

## Mixed valence $\eta^6$ -arene cobalt(i) and cobalt(ii) compound†‡

Cite this: *Dalton Trans.*, 2013, **42**, 10277

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Received 9th April 2013,  
Accepted 13th May 2013

DOI: 10.1039/c3dt50939g

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The first carbonyl free mixed valence cobalt(i)/cobalt(ii) compound  $[2\{L_2Co(i)(\eta^6-C_7H_8)\}]^{2+} [Co(ii)_2Cl_6]^{2-}$  (**1**) [ $L = PhC(N^tBu)_2SiCl$ ] was obtained by the reaction of four equivalents of anhydrous  $CoCl_2$  with five equivalents of *N*-heterocyclic chlorosilylene **L**. In contrast, the reaction of **L** with  $CoBr_2$  yielded  $[L_2CoBr_2]$  (**2**). Compound **1** was formed by the cleavage of Co–Cl bonds, the reduction of Co(ii) to Co(i) and by the coordination of a toluene molecule. The chlorosilylene (**L**) functions as a reducing agent as well as a neutral  $\sigma$ -donor ligand. The toluene molecule coordinates to the Co(i) atom in an  $\eta^6$ -fashion.

Transition metal–arene complexes have attracted considerable attention because of their potential useful applications in organic synthesis and catalysis.<sup>1</sup> Activation of an arene molecule on coordination to a transition metal significantly modifies the reactivity of the arene molecule in several distinct ways.<sup>2</sup> One important consequence is the increased acidity of the arene protons, thereby facilitating the functionalization of rather inert C–H bonds.<sup>1b,3</sup> High yield access to stable chlorosilylenes **L** [ $PhC(N^tBu)_2SiCl$ ]<sup>4</sup> and NHC·SiCl<sub>2</sub> [NHC = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr) or 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene]<sup>5</sup> by convenient synthetic routes permitted us to explore their chemistry.<sup>6–9</sup> In particular, their application as reducing agents<sup>6</sup> as well as neutral  $\sigma$ -donor ligands<sup>7</sup> provides a new area of investigation in transition metal chemistry. A striking example is the isolation of the mixed valence cobalt(i/ii) compound  $[(IPr-SiCl_2)_2Co(CO)_3]^+ [CoCl_3(THF)]^-$  on reaction of  $Co_2(CO)_8$  with IPr·SiCl<sub>2</sub>.<sup>7a</sup> Carbonyl free complexes with low-valent 3d transition metals are scarce but show interesting applications in the activation of small molecules and as enzyme mimics.<sup>2</sup> Among the first row transition metal complexes, some carbonyl free cobalt(i) complexes have been prepared using sterically crowded monodentate or chelating di-, tri-, or poly-dentate ligands. Such complexes have been prepared by the reduction of Co(ii) halides using alkali metals (e.g., K<sub>C<sub>8</sub></sub>) as reducing agents.<sup>10</sup> In continuation of our ongoing research work to develop safer and more convenient synthetic methods for compounds with

low-valent elements and their further applications, we became interested in establishing facile methods for transition metal complexes with low-valent main group elements. Herein, we report on a carbonyl-free mixed valence cobalt compound of composition  $[2\{L_2Co(i)(\eta^6-C_7H_8)\}]^{2+} [Co(ii)_2Cl_6]^{2-}$  (**1**) using anhydrous  $CoCl_2$  and a chlorosilylene (**L**) and  $[L_2CoBr_2]$  (**2**) which was obtained by the reaction of **L** and  $CoBr_2$ . Interestingly, protocols for preparation of mixed valence cobalt(i)/cobalt(ii) compounds are extremely rare.<sup>7a,11</sup> To the best of our knowledge this is the first report of a carbonyl free mixed valence cobalt(i)/cobalt(ii) compound.

## Results and discussion

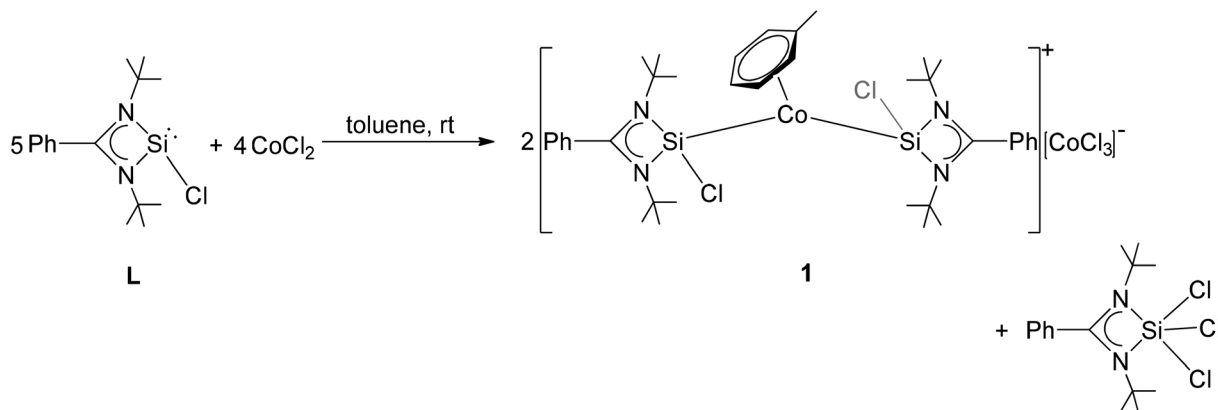
Compound **1** was obtained in a one pot synthesis of chlorosilylene **L** with anhydrous  $CoCl_2$  (Scheme 1). The reaction proceeds in a 5 : 4 ratio even when equivalent amounts of **L** and anhydrous  $CoCl_2$  were used. Compound **1** was formed by the cleavage of Co–Cl bonds, the reduction of Co(ii) to Co(i) and by the coordination of a toluene molecule, which coordinates to the Co(i) in an  $\eta^6$ -fashion. The chlorosilylene **L** functions as a reducing agent as well as a neutral  $\sigma$ -donor ligand. One equivalent of **L** is oxidized to a Si(iv) compound of composition  $PhC(N^tBu)_2SiCl_3$ . Compound **1** was isolated as green coloured crystals (68%) and is soluble in THF. Compound **1** is stable both in solution and in the solid state for a long period of time without any decomposition under an inert gas atmosphere. Compound **1** was characterized by NMR spectroscopy and elemental analysis and its molecular structure was established unambiguously by single crystal X-ray structural analysis.

The <sup>1</sup>H NMR spectrum of compound **1** exhibits broad resonances even in the temperature range of +50 to –90 °C,

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† This work celebrates 300 years of chemistry at the University of Edinburgh.

‡ CCDC 868295 (**1**) and 929864 (**2**). For crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt50939g

Scheme 1 Synthesis of **1**.

which might be due to the presence of the paramagnetic Co(II) anion. The  $^{29}\text{Si}$  NMR spectrum of **1** exhibits two close single resonances at  $\delta$  48.27 and 49.48 ppm, which are tentatively assigned to the two silicon atoms. The appearance of two resonances may be due to the slight variance in the geometrical environment around the silicon atoms. These values are consistent with those observed for other transition metal–silylene complexes.<sup>7</sup>

Compound **1** crystallizes with two solvent molecules in the monoclinic space group  $P2_1/n$  as green coloured crystals. The cationic part of **1** is shown in Fig. 1. Compound **1** contains cobalt in two different oxidation states; one exhibits the central atom in the cation which is in the +I oxidation state and the other in the anion which is in the +II oxidation state. The cobalt atom present in the cationic part is coordinated to the two silicon atoms and by the toluene molecule. The toluene molecule coordinates to Co(I) in an  $\eta^6$ -fashion. Both silicon atoms are tetra-coordinate and in a distorted tetrahedral geometry comprising two nitrogen atoms from the supporting amidinato ligand, one chlorine and one cobalt atom. The bond angle Si1–Co1–Si2 is  $92.99(3)^\circ$ . The Si–Co bond lengths in **1** are 2.1553(9) and 2.1501(10) Å, which are close to

those reported in the literature.<sup>7a</sup> The Co–centroid distance of the toluene  $\text{C}_6$ -perimeter is 1.5920(13) Å [the coordinating toluene molecule is disordered over two positions; all twelve atoms were taken into account for the distance and its e.s.d. value]. The anion part exists as a dimer  $[\text{Co(II)Cl}_3]_2^{2-}$  in the crystal structure of **1**. The cobalt atom present in the anion is tetra-coordinate and is in a tetrahedral geometry. The terminal Co–Cl bond lengths present in the anion part are 2.2185(9) and 2.2329(9) Å, respectively, while the bridging Co–Cl bond lengths are 2.3311(9) and 2.3320(9) Å, which are quite comparable with those of other anionic Co–Cl bond distances.<sup>12</sup> There is also a variation of the bond lengths and the angles of the amidinate moiety of **1** coordinate to the cobalt atom. The average Si–Cl bond length in **1** is 2.1172(12) Å [Si–Cl of **L** 2.156(1) Å] and the N–Si–N angles are  $71.27(10)$  and  $70.86(11)^\circ$  [N–Si–N of **L**  $71.15(7)^\circ$ ]. Compound **1** exhibits two characteristic absorption bands at 589 and 699 nm which are characteristic of the  $^4\text{A}_2 \rightarrow ^4\text{T}_1(\text{P})$  d–d transitions for a high spin Co(II) ion in a tetrahedral environment.<sup>13</sup>

Compound **2** was synthesized by the reaction of chlorosilylene **L** with anhydrous  $\text{CoBr}_2$  in a 2 : 1 ratio (Scheme 2) and it crystallized as violet coloured crystals. It is stable under an inert gas atmosphere. No resonance was observed for compound **2** in its  $^{29}\text{Si}$  NMR spectrum, which might be due to the presence of paramagnetic cobalt(II) ions. The molecular structure of compound **2** was established unambiguously by single crystal X-ray structural analysis.

Compound **2** crystallizes in the monoclinic space group  $P2_1/n$ . The molecular structure of **2** is shown in Fig. 2. Compound **2** contains cobalt in the +II oxidation state. The cobalt atom exhibits a distorted tetrahedral coordination sphere consisting of two silicon and two bromine atoms, with a slight bromine/chlorine disorder. The silicon atoms are tetra-coordinate and in a distorted tetrahedral geometry made up of two nitrogen atoms from the supporting amidinato ligand, one chlorine, and one cobalt atom. The bond angles of Si1–Co1–Si2 are  $95.00(2)$  and  $\text{Br1–Co1–Br2}$   $98.940(16)^\circ$ . The Si–Co bond lengths in **2** are 2.1793(5) and 2.1940(5) Å. There is also a variation of the bond lengths and the angles in the amidinate moiety of **2** after coordination to the cobalt atom. The average

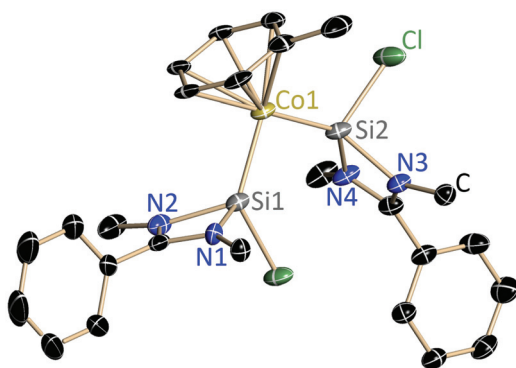
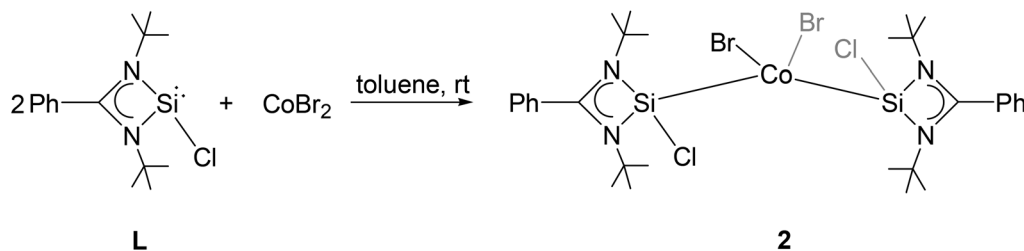
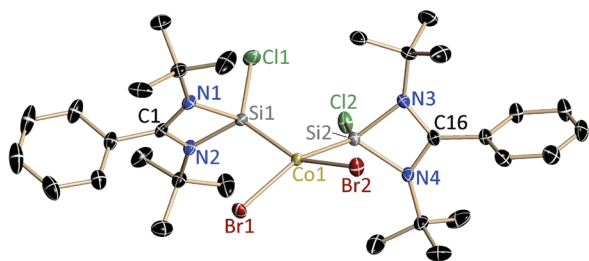


Fig. 1 Molecular structure of **1** (cationic part). Anisotropic displacement parameters are depicted at the 50% probability level. Hydrogen atoms and the anion are omitted. Selected bond lengths (Å) and bond angles ( $^\circ$ ): Co1–Si1 2.1553(9), Co1–Si2 2.1501(10), Si–Cl<sub>av</sub> 2.1172(11); N3–Si2–N4  $71.27(10)$ , N2–Si1–N1  $70.86(11)$ , Si2–Co1–Si1  $92.99(3)$ .



Scheme 2 Synthesis of 2.



**Fig. 2** Molecular structure of **2**. Anisotropic displacement parameters are depicted at the 50% probability level. Hydrogen atoms and the disorder are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Co1–Si1 2.1940(5), Co1–Si2 2.1793(5), Si–Cl<sub>av</sub> 2.0986(10), Co–Br<sub>av</sub> 2.3609(4); N3–Si2–N4 72.14(5), N2–Si1–N1 71.96(5), Si2–Co1–Si1 95.00(2), Br1–Co1–Br2 98.940(16).

Si–Cl bond length in **2** is 2.0986(10) Å and the N–Si–N angles are 71.96(5) and 72.14(5)°. The high spin Co(II) ion of **2** shows two characteristic absorption bands at 574 and 675 nm {<sup>4</sup>A<sub>2</sub> → <sup>4</sup>T<sub>1</sub>(P)}.<sup>13</sup>

## Conclusions

In summary, the first carbonyl free mixed valence cobalt(I)/cobalt(II) compound of composition [2{L<sub>2</sub>Co(I)(η<sup>6</sup>-C<sub>7</sub>H<sub>8</sub>)}]<sup>2+</sup>[Co(II)<sub>2</sub>Cl<sub>6</sub>]<sup>2-</sup> (**1**) was prepared with a stable chlorosilylene (L). Compound **1** was formed by the cleavage of Co–Cl bonds, the reduction of Co(II) to Co(I) by L and by coordination of a toluene molecule. However, the reaction of L with CoBr<sub>2</sub> yielded [L<sub>2</sub>CoBr<sub>2</sub>] (**2**). In the case of the reaction of L with CoCl<sub>2</sub>, we surmise that the formation of [Co(II)Cl<sub>3</sub>]<sup>-</sup> and PhC(N<sup>t</sup>Bu)<sub>2</sub>SiCl<sub>3</sub> is thermodynamically favoured compared to adduct formation of L with CoBr<sub>2</sub>.

## Experimental section

The synthesis was carried out in an inert gas atmosphere of dinitrogen in oven dried glassware using standard Schlenk techniques and other manipulations were accomplished in a dinitrogen filled glove box. Solvents were purified by the MBRAUN solvent purification system MB SPS-800. All chemicals were purchased from Aldrich and used without further purification. L was prepared as reported in the literature.<sup>4</sup> <sup>1</sup>H and <sup>29</sup>Si NMR spectra were recorded with a Bruker Avance DRX 500 spectrometer using C<sub>6</sub>D<sub>6</sub> as a solvent. Chemical shifts δ

are given relative to SiMe<sub>4</sub>. UV/Vis spectra were recorded with an Analytik Jena Specord S100 using quartz cuvettes. Elemental analyses were performed at the Institut für Anorganische Chemie, Universität Göttingen. For elemental analysis, 1-toluene was treated under vacuum for eight hours to remove the toluene molecule.

### Synthesis of 1

Toluene (30 mL) was added to a 50 mL Schlenk flask already containing L (0.30 g, 1.02 mmol) and anhydrous CoCl<sub>2</sub> (0.11 g, 0.84 mmol). The reaction mixture was stirred for one week at room temperature. The reaction mixture was filtered and left at room temperature for 45 days to yield green coloured single crystals of **1** (0.25 g, 68.0%). Elemental analysis (%) calcd for C<sub>74</sub>H<sub>108</sub>Cl<sub>10</sub>Co<sub>4</sub>N<sub>8</sub>Si<sub>4</sub> (1812.3): C, 49.04; H, 6.01; N, 6.18. Found: C, 48.95; H, 6.03; N, 6.12. <sup>1</sup>H NMR (500 MHz, THF-d<sub>8</sub>, 50 °C): δ -1.95, -1.08, 0.15, 0.81, 2.33, 2.94, 4.20, 4.83, 5.88, 6.42, 6.75, 7.16, 7.29, 7.33, 7.47 ppm. <sup>1</sup>H NMR (500 MHz, THF-d<sub>8</sub>, 25 °C): δ -2.22, -1.26, 0.14, 0.81, 1.92, 2.33, 3.11, 4.24, 4.51, 5.74, 6.28, 6.58, 7.16, 7.21, 7.33, 7.46 ppm. <sup>1</sup>H NMR (500 MHz, THF-d<sub>8</sub>, 0 °C): δ -2.46, -1.43, 0.14, 0.83, 2.10, 2.34, 4.93, 5.60, 6.14, 6.39, 7.13, 7.18, 7.24, 7.35, 7.50 ppm. <sup>1</sup>H NMR (500 MHz, THF-d<sub>8</sub>, -25 °C): δ -2.79, -1.63, 0.14, 0.86, 2.35, 2.57, 3.79, 4.09, 5.43, 5.96, 6.11, 7.15, 7.19, 7.25, 7.37, 7.55 ppm. <sup>1</sup>H NMR (500 MHz, THF-d<sub>8</sub>, -50 °C): δ -3.10, -1.81, 0.14, 0.92, 2.35, 2.66, 4.46, 4.98, 5.26, 5.75, 7.17, 7.21, 7.27, 7.39, 7.46, 7.62 ppm. <sup>1</sup>H NMR (500 MHz, THF-d<sub>8</sub>, -90 °C): δ -1.70, 0.14, 1.12, 2.36, 4.96, 5.18, 5.40, 5.97, 7.24, 7.30, 7.42, 7.54, 7.66, 7.82 ppm. <sup>29</sup>Si{<sup>1</sup>H} NMR (99.36 MHz, THF-d<sub>8</sub>, 25 °C): δ 48.27, 49.48 ppm. UV-vis {THF, λ<sub>max</sub>/nm (ε/L mol<sup>-1</sup> cm<sup>-1</sup>): 589 (285), 699 (515).

### Synthesis of 2

Toluene (60 mL) was added to a 100 mL Schlenk flask already containing L (0.52 g, 1.76 mmol) and anhydrous CoBr<sub>2</sub> (0.39 g, 1.78 mmol). The reaction mixture was stirred for 16 h at room temperature. Then the volume was reduced to 40 mL followed by placing the flask at -27 °C to obtain the violet coloured crystals of **2** (0.60 g, 84.5%). Elemental analysis (%) calcd for C<sub>30</sub>H<sub>46</sub>Br<sub>2</sub>Cl<sub>2</sub>CoN<sub>4</sub>Si<sub>2</sub> (808.53): C, 44.56; H, 5.73; N, 6.93. Found: C, 44.48; H, 5.71; N, 6.92. <sup>1</sup>H NMR (500 MHz, THF-d<sub>8</sub>, 25 °C): δ -2.99, -2.41, -1.04, 0.11, 0.55, 2.30, 5.52, 6.10, 6.47, 7.35, 7.52, 7.65, 7.93, 8.08, 8.61 ppm. UV-vis {THF, λ<sub>max</sub>/nm (ε/mol<sup>-1</sup> L cm<sup>-1</sup>): 574 (298), 675 (198).

**Table 1** Crystal and structure refinement parameters for compounds **1** and **2**

Parameters	<b>1</b> -toluene	<b>2</b>
CSD number	868295	929864
Empirical formula	C <sub>88</sub> H <sub>124</sub> Cl <sub>10</sub> Co <sub>4</sub> N <sub>8</sub> Si <sub>4</sub>	C <sub>30</sub> H <sub>46</sub> Br <sub>2</sub> Cl <sub>2</sub> CoN <sub>4</sub> Si <sub>2</sub>
Formula weight	1996.52	808.54
Crystal system	Monoclinic	Monoclinic
Space group	<i>P2</i> <sub>1</sub> / <i>n</i>	<i>P2</i> <sub>1</sub> / <i>n</i>
Unit cell dimensions	<i>a</i> = 10.4803(19) Å <i>b</i> = 32.015(6) Å <i>c</i> = 14.974(3) Å $\beta$ = 99.675(7)°	<i>a</i> = 18.568(3) Å <i>b</i> = 9.504(2) Å <i>c</i> = 21.378(3) Å $\beta$ = 102.95(2)°
Volume, <i>Z</i>	4952.6(16) Å <sup>3</sup> , 2	3676.6(11) Å <sup>3</sup> , 4
Density (calcd)	1.339 g cm <sup>-3</sup>	1.461 g cm <sup>-3</sup>
Absorption coefficient	1.022 mm <sup>-1</sup>	1.530 mm <sup>-1</sup>
<i>F</i> (000)	2084	1652
Crystal size	0.06 × 0.05 × 0.04 mm <sup>3</sup>	0.11 × 0.10 × 0.10 mm <sup>3</sup>
$\theta$ range for data collection	1.27 to 24.76°	1.54 to 25.27°
Limiting indices	-12 ≤ <i>h</i> ≤ 12, -0 ≤ <i>k</i> ≤ 37, -0 ≤ <i>l</i> ≤ 17	-28 ≤ <i>h</i> ≤ 28, -14 ≤ <i>k</i> ≤ 14, -32 ≤ <i>l</i> ≤ 32
Reflections collected	297 646	92 551
Independent reflections	9721 ( <i>R</i> <sub>int</sub> = 0.0862)	13 567 ( <i>R</i> <sub>int</sub> = 0.0474)
Completeness to $\theta$	99.5% ( $\theta$ = 24.76°)	99.7% ( $\theta$ = 25.27°)
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data/restraints/parameters	9721/489/651	13 567/79/420
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.024	1.047
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0428, <i>wR</i> <sub>2</sub> = 0.0824	<i>R</i> <sub>1</sub> = 0.0266, <i>wR</i> <sub>2</sub> = 0.0588
<i>R</i> indices (all data)	<i>R</i> <sub>1</sub> = 0.0713, <i>wR</i> <sub>2</sub> = 0.0912	<i>R</i> <sub>1</sub> = 0.0374, <i>wR</i> <sub>2</sub> = 0.0614
Largest diff. peak and hole	0.394 and -0.349 e Å <sup>-3</sup>	0.477 and -0.311 e Å <sup>-3</sup>

### Crystal structure determination

Suitable single crystals for the X-ray structural analysis of **1** and **2** were mounted at low temperature in inert oil under argon atmosphere by applying the X-Temp2 device.<sup>14</sup> Both data sets were collected at 100 K on a Bruker D8 three circle diffractometer equipped with an Apex II CCD detector and an Incoatec microsource with mirror optics. The data set of **1** was measured using an Incoatec Mo microsource<sup>15</sup> ( $K_{\alpha}$ - $\lambda$  = 0.71073 Å) and **2** was measured using an Incoatec Ag microsource ( $K_{\alpha}$ - $\lambda$  = 0.56086 Å). The batch of crystals grown from compound **1** were very small and of poor quality. A split crystal with three domains (one major and two minor domains) eventually was chosen because of its comparatively large size. The data were integrated with Saint.<sup>16</sup> In the case of **1**, integration of data with a higher resolution than  $\sin(\theta)/\lambda$  = 0.589 (as compared to the standard resolution of  $\sin(\theta)/\lambda$  = 0.590) was neglected in favour of higher data quality. An empirical absorption correction with Sadabs<sup>17</sup> (TWINABS in the case of **1**) was applied. A reflection file of HKLF4 format as well as a HKLF5 reflection file only including reflections of the strongest domain was written for **1**; the HKLF4 file was used for structure solution while the HKLF5 file was used for structure refinement. The structures were solved by direct methods (Shelxs-97)<sup>18a</sup> and refined against all data by full-matrix least-squares methods on *F*<sup>2</sup> (Shelxl-97)<sup>18b,c</sup> using the Shelxle GUI.<sup>18d</sup> All non-hydrogen-atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically on calculated positions using a riding model with their *U*<sub>iso</sub> values constrained to 1.5*U*<sub>eq</sub> of their pivot atoms for terminal sp<sup>3</sup> carbon atoms and 1.2 times for all other carbon atoms. The chlorine/bromine disorder (relative occupancies

97 : 3) and the rotational disorder of the <sup>t</sup>Bu-group attached to N1 were refined using bond length and angle restraints and anisotropic displacement parameters restraints and constraints. The refinement of the minor chlorine/bromine disorder gave a considerable improvement in *wR*<sub>2</sub> from 0.0681 to 0.0588 and in goodness-of-fit from 1.062 to 1.047 as well as a decrease in residual density (the highest peak without disorder: 0.60 e Å<sup>-3</sup>). Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited at the Cambridge Crystallographic Data Centre. The CCDC numbers, crystal data and experimental details for the X-ray measurements are listed in Table 1.

### Acknowledgements

We thank the Deutsche Forschungsgemeinschaft for supporting this work. R. A. is thankful to the Alexander von Humboldt Stiftung for a research fellowship. D. S. and J. H. are grateful to the DNRF funded *Center for Materials Crystallography* (CMC) for support and the Land Niedersachsen for providing a fellowship under the *Catalysis of Sustainable Synthesis* (CaSuS) PhD program.

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