benzophenone), DMF (p.a. grade dried, over molecular sieves 4 Å), hexane (degassed, HPLC grade without further purification).

Column chromatography was performed on Merck silica gel 60 (0.040–0.063 mm). ^{1}H and ^{13}C NMR spectra were recorded on either an ARX 300 or an AMX 400 spectrometer (Bruker). Standards for the calibration of the chemical shifts were residual protonated $CHCl_3$ (^{1}H: δ = 7.26 ppm, ^{13}C: δ = 77.0 ppm) or THF (^{1}H: δ = 1.73 ppm, ^{13}C: δ = 25.5 ppm) unless otherwise noted. IR spectra were recorded on a FT-IR 3100 Excalibur Series (Varian Associated). HRMS were recorded either on MicroTof (Bruker), a Finnigan LTQ FT or TSQ 700. Elemental analyses were recorded on Vario EL III (Elementar Analysensystem GmbH).

4-Methylthiazole-2-carbaldehyde

To a solution of compound **8** (500 mg, 5.00 mmol, 1.0 equiv) in anhydrous THF (20 mL) was added, dropwise, *n*-BuLi (3.75 mL, 1.6 M in hexane, 6.00 mmol, 1.2 equiv) at –78 °C. The solution was stirred for 1 h then DMF (0.77 mL, 10.00 mmol, 2.0 equiv) was added. After 3 h stirring (–78 °C to 20 °C), the mixture was acidified with aq HCl (4 M, 15 mL). The organic phase was separated and extracted with aq HCl (4 M, 3 × 20 mL), the aqueous phase was made basic with K_2CO_3 and extracted with CH_2Cl_2 (3 × 20 mL). The combined organic phases were dried over Na_2SO_4. After removal of the

solvent in vacuo, the residue was purified by column chromatography (*n*-pentane–EtOAc, 5:1) to give the desired product.[14]

Yield: 90%; yellow solid; R_f = 0.43 (*n*-pentane–EtOAc, 1:1).

IR (ATR): 3106, 2926, 2848, 2670, 1686, 1503, 1442, 1299, 1233, 964, 868, 742, 657, 632, 553 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 2.59 (s, 3 H, CH_3), 7.34 (s, 1 H, ArH), 9.98 (s, 1 H, CHO).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 17.0 (CH_3), 121.0 (C_{Ar}), 156.3 (C_{Ar}), 165.2 (C_{Ar}), 183.8 (CHO).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_5H_5NNaOS^+$: 149.9990; found: 149.9992.

Formation of Bisimines; General Procedure

Carbaldehyde (1 equiv) and 2,4,6-trimethylaniline (2 equiv) were dissolved in EtOH (3 mL per mmol) and heated to reflux for 3 h. The solvent was removed in vacuo and the residue was purified by column chromatography (*n*-pentane–EtOAc–Et_3N, 100:10:1) to give the desired product.[15]

4,4′-Di-*tert*-butyl[2,2′]bithiazolyl (5)

Yield: 53%; pale-yellow crystals; R_f = 0.70 (*n*-pentane–EtOAc, 4:1).

IR (ATR): 3119, 2970, 2874, 2357, 1739, 1701, 1545, 1481, 1369, 1260, 1225, 1133, 1029, 912, 821, 636, 618, 574 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.37 (s, 18 H, *t*-Bu), 6.95 (s, 2 H, ArH).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 30.0 (*t*-Bu), 34.9 (*t*-Bu), 117.0 (C_{Ar}), 158.6 (C_{Ar}), 165.6 (N=C).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{21}N_2S_2^+$: 281.1141; found: 281.1144.

[(*E*)-1-(4-Methylthiazol-2-yl)methylidene]-2,4,6-trimethylphenylamine (9)

Yield: 63%; yellow solid; R_f = 0.63 (*n*-pentane–EtOAc, 1:1).

IR (ATR): 2954, 2922, 2853, 1627, 1590, 1456, 1376, 1316, 1258, 1204, 1014, 852, 823, 759, 729, 670, 632, 568 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.15 (s, 6 H, *o*-Me), 2.28 (s, 3 H, *p*-Me), 2.54 (s, 3 H, N-Me), 6.89 (s, 2 H, ArH), 7.07 (s, 1 H, ArH), 8.35 (s, 1 H, N=CH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.3 (Me), 18.5 (Me), 21.0 (Me), 117.5 (C_{Ar}), 122.0 (C_{Ar}), 127.4 (C_{Ar}), 129.0 (C_{Ar}), 129.1 (C_{Ar}), 134.2 (C_{Ar}), 147.1 (C_{Ar}), 154.8 (C_{Ar}), 156.3 (C_{Ar}), 166.6 (N=CH).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{14}H_{16}N_2NaS^+$: 267.0932; found: 267.0930.

[(*E*)-1-(Benzothiazol-2-yl)methylidene]-2,4,6-trimethylphenylamine (12)

Yield: 81%; yellow solid; R_f = 0.85 (*n*-pentane–EtOAc, 1:1).

IR (ATR): 3371, 3007, 2968, 2914, 2856, 2732, 2361, 1628, 1807, 1468, 1443, 1307, 1251, 1208, 1156, 1010, 854, 877, 744 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.20 (s, 6 H, *o*-Me), 2.31 (s, 3 H, *p*-Me), 6.93 (s, 2 H, ArH), 7.48–7.55 (m, 3 H, ArH), 7.96 (d, *J* = 8.2 Hz, 1 H, ArH), 8.54 (s, 1 H, N=CH).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 18.3 (Me), 20.82 (Me), 122.8 (C_{Ar}), 124.3 (C_{Ar}), 126.6 (C_{Ar}), 127.3 (C_{Ar}), 127.6 (C_{Ar}), 129.7 (C_{Ar}), 132.1 (C_{Ar}), 135.3 (C_{Ar}), 136.3 (C_{Ar}), 147.3 (C_{Ar}), 154.5 (C_{Ar}), 157.5 (C_{Ar}), 168.2 (N=CH).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{17}N_2S^+$: 281.1112; found: 281.1111.

Anal. Calcd for $C_{17}H_{16}N_2S$: C, 72.82; H, 5.75; N, 9.99. Found: C, 72.79; H, 5.79; N, 9.75.

Synthesis of Imidazolium Triflates; General Procedure

To a suspension of AgOTf (1.5 equiv) in CH_2Cl_2 (0.3 M) was added chloromethyl pivalate (1.5 equiv), and the resulting suspension was stirred for 45 min in the dark. The supernatant was transferred via syringe to the bisimine (1 equiv), and the resulting solution was stirred in a sealed tube in the dark at 40 °C for 16 h. The solution was cooled to r.t., quenched with MeOH (5 mL/mmol) and the solvent was evaporated in vacuo. The resulting oil was purified by chromatography on silica gel (CH_2Cl_2–MeOH, 98:2) to give the imidazolium triflate as yellow crystals.[7]

4,4′-Di-*tert*-butyl-3-(2,2-dimethylpropionyloxymethyl)-[2,2′]bithiazol-3-ylium Trifluoromethanesulfonate (7)

Yield: 89%; pale-yellow crystals; R_f = 0.24 (CH_2Cl_2–MeOH, 10:1).

IR (ATR): 3121, 3100, 2970, 2940, 2909, 2874, 2348, 1740, 1546, 1480, 1355, 1225, 1194, 1162, 1120, 1077, 1029, 1015, 1003, 912, 871, 821, 636 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.11 (s, 9 H, *t*Bu), 1.40 (s, 9 H, *t*Bu), 1.57 (s, 9 H, *t*Bu), 1.85 (s, 2 H, CH_2), 7.55 (s, 1 H, ArH), 8.28 (s, 1 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.8 (*t*Bu), 30.1 (*t*Bu), 30.3 (*t*Bu), 35.5 (C_q), 35.7 (C_q), 38.9 (C_q), 72.5 (NCH_2O), 120.0 (C_{Ar}), 122.1 (C_{Ar}), 150.0 (C_{Ar}), 158.7 (C_{Ar}), 166.0 (C_{Ar}), 171.5 (C_{Ar}), 176.1 (C=O).

HRMS (ESI): *m*/*z* [M – OTf^-]$^+$ calcd for $C_{20}H_{31}N_2O_2S_2^+$: 395.1821; found: 395.1819.

3-Methyl-6-(2,4,6-trimethylphenyl)-6*H*-imidazo[5,1-*b*]thiazol-4-ylium Trifluoromethanesulfonate (10)

Yield: 66%; pale-yellow crystals; R_f = 0.39 (CH_2Cl_2–MeOH, 10:1).

IR (ATR): 3130, 1547, 1524, 1485, 1388, 1266, 1250, 1222, 1188, 1158, 1028, 861, 782, 661, 635 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.04 (s, 6 H, *o*-Me), 2.34 (s, 3 H, *p*-Me), 2.67 (s, 3 H, Me), 7.00 (s, 2 H, 2 × ArH), 7.10 (s, 1 H, ArH), 7.47 (s, 1 H, ArH), 9.58 (s, 1 H, NCHN).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.9 (Me), 17.3 (Me), 21.2 (Me), 113.0 (NCHN), 117.1 (C_{Ar}), 122.9 (C_{Ar}), 126.6 (C_{Ar}), 126.9 (C_{Ar}), 129.7 (C_{Ar}), 131.2 (C_{Ar}), 134.2 (C_{Ar}), 141.6 (C_{Ar}).

HRMS (ESI): *m*/*z* [M – OTf^-]$^+$ calcd for $C_{15}H_{17}N_2S^+$: 257.1107; found: 257.1109.

2-(2,4,6-Trimethylphenyl)-2*H*-benzo[*d*]imidazo-[5,1-*b*]thiazol-9-ylium Trifluoromethanesulfonate (13)

Yield: 53%; yellow crystals; R_f = 0.36 (CH_2Cl_2–MeOH, 10:1).

IR (ATR): 3316, 3055, 2989, 2952, 2877, 2792, 1667, 1579, 1467, 1393, 1290, 1265, 1182, 896, 736, 706, 629, 584 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.11 (s, 6 H, *o*-Me), 2.37 (s, 3 H, *p*-Me), 7.05 (s, 2 H, 2 × ArH), 7.10 (s, 1 H, ArH), 7.40 (d, *J* = 8.3 Hz, 1 H, ArH), 7.64–7.68 (m, 1 H, ArH), 7.78–7.81 (m, 1 H, ArH), 8.68–8.74 (m, 1 H, ArH), 10.47 (s, 1 H, NCHN).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.3 (Me), 21.4 (Me), 114.3 (NCHN), 117.7 (C_{Ar}), 122.8 (C_{Ar}), 124.1 (C_{Ar}), 128.0 (C_{Ar}), 129.3 (C_{Ar}), 129.7 (C_{Ar}), 129.8 (C_{Ar}), 130.1 (C_{Ar}), 131.9 (C_{Ar}), 132.5 (C_{Ar}), 134.2 (C_{Ar}), 141.6 (C_{Ar}).

HRMS (ESI): *m*/*z* [M – OTf^-]$^+$ calcd for $C_{18}H_{17}N_2S^+$: 293.1107; found: 293.1107.

Formation of Free Carbenes; General Procedure
To a mixture of the imidazolium salt **10** or **13** (1.0 equiv) and *t*-BuOK (1.10 equiv) in a standard NMR tube was added THF-d_8 (1 mL per 0.1 mmol) affording the free carbenes in solution.

Carbene 14
^{1}H NMR (300 MHz, THF-d_8): δ = 1.97 (s, 6 H, *o*-Me), 2.30 (s, 3 H, *p*-Me), 2.47 (s, 3 H, Me), 6.52 (s, 1 H, ArH), 6.94 (s, 3 H, ArH).

^{13}C NMR (75.5 MHz, THF-d_8): δ = 13.9 (Me), 18.1 (Me), 21.3 (Me), 109.0 (C_{Ar}), 111.5 (C_{Ar}), 128.3 (C_{Ar}), 129.5 (C_{Ar}), 130.3 (C_{Ar}), 133.8 (C_{Ar}), 135.8 (C_{Ar}), 138.2 (C_{Ar}), 140.4 (C_{Ar}), 207.5.

Carbene 16
^{1}H NMR (300 MHz, THF-d_8): δ = 1.98 (s, 6 H, *o*-Me), 2.25 (s, 3 H, *p*-Me), 6.92 (s, 2 H, 2 × ArH), 7.33–7.44 (m, 2 H, ArH), 7.85–7.92 (m, 2 H, ArH), 8.04 (s, 1 H, ArH).

^{13}C NMR (75.5 MHz, THF-d_8): δ = 18.6 (Me), 21.2 (Me), 111.1 (C_{Ar}), 122.9 (C_{Ar}), 124.2 (C_{Ar}), 126.3 (C_{Ar}), 126.9 (C_{Ar}), 130.6 (C_{Ar}), 137.1 (C_{Ar}), 137.3 (C_{Ar}), 137.9 (C_{Ar}), 139.4 (C_{Ar}), 153.7 (C_{Ar}), 163.73 (C_{Ar}), 166.84 (C_{Ar}), 202.32.

Synthesis of Thiourea Derivatives; General Procedure
A suspension of compound **10** or **13** (1.0 equiv) in THF (1.00 mL per 0.1 mmol) was treated with *t*-BuOK (1.4 equiv). After stirring for 5 min, elemental sulphur (S_8, 1.4 equiv) was added and stirring was continued overnight. The solvent was removed in vacuo and the residue was purified by flash chromatography (*n*-pentane–EtOAc, 10:1) affording thiones **15** or **17** as yellow solids.[9]

3-Methyl-6-(2,4,6-trimethylphenyl)-6*H*-imidazo[5,1-*b*]thiazole-5-thione (15)
Yield: 78%; yellow solid; R_f = 0.73 (*n*-pentane–EtOAc, 1:1).

IR (ATR): 2987, 2957, 2878, 2392, 2348, 1669, 1472, 906, 730, 705 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.07 (s, 6 H, *o*-Me), 2.34 (s, 3 H, *p*-Me), 2.97 (s, 3 H, Me), 6.18 (s, 1 H, ArH), 6.58 (s, 1 H, ArH), 6.98 (s, 2 H, ArH).

^{13}C NMR (75.5 MHz, THF-d_8): δ = 15.6 (Me), 18.6 (Me), 21.5 (Me), 107.7 (C_{Ar}), 109.3 (C_{Ar}), 129.1 (C_{Ar}), 129.5 (C_{Ar}), 129.8 (C_{Ar}), 133.9 (C_{Ar}), 137.0 (C_{Ar}), 139.6 (C_{Ar}), 158.9 (C=S).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{15}H_{16}N_2NaS_2^+$: 311.0653; found: 311.0651.

2-(2,4,6-Trimethylphenyl)-2*H*-benzo[*d*]imidazo[5,1-*b*]thiazole-1-thione (17)
Yield: 83%; pale-yellow solid; R_f = 0.69 (*n*-pentane–EtOAc, 1:1).

IR (ATR): 3052, 2985, 2876, 2360, 1613, 1508, 1420, 1265, 737, 563, 561, 551 cm^{-1}.

^{1}H NMR (400 MHz, THF-d_8): δ = 2.03 (s, 6 H, *o*-Me), 2.28 (s, 3 H, *p*-Me), 6.61 (s, 1 H, ArH), 6.94 (s, 2 H, 2 × ArH), 7.28–7.38 (m, 3 H, ArH), 7.48 (dd, *J* = 17.6, 8.1 Hz, 1 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.4 (Me), 22.1 (Me), 109.3 (C_{Ar}), 117.0 (C_{Ar}), 124.0 (C_{Ar}), 125.8 (C_{Ar}), 126.4 (C_{Ar}), 126.9 (C_{Ar}), 129.8 (C_{Ar}), 132.5 (C_{Ar}), 135.0 (C_{Ar}), 135.7 (C_{Ar}), 137.1 (C_{Ar}), 139.8 (C_{Ar}), 157.5 (C=S).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{18}H_{16}N_2NaS_2^+$: 347.0647; found: 347.0649.

Synthesis of [(NHC)Ir(COD)Cl] Complexes; General Procedure
A suspension of compound **10** or **13** (1.8 equiv) in THF (1 mL per 0.1 mmol) was treated with *t*-BuOK (2.0 equiv). After stirring for 10 min, $[Ir(COD)Cl]_2$ (1.0 equiv) was added and stirring was continued overnight. The solvent was evaporated and the residue was purified by chromatography on silica gel (*n*-pentane–EtOAc, 10:1) to give the corresponding product.

[(NHC)Ir(COD)Cl]
Yield: 89%; yellow solid; R_f = 0.70 (*n*-pentane–EtOAc, 1:1).

IR (ATR): 2915, 2877, 2830, 1734, 1608, 1558, 1488, 1360, 1327, 1241, 1159, 1038, 1000, 971, 884, 852, 817, 735, 644, 611 cm^{-1}.

^{1}H NMR (400 MHz, THF-d_8): δ = 1.10–1.79 [m, 2 H, $(CH_2)_{COD}$], 2.01–2.25 [m, 6 H, $(CH_2)_{COD}$], 2.28 (s, 6 H, *o*-Me), 3.17–3.26 (m, 2 H, CH_{COD}), 3.31 (s, 3 H, *p*-Me), 4.09 (s, 3 H, Me), 4.38–4.54 (m, 2 H, CH_{COD}), 6.39 (s, 1 H, ArH), 6.83 (s, 1 H, ArH), 6.93 (s, 1 H, ArH), 7.05 (s, 1 H, ArH).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ= 17.9, 19.6, 21.1, 28.2, 30.1, 50.6, 81.6, 109.7, 112.5, 127.9, 129.5, 132.8, 134.2, 138.0, 138.8, 171.5 (NCIrCl).

HRMS (ESI): *m*/*z* [M – Cl$^-$]$^+$ calcd for $C_{23}H_{28}IrN_2S^+$: 557.1596; found: 557.1592.

[(NHC)Ir(COD)Cl]
Yield: 58%; yellow solid; R_f = 0.69 (*n*-pentane–EtOAc, 1:1).

IR (ATR): 3054, 2994, 2936, 2833, 2816, 1264, 759, 735, 631 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.18–1.26 [m, 2 H, $(CH_2)_{COD}$], 1.36–1.88 [m, 6 H, $(CH_2)_{COD}$], 1.98 (s, 6 H, *o*-Me), 2.39 (s, 6 H, *p*-Me), 2.78–2.86 [m, 2 H, CH_{COD}], 3.19–3.22 (m, 2 H, CH_{COD}), 6.87 (s, 1 H, ArH), 6.90 (s, 1 H, ArH), 7.02 (s, 1 H, ArH), 7.38–7.52 (m, 1 H, ArH), 7.54–7.59 (m, 2 H, ArH), 9.92 (d, *J* = 7.8 Hz, 1 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.7, 19.3, 20.9, 28.2, 29.9, 31.7, 34.7, 51.0, 52.3, 83.0, 84.9, 112.6, 119.7, 123.2, 126.3, 128.2, 129.4, 129.8, 131.7, 134.3, 136.9, 139.2, 174.40 (C-Ir).

HRMS (ESI): *m*/*z* [M – Cl$^-$]$^+$ calcd for $C_{26}H_{28}ClIrN_2S^+$: 593.1602; found: 593.1596.

Formation of [(NHC)Ir(CO)$_2$Cl] Complexes; General Procedure
CO gas (balloon) was passed through an ice-cold solution of the complex **21** or **22** in CH_2Cl_2 (5 mL) for 15 min. Solvent was evaporated and the residue was washed several times with cold hexane to afford the complex.[11c]

[(NHC)Ir(CO)$_2$Cl] (18)
Yield: 41%; yellow solid; R_f = 0.76 (CH_2Cl_2–MeOH, 10:1).

IR (ATR): 3095, 2923, 2858, 2056, 1971, 1609, 1552, 1489, 1435, 1385, 1339, 1260, 1187, 1160, 1093, 1042, 854, 819, 741, 662, 615 cm^{-1}.

IR (solution in CH_2Cl_2): 2065.81, 1982.33 (C=O) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.06 (s, 6 H, *o*-Me), 2.40 (s, 3 H, *p*-Me), 3.01 (s, 3 H, Me), 6.61 (s, 1 H, ArH), 7.02 (s, 1 H, ArH), 7.04 (s, 2 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.9 (Me), 18.8 (Me), 21.4 (Me), 111.8 (C_{Ar}), 112.9 (C_{Ar}), 130.0 (C_{Ar}), 131.4 (C_{Ar}), 131.6 (C_{Ar}), 132.3 (C_{Ar}), 134.0 (C_{Ar}), 136.0 (C_{Ar}), 140.0 (C_{Ar}), 165.5 (C=O), 167.9 (C=O), 180.6 (C-Ir).

HRMS (ESI): *m*/*z* [M – Cl$^-$]$^+$ calcd for $C_{17}H_{16}IrN_2O_2S^+$: 505.0562; found: 505.0566.

[(NHC)Ir(CO)$_2$Cl] (19)
Yield: 62%; yellow solid; R_f = 0.82 (CH_2Cl_2–MeOH, 10:1).

IR (ATR): 3687, 3599, 3164, 3055, 2982, 2957, 2855, 2926, 2534, 2348, 2278, 2068, 1985, 1671, 1590, 1251, 1277, 1243, 1137, 895, 651 cm^{-1}.

IR (solution in CH_2Cl_2): 2068.95, 1985.93 (C=O) cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.98 (s, 6 H, *o*-Me), 2.39 (s, 3 H, *p*-Me), 6.99 (s, 2 H, ArH), 7.06 (s, 1 H, ArH), 7.44 (m, 2 H, ArH), 7.64 (m, 1 H, ArH), 9.41 (m, 1 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.8 (C, Me), 18.9 (Me), 21.3 (Me), 113.3 (C_{Ar}), 120.0 (C_{Ar}), 123.6 (C_{Ar}), 127.6 (C_{Ar}), 129.1 (C_{Ar}), 129.6 (C_{Ar}), 131.0 (C_{Ar}), 131.7 (C_{Ar}), 133.7 (C_{Ar}), 133.9 (C_{Ar}), 136.0 (C_{Ar}), 136.3 (C_{Ar}), 140.1 (C_{Ar}), 167.7 (C=O), 168.1 (C=O), 180.5 (C-Ir).

HRMS (ESI): *m*/*z* [M – Cl^-]$^+$ calcd for $C_{20}H_{16}IrN_2O_2S^+$: 541.0562; found: 541.0566.

Formation of (NHC)–$PdCl_2$–(3-Chloropyridine) Complex (20)

A mixture of $PdCl_2$ (21.8 mg, 0.123 mmol, 1 equiv), imidazolium salt **10** (50 mg, 0.123 mmol, 1.0 equiv) and K_2CO_3 (84 mg, 0.651 mmol, 5.0 equiv) was suspended in 3-chloropyridine (0.5 mL) and stirred at 80 °C for 16 h. After cooling to ambient temperature, the reaction mixture was diluted with CH_2Cl_2 and filtered through a short pad of Celite®. Solvents were removed in vacuo and the residue was purified by chromatography on silica gel (CH_2Cl_2–MeOH, 50:1) to give the desired product.[13]

Yield: 49%; yellow solid; R_f = 0.84 (CH_2Cl_2–MeOH, 10:1).

IR (ATR): 2921, 2852, 1462, 1347, 1187, 747, 740, 716, 640, 625, 567 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.18 (s, 6 H, *o*-Me), 2.31 (s, 3 H, *p*-Me), 3.45 (s, 3 H, Me), 6.62 (s, 1 H, ArH), 6.94 (s, 1 H, ArH), 6.99 (s, 2 H, ArH), 7.60–7.63 (m, 2 H, ArH), 8.67 (dd, *J* = 6.5, 4.3 Hz, 1 H, ArH), 8.75 (d, *J* = 2.1 Hz, 1 H, ArH).

^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 17.5 (Me), 19.4 (Me), 21.8 (Me), 112.4 (C_{Ar}), 115.1 (C_{Ar}), 124.8 (C_{Ar}), 129.5 (C_{Ar}), 131.6 (C_{Ar}), 132.5 (C_{Ar}), 133.5 (C_{Ar}), 136.4 (C_{Ar}), 136.9 (C_{Ar}), 138.0 (C_{Ar}), 139.7 (C_{Ar}), 149.4 (C_{Ar}), 150.0 (C_{Ar}), 151.0 (C_{Ar}).

HRMS (ESI): *m*/*z* [M – Cl^-]$^+$ calcd for $C_{20}H_{20}Cl_2N_3PdS^+$: 509.9790; found: 509.9786.

X-ray Crystal Structure Analysis of 7[8]

CCDC 68504. Empirical formula $C_{21}H_{31}F_3N_2O_5S_3$; Formula weight 544.66; light-yellow crystal 0.40 × 0.30 × 0.15 mm; Unit cell dimensions: *a* = 9.2232(2) Å, *b* = 16.6824(2) Å, *c* = 36.5487(6) Å; *V* = 5623.57(17) Å^3; D (calculated) = 1.287 g cm^{-3}; μ = 0.315 mm^{-1} empirical absorption correction (0.884 ≤ *T* ≤ 0.954); *Z* = 8; orthorhombic, space group *P*bca (No. 61); λ = 0.71073 Å; *T* = 223(2) K; ω and φ scans, 37182 reflections collected (±*h*, ±*k*, ±*l*), [(sin θ)/λ] = 0.66 Å^{-1}, 6566 independent (R_{int} = 0.051) and 4133 observed reflections [*I* ≥ 2 σ(*I*)]; 316 refined parameters; *R* = 0.048, wR^2 = 0.138; max. (min.) residual electron density 0.30 (–0.27) e Å^{-3}; hydrogen atoms calculated and refined as riding atoms.

X-ray Crystal Structure Analysis of 10[8]

CCDC 68503. Empirical formula $C_{16}H_{17}F_3N_2O_3S_2$; Formula weight 406.44; colorless crystal 035 × 0.35 × 0.25 mm; Unit cell dimensions: *a* = 19.5592(5) Å, *b* = 13.6605(3) Å, *c* = 22.2651(6) Å, *β* = 91.592(1)°; *V* = 5946.7(3) Å^3; D (calculated) = 1.362 g cm^{-3}; μ = 2.854 mm^{-1} empirical absorption correction (0.435 ≤ *T* ≤ 0.536); *Z* = 12; monoclinic, space group $P2_1/c$ (No. 14); λ = 1.54178 Å; *T* = 223(2) K; ω and φ scans, 566606 reflections collected (±*h*, ±*k*, ±*l*), [(sin θ)/λ] = 0.60 Å^{-1}; 10659 independent (R_{int} = 0.057) and 8617 observed reflections [*I* ≥ 2 σ(*I*)]; 715 refined parameters, *R* = 0.063, wR^2 = 0.174; max. (min.) residual electron density 1.07 (–0.37) e Å^{-3}; three almost identical molecules in the asymmetric unit, hydrogen atoms calculated and refined as riding atoms.

X-ray Crystal Structure Analysis of 13[8]

CCDC 68505. Empirical formula $C_{19}H_{17}F_3N_2O_3S_2$; Formula weight 442.47; colorless crystal 0.35 × 0.10 × 0.05 mm; Unit cell dimensions: *a* = 12.8722(5) Å, *b* = 18.9645(8) Å, *c* = 17.1399(7) Å, *β* = 104.237(3)°; *V* = 4055.6(3) Å^3; D (calculated) = 1.449 g cm^{-3}; μ = 2.843 mm^{-1}, empirical absorption correction (0.436 ≤ *T* ≤ 0.871); *Z* = 8; monoclinic, space group $P2_1/c$ (No. 14); λ = 1.54178 Å; *T* = 223(2) K; ω and φ scans, 32123 reflections collected (±*h*, ±*k*, ±*l*), [(sin θ)/λ] = 0.60 Å^{-1}; 6649 independent (R_{int} = 0.053) and 4080 observed reflections [*I* ≥ 2 σ(*I*)]; 602 refined parameters, *R* = 0.072, wR^2 = 0.205; max. (min.) residual electron density 0.56 (–0.37) e Å^{-3}; two almost identical molecules in the asymmetric unit, one anion refined with split positions and geometrical restraints, hydrogen atoms calculated and refined as riding atoms.

X-ray Crystal Structure Analysis of 18[8]

CCDC 68506. Empirical formula $C_{17}H_{16}ClIrN_2O_2S$; Formula weight 540.03; yellow crystal 0.50 × 0.40 × 0.20 mm; Unit cell dimensions: *a* = 8.1949(1) Å, *b* = 11.0607(2) Å, *c* = 19.9746(3) Å, *β* = 92.430(1)°; *V* = 1808.90(5) Å^3; D (calculated) = 1.983 g cm^{-3}; μ = 7.655 mm^{-1}, empirical absorption correction (0.114 ≤ *T* ≤ 0.310); *Z* = 4; monoclinic, space group $P2_1/c$ (No. 14); λ = 0.71073 Å; *T* = 223(2) K; ω and φ scans, 11467 reflections collected (±*h*, ±*k*, ±*l*), [(sin θ)/λ] = 0.66 Å^{-1}; 4288 independent (R_{int} = 0.060) and 3765 observed reflections [*I* ≥ 2 σ(*I*)]; 221 refined parameters, *R* = 0.033, wR^2 = 0.089; max. (min.) residual electron density 2.35 (–1.23) e Å^{-3}; close to Ir, hydrogen atoms calculated and refined as riding atoms.

X-ray Crystal Structure Analysis of 20[8]

CCDC 68507. Empirical formula $C_{20}H_{20}Cl_3N_3PdS$; Formula weight 547.20; light-yellow crystal 0.35 × 0.06 × 0.05 mm; Unit cell dimensions: *a* = 16.5972(2) Å, *b* = 11.9804(2) Å, *c* = 21.8986(1) Å; *V* = 4354.34(12) Å^3; D (calculated) = 1.669 g cm^{-3}; μ = 1.328 mm^{-1}, empirical absorption correction (0.654 ≤ *T* ≤ 0.937); *Z* = 8; orthorhombic, space group $Pca2_1$ (No. 29); λ = 0.71073 Å; *T* = 223(2) K; ω and φ scans, 23959 reflections collected (±*h*, ±*k*, ±*l*), [(sinθ)/λ] = 0.66 Å^{-1}; 8304 independent (R_{int} = 0.071) and 5718 observed reflections [*I* ≥ 2 σ(*I*)]; 524 refined parameters, *R* = 0.048, wR^2 = 0.102, Flack parameter –0.45(3); max. (min.) residual electron density 0.89 (–1.32) e Å^{-3}; two almost identical molecules in the asymmetric unit, disorder of the chloropyridine ligand of molecule B refined with split positions, hydrogen atoms calculated and refined as riding atoms.

Acknowledgment

We thank the Fonds der Chemischen Industrie, the Alfried-Krupp von Bohlen und Halbach-Stiftung and the Deutsche Forschungsgemeinschaft for generous financial support.

References

(1) (a) Herrmann, W. A. *Angew. Chem. Int. Ed.* **2002**, *41*, 1290. (b) Kantchev, E. A. B.; O'Brien, C. J.; Organ, M. G. *Angew. Chem. Int. Ed.* **2007**, *46*, 2768. (c) *N-Heterocyclic carbenes in synthesis*; Nolan, S. P., Ed.; Wiley-VCH: Weinheim, **2006**. (d) *N-Heterocyclic carbenes in transition metal catalysis*; Glorius, F., Ed.; Springer: Berlin, **2007**.

(2) For an excellent review on applications in organocatalysis, see: Enders, D.; Niemeier, O.; Henseler, A. *Chem. Rev.* **2007**, *107*, 5606.

(3) For an excellent overview on the variety of NHC structures and their coordination chemistry, see: (a) Hahn, F. E.; Jahnke, M. C. *Angew. Chem. Int. Ed.* **2008**, *47*, 3122. See also: (b) Scott, N. M.; Nolan, S. P. *Eur. J. Inorg. Chem.* **2005**, 1815.

(4) For the design and application of the IBiox series of NHC ligands with different steric demand, see: (a) Glorius, F.; Altenhoff, G.; Goddard, R.; Lehmann, C. *Chem. Commun.* **2002**, 2704. (b) Altenhoff, G.; Goddard, R.; Lehmann, C. W.; Glorius, F. *Angew. Chem. Int. Ed.* **2003**, *42*, 3690. (c) Altenhoff, G.; Goddard, R.; Lehmann, C. W.; Glorius, F. *J. Am. Chem. Soc.* **2004**, *126*, 15195. (d) Altenhoff, G.; Würtz, S.; Glorius, F. *Tetrahedron Lett.* **2006**, *47*, 2925.
(5) (a) Burstein, C.; Lehmann, C. W.; Glorius, F. *Tetrahedron* **2005**, *61*, 6207. (b) Alcarazo, M.; Roseblade, S. J.; Cowley, A. R.; Fernandez, R.; Brown, J. M.; Lassaletta, J. M. *J. Am. Chem. Soc.* **2005**, *127*, 3290.
(6) For related NHCs, see: Nonnenmacher, M.; Kunz, D.; Rominger, F.; Oeser, T. *Chem. Commun.* **2006**, 1378; and references cited therein.
(7) Wong, W.-Y.; Chan, S.-M.; Choi, K.-H.; Cheah, K.-W.; Chan, W.-K. *Macromol. Rapid Commun.* **2000**, *21*, 453.
(8) CCDC 685503–685507 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44(1223)336033; E-mail: deposit@ccdc.cam.ac.uk]. Data sets were collected with Nonius KappaCCD diffractometers, in the case of Mo-radiation equipped with a rotating anode generator. Programs used: (a) COLLECT – data collection software: Nonius B. V., **1998** (b) Data reduction Denzo-SMN: Otwinowski, Z.; Minor, W. *Methods in Enzymology* **1997**, *276*, 307. For absorption correction SORTAV, see: (c) Blessing, R. H. *Acta Crystallogr. Sect. A* **1995**, *51*, 33. (d) Blessing, R. H. *J. Appl. Crystallogr.* **1997**, *30*, 421. (e) Denzo: Otwinowski, Z.; Borek, D.; Majewski, W.; Minor, W. *Acta Crystallogr., Sect. A* **2003**, *59*, 228. (f) Structure solution SHELXS-97: Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467. (g) Structure refinement SHELXL-97: Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, *64*, 112. (h) Graphics SCHAKAL: Keller, E. Universität Freiburg; **1997**.
(9) Arduengo, A. J. III *Acc. Chem. Res.* **1999**, *32*, 913.
(10) See for example: (a) Magill, A. M.; Cavell, K. J.; Yates, B. F. *J. Am. Chem. Soc.* **2004**, *126*, 8717. (b) Huang, J.; Schanz, H.-J.; Stevens, E. D.; Nolan, S. P. *Organometallics* **1999**, *18*, 2370. (c) Luo, L.; Nolan, S. P. *Organometallics* **1994**, *13*, 4781.
(11) (a) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313. (b) Chianese, A. R.; Li, X.; Janzen, M. C.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2003**, *22*, 1663. (c) Chianese, A. R.; Kovacevic, A.; Zeglis, B. M.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2004**, *23*, 2461. (d) Kelly, R. A. III; Clavier, H.; Giudice, S.; Scott, N. M.; Stevens, E. D.; Bordner, J.; Samardjiev, I.; Hoff, C. D.; Cavallo, L.; Nolan, S. P. *Organometallics* **2008**, *27*, 202.
(12) Additional reference data and a pertinent discussion of NHC donor abilities can be found in the supporting information of the following publication: Fürstner, A.; Alcazaro, M.; Krause, H.; Lehmann, C. W. *J. Am. Chem. Soc.* **2007**, *129*, 12676.
(13) (a) Organ, M. G.; Abdel-Hadi, M.; Avola, S.; Dubovyk, I.; Hadei, N.; Kantchev, E. A. B.; O'Brien, C. J.; Sayah, M.; Valente, C. *Chem. Eur. J.* **2008**, *14*, 2443. (b) O'Brien, C. J.; Kantchev, E. A. B.; Valente, C.; Hadei, N.; Chass, G. A.; Lough, A.; Hopkinson, A. C.; Organ, M. G. *Chem. Eur. J.* **2006**, *12*, 4743.
(14) Katritzky, A. R.; He, H.-Y.; Long, Q.; Cui, X.; Level, J.; Wilcox, A. L. *ARKIVOC* **2000**, *(iii)*, 240.
(15) Kennedy, D. F.; Messerle, B. A.; Smith, M. K. *Eur. J. Inorg. Chem.* **2007**, *1*, 80.