

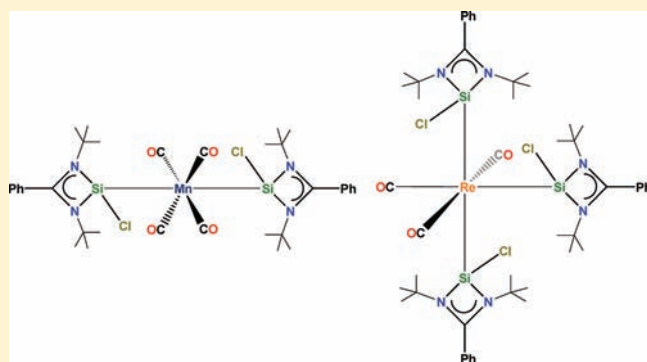
Syntheses of Group 7 Metal Carbonyl Complexes with a Stable N-Heterocyclic Chlorosilylene

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Supporting Information

ABSTRACT: Two structurally characterized manganese [$L_2Mn(CO)_4$] $^+$ [$Mn(CO)_5$] $^-$ (**1**) and rhenium [$L_3Re(CO)_3$] $^+$ [$ReCO_5$] $^-$ (**2**) silylene complexes were prepared in one pot syntheses by reacting 1 equivalent of $Mn_2(CO)_{10}$ with 2 equivalents of stable N-heterocyclic chlorosilylene **L** {**L** = $PhC(NtBu)_2SiCl$ } and 1 equivalent of $Re_2(CO)_{10}$ with 3 equivalents of **L** in toluene at room temperature. Both complexes **1** and **2** were characterized by single-crystal X-ray structural analysis, NMR and IR spectroscopy, EI-MS spectrometry, and elemental analysis.



INTRODUCTION

The coordination chemistry of N-heterocyclic carbenes (NHCs) has been studied extensively, and these complexes have shown diverse applications.^{1,2} The NHCs have found increasing use as reagents for organic transformations and in asymmetric organocatalysis. Considering the great importance of NHC-transition metals in coordination chemistry, the analogous compounds of N-heterocyclic silylene (NHSi) with transition metals^{3,4} are still scarce and have to be studied more extensively. A challenge in the case of NHSi's is the synthetic procedure available for the preparation of NHSi's.⁵ Usually, the conventional synthetic procedure for the preparation of NHSi's involves the use of strong reducing agents, such as potassium metal or potassium graphite. These reducing agents and harsh conditions often lower the yields. Recently, we synthesized NHC-stabilized dichlorosilylene $RSiCl_2$ [**R** = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene] in high yield by employing a new synthetic procedure comprising the reductive elimination of HCl from trichlorosilane in the presence of NHC under mild reaction conditions.⁶ Furthermore, we reported the high yield synthesis of stable N-heterocyclic chlorosilylene **L** [**L** = $PhC(NtBu)_2SiCl$] using lithium bis(trimethylsilyl) amide as a dehydrochlorinating agent.⁷ Currently, we are in the process of investigating the reactivity of the chlorosilylene **L** toward organic substrates and transition metal complexes.^{4c,7,8} In order to gain further insight into the reactivity of **L** toward transition metals, we carried out the reaction with group 7 metal carbonyls $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$, which form complexes of composition [$L_2Mn(CO)_4$] $^+$ [$Mn(CO)_5$] $^-$ (**1**) and rhenium [$L_3Re(CO)_3$] $^+$ [$ReCO_5$] $^-$ (**2**), respectively.

RESULTS AND DISCUSSION

Compounds **1** and **2** were obtained in good yields in one pot reactions of **L** with $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ in 2:1 and 3:1

ratios, respectively (Schemes 1 and 2). In the case of treating **L** with $Re_2(CO)_{10}$, the reaction proceeds in a 3:1 ratio even though a 2:1 ratio was used. Both compounds **1** and **2** are soluble in benzene, toluene, and THF. Furthermore, they are stable both in solution and in the solid state for a long period of time without any decomposition under an inert gas atmosphere. Compounds **1** and **2** were fully characterized by NMR spectroscopy, EI-MS spectrometry, elemental analysis, and single crystal X-ray structural analysis.

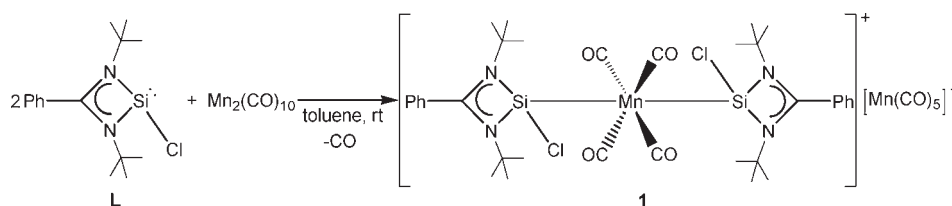
The ^{29}Si NMR spectrum of **1** shows a single resonance at δ 92.5 ppm, which is downfield shifted compared to **L** (δ 14.6 ppm),^{5a} because in **1** the silicon atom is deshielded upon coordination of the manganese atom to silicon. This chemical shift is pertinent to the reported value of δ 62.69 ppm for $L \cdot Ni(CO)_3$.^{4c} The *t*Bu protons for compound **1** in the 1H NMR spectrum show a broad singlet which is observed at δ 1.39 ppm and is downfield shifted compared to that of **L** (δ 1.08 ppm). The ^{13}C NMR spectrum reveals the presence of carbonyl groups which resonate at 221.20 and 239.86 ppm. Moreover, **1** shows its fragment ions for [$M-CO$] $^+$ and [$M-4CO$] $^+$ in its mass spectrum at m/z 728 and 644, respectively.

Compound **1** crystallizes in the monoclinic space group $P2_1/n$ (Table 1). The molecular structure of **1** is shown in Figure 1. The bond parameters for compound **1** are given in Table 2. In **1**, both silicon atoms are tetracoordinate, and in a distorted tetrahedral geometry comprising two nitrogen atoms from the supporting amidinato ligand, one chlorine, and one manganese atom. Two manganese atoms are present in the structure; one exhibits the central atom in the cation and the other in the anion. The manganese

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Scheme 1. Synthesis of 1



Scheme 2. Synthesis of 2

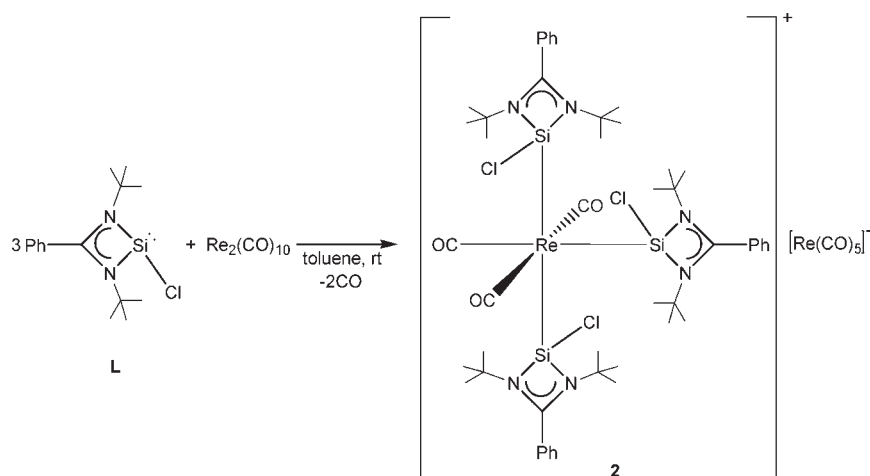


Table 1. Crystal and Structure Refinement Parameters for Compounds 1 and 2

parameters	1 · 2toluene	2 · toluene
empirical formula	C ₅₃ H ₆₂ Cl ₂ Mn ₂ N ₄ O ₉ Si ₂	C ₆₀ H ₇₇ Cl ₃ N ₆ O ₈ Re ₂ Si ₃
fw	1136.03	1573.32
cryst syst	monoclinic	monoclinic
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
unit cell dimensions	<i>a</i> = 8.8470 (14) Å <i>b</i> = 34.141 (5) Å <i>c</i> = 19.096 (3) Å α = 90° β = 100.555 (4)° γ = 90°	<i>a</i> = 12.4470 (4) Å <i>b</i> = 37.8010 (13) Å <i>c</i> = 14.4401 (5) Å α = 90° β = 90.4560(10)° γ = 90°
volume, <i>Z</i>	5670.20 (16) Å ³ , 4	6794.0 (4) Å ³ , 4
density (calcd)	1.331 g/cm ³	1.538 g/cm ³
absorption coefficient	0.637 mm ^{−1}	3.785 mm ^{−1}
<i>F</i> (000)	2368	3144
cryst size	0.12 × 0.05 × 0.05 mm ³	0.21 × 0.09 × 0.06 mm ³
θ range for data collection	1.19 to 25.43°	1.08 to 26.74°
limiting indices	−10 ≤ <i>h</i> ≤ 10, −41 ≤ <i>k</i> ≤ 41, −23 ≤ <i>l</i> ≤ 23	−15 ≤ <i>h</i> ≤ 15, −47 ≤ <i>k</i> ≤ 47, −18 ≤ <i>l</i> ≤ 18
reflns collected	122803	272786
independent reflns	10441 (<i>R</i> _{int} = 0.0728)	14417 (<i>R</i> _{int} = 0.0509)
completeness to θ	99.6% (θ = 25.43)	99.9% (θ = 26.74)
refinement method	full-matrix least-squares on <i>F</i> ²	full-matrix least-squares on <i>F</i> ²
data/restraints/params	10441/40/663	14417/119/818
goodness of fit on <i>F</i> ²	1.022	1.299
final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0367, <i>wR</i> 2 = 0.0747	<i>R</i> 1 = 0.0484, <i>wR</i> 2 = 0.1074
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0582, <i>wR</i> 2 = 0.0838	<i>R</i> 1 = 0.0536, <i>wR</i> 2 = 0.1093
largest diff. peak and hole	0.352 and −0.347 eÅ ^{−3}	3.867 and −1.939 eÅ ^{−3}

atom present in the cationic part is coordinated in a distorted octahedral geometry derived from the two silicon and four carbon atoms of the carbonyl groups. The environment of manganese in the cationic part of the *trans* isomer $[\text{L}_2\text{Mn}(\text{CO})_4]^+$ is depicted in Figure 1a. The silylene ligands are located in *trans* positions, and the Si(2)–Mn(1)–Si(1) bond angle exhibits $178.30(3)^\circ$. The Si–Mn bond distances in **1** are 2.2816(8) and 2.2789(8) Å. The average manganese carbonyl bond length in the cation is 1.842(3) Å. The manganese atom present in the anion is pentacoordinate and comprises a trigonal bipyramidal geometry (Figure 1b). The average Mn–CO bond distance present in the anion part is 1.822(3) Å for the axial and 1.807(3) Å for the equatorial sites, which is quite comparable with that of the cationic Mn–CO bond distance and also with literature values.⁹ Moreover, there is also a variation of the bond lengths and the angles of L after coordination to the manganese atom. The average Si–Cl bond length in **1** is 2.0867(9) Å [Si–Cl of L, 2.156(1) Å], and the $\angle\text{N–Si–N}$ angles are $72.53(9)$ and $72.38(9)^\circ$ [$\angle\text{N–Si–N}$ of L, $71.15(7)^\circ$].

The *t*Bu protons for compound **2** in the ^1H NMR spectrum show two broad singlets (δ 1.27 and δ 1.32 ppm) with an intensity ratio of 1:2. Like in **1**, compound **2** shows downfield resonances (δ 40.32 and δ 47.38 ppm) in its ^{29}Si NMR spectrum. These data indicate the possibility of two types of silylene coordination to the

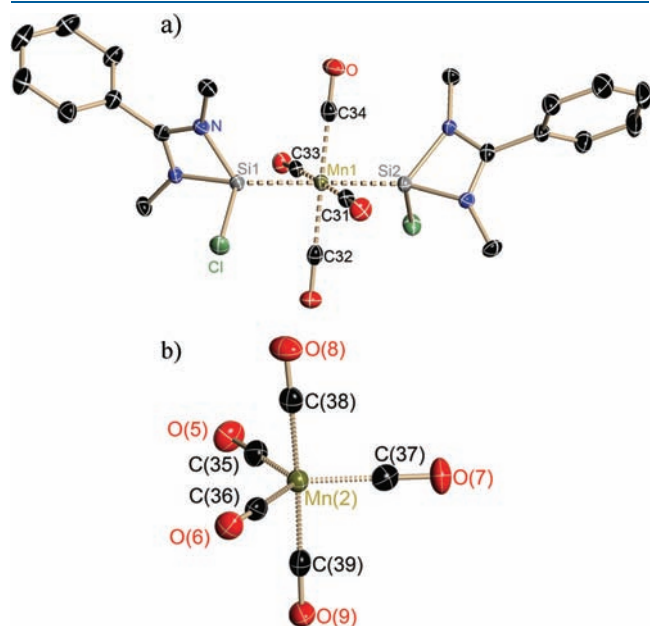


Figure 1. Molecular structure of **1**. (a) Cationic part of complex **1**, where the silylene ligands are arranged in *trans* positions. (b) Anionic part of complex **1**. The anisotropic displacement parameters are depicted at the 50% probability level.

rhenium atom in **2** (two silylenes in one coordination environment and another one in a different coordination environment). The ^{13}C NMR spectrum of **2** shows carbonyl resonances at 198.23, 200.42, and 219.81 ppm. Complex **2** exhibits the $[\text{M–2CO}]^+$ fragment ion in its mass spectrum at m/z 1100.

The molecular structure of compound **2** possesses two types of silylene coordination environments, two equatorial and one axial unambiguously established by single crystal X-ray structural analysis. Like **1**, **2** also crystallizes in the monoclinic space group $P2_1/n$ (Table 1). The molecular structure is shown in Figure 2, and the bond parameters are given in Table 3. Similar to **1**, the three silicon atoms present in the cationic part of **2** are tetra-coordinate and arranged in a distorted tetrahedral geometry, where the coordination environment of all three silicon atoms comprises two nitrogen atoms from the chelating amidinato ligand, one chlorine, and one rhenium atom. The rhenium atom in the cationic part is coordinated in a distorted octahedral geometry regarding the coordination environment derived from

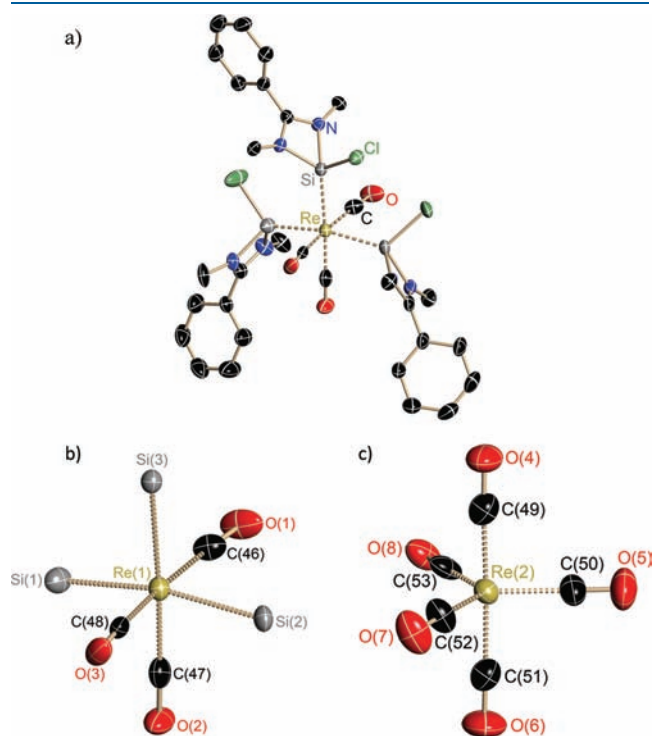


Figure 2. Molecular structure of **2**. (a) Cationic part of complex **2**. (b) Coordination environment around the Re atom in the cation, where the silylene ligands are arranged in meridional fashion. (c) Anionic part of complex **2**. The anisotropic displacement parameters are depicted at the 50% probability level.

Table 2. Selected Bond Parameters for Compound **1**

bond lengths/Å		bond angles/deg			
Mn(1)–Si(1)	2.2816(8)	Si(2)–Mn(1)–Si(1)	178.30(3)	N(4)–Si(2)–N(3)	72.53(9)
Mn(1)–Si(2)	2.2789(8)	C(33)–Mn(1)–C(31)	178.48(11)	N(1)–Si(1)–N(2)	72.38(9)
Mn–C _{av} (cationic)	1.842(3)	C(32)–Mn(1)–C(34)	178.62(11)	C(39)–Mn(2)–C(38)	177.09(12)
Si–Cl _{av}	2.0867(9)	C(32)–Mn(1)–C(33)	89.19(11)	C(35)–Mn(2)–C(36)	122.65(12)
Si–N _{av}	1.814(2)	C(34)–Mn(1)–C(31)	92.03(11)	C(36)–Mn(2)–C(37)	120.27(12)
Mn–C _{av} (eq:anionic)	1.807(3)	C(32)–Mn(1)–Si(1)	89.23(8)	C(37)–Mn(2)–C(39)	90.04(12)
Mn–C _{av} (ax:anionic)	1.822(3)	C(34)–Mn(1)–Si(2)	90.06(8)	C(35)–Mn(2)–C(37)	117.06(12)

Table 3. Selected Bond Parameters for Compound 2

bond lengths/Å		bond angles/deg			
Re(1)–Si(1)	2.4384(18)	Si(2)–Re(1)–Si(1)	167.24(6)	N(2)–Si(1)–N(1)	70.8(3)
Re(1)–Si(2)	2.4354(17)	Si(2)–Re(1)–Si(3)	96.74(6)	N(4)–Si(2)–N(3)	71.2(3)
Re(1)–Si(3)	2.4928(17)	Si(1)–Re(1)–Si(3)	95.89(6)	N(5)–Si(3)–N(6)	71.1(2)
Re–C _{av} (cationic)	1.958(7)	C(46)–Re(1)–C(48)	171.3(3)	C(53)–Re(2)–C(52)	120.2(4)
Si–Cl _{av}	2.087(2)	C(47)–Re(1)–C(46)	93.6(3)	C(49)–Re(2)–C(51)	177.9(4)
Si–N _{av}	1.837(6)	C(47)–Re(1)–C(48)	90.1(3)	C(53)–Re(2)–C(50)	118.5(4)
Re–C _{av} (eq:anionic)	1.937(7)	C(47)–Re(1)–Si(3)	176.84(19)	C(49)–Re(2)–C(50)	90.6(4)
Re–C _{av} (ax:anionic)	1.946(8)	C(48)–Re(1)–Si(1)	94.45(18)	C(52)–Re(2)–C(50)	121.3(4)

the three silicon and three carbon atoms of the carbonyl groups (Figure 2b). Here, the coordination environment of rhenium is that of a meridional isomer (i.e., the silylene ligand and carbonyl groups are coplanar) $[\text{L}_3\text{Re}(\text{CO})_3]^+$ (Figure 2b). There are two types of Si–Re bond lengths observed in **2**: one is longer [Re(1)–Si(3), 2.4928(17) Å], while the other two are shorter and their bond lengths similar [Re(1)–Si(1), 2.4384(18) and Re(1)–Si(2), 2.4354(17) Å]. The average Re–CO bond distance present in the cation is 1.958(7) Å, which is close to those found before.¹⁰ The counteranion has a trigonal bipyramidal geometry, as expected, which is shown in Figure 2c. The average bond distance of Si–Cl in **1** is 2.087(2) Å, and the $\angle \text{N}–\text{Si}–\text{N}$ angles are 70.8(3), 71.2(3), and 71.1(2)°.

CONCLUSION

Chlorosilylene **L** is a versatile ligand for the synthesis of silylene transition metal carbonyl complexes. The size of the metal ion imposes the substitution of carbonyl groups from the carbonyl precursor compounds under the same experimental conditions. In the case of $\text{Mn}_2(\text{CO})_{10}$, one carbonyl group is eliminated to give $[\text{L}_2\text{Mn}(\text{CO})_4]^+[\text{Mn}(\text{CO})_5]^-$ (**1**), but with $\text{Re}_2(\text{CO})_{10}$, two carbonyl groups are eliminated to yield $[\text{L}_3\text{Re}(\text{CO})_3]^+[\text{Re}(\text{CO})_5]^-$ (**2**). The above two compounds are the first structurally characterized manganese and rhenium silylene complexes. In comparison to metal complexes with stable carbenes, the metal complexes of silylenes are quite scarce, and the chemistry has to be explored to find useful applications of these systems.

EXPERIMENTAL SECTION

Syntheses were carried out under an inert gas atmosphere of dinitrogen in oven-dried glassware using standard Schlenk techniques, and other manipulations were accomplished in a dinitrogen filled glovebox. Solvents were purified using 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.⁷ ¹H, ¹³C, and ²⁹Si NMR spectra were recorded with a Bruker Avance DPX 200, or a Bruker Avance DRX 500 spectrometer, using C₆D₆ as the solvent. Chemical shifts δ are given relative to SiMe₄. IR spectra were recorded on a Bio-Rad Digilab FTS7 spectrometer in the range 4000–350 cm⁻¹ as nujol mulls. EI-MS spectra were obtained using a Finnigan MAT 8230 instrument. Elemental analyses were performed by the Institut für Anorganische Chemie, Universität Göttingen. Melting points were measured in sealed glass capillaries on a Büchi B-540 melting point apparatus.

Synthesis of 1. Toluene (60 mL) was added to a 100 mL Schlenk flask containing **L** (0.31 g, 1.05 mmol) and $\text{Mn}_2(\text{CO})_{10}$ (0.21 g, 0.54 mmol). The reaction mixture was stirred at room temperature for 12 h. The solution was filtered, and the solvent from the filtrate was reduced *in*

vacuo to 20 mL and stored in a freezer at –32 °C for 3 days to obtain pale yellow single crystals (0.36 g, 72.0%). Mp: 115–118 °C. For elemental analysis, **1**·2toluene was treated under vacuum conditions for 6 h to remove the toluene molecules. Elemental analysis (%) calcd for C₃₉H₄₆Cl₂Mn₂N₄O₉Si₂ (951.76): C, 49.22; H, 4.87; N, 5.89. Found: C, 49.85; H, 4.82; N, 5.80. ¹H NMR (200 MHz, C₆D₆, 25 °C): δ 1.39 (s(br), 36H, C(CH₃)₃), 6.80–7.01 (br, 10H, C₆H₅) ppm. ¹³C{¹H} NMR (125.75 MHz, C₆D₆, 25 °C): δ 32.10 C(CH₃)₃, 56.33 (C(CH₃)₃), 125.64, 129.98, 130.16, 130.45, 132.61, 137.82 (C₆H₅), 172.72 (NCN), 221.20 (br, CO), 239.86 (CO) ppm. ²⁹Si{¹H} NMR (99.36 MHz, C₆D₆, 25 °C): δ 92.50 ppm. EI-MS: *m/z* 728 [M – CO]⁺, 644 [M – 4CO]⁺. FT-IR (Nujol, cm⁻¹): ν 2080 (s), 2045 (s), 2012 (s), 1982 (s), 1921(b) (CO).

Synthesis of 2. Toluene (60 mL) was added to a 100 mL Schlenk flask containing **L** (0.20 g, 0.68 mmol) and $\text{Re}_2(\text{CO})_{10}$ (0.15 g, 0.23 mmol). The reaction mixture was stirred at room temperature for 12 h. The solution was filtered, and the solvent from the filtrate was reduced *in vacuo* to 15 mL and stored in a freezer at –32 °C overnight to obtain yellow colored single crystals (0.24 g, 70.6%). Mp: 157–159 °C. For elemental analysis, **2**·toluene was treated under vacuum conditions for 6 h to remove the toluene molecule. Elemental analysis (%) calcd for C₅₃H₆₉Cl₃N₆O₈Re₂Si₃ (1481.18): C, 42.98; H, 4.70; N, 5.67. Found: C, 42.68; H, 4.42; N, 4.95. ¹H NMR (200 MHz, C₆D₆, 25 °C): δ 1.27 (s(br), 18H, C(CH₃)₃), 1.32 (s(br), 36H, C(CH₃)₃), 6.74–7.13 (br, 15H, C₆H₅) ppm. ¹³C{¹H} NMR (125.75 MHz, C₆D₆, 25 °C): δ 30.58 C(CH₃)₃, 31.40 C(CH₃)₃, 55.10 (C(CH₃)₃), 55.87 (C(CH₃)₃), 125.62, 127.89, 128.27, 128.49, 129.26, 129.45, 129.84, 130.88, 131.55, 137.82 (C₆H₅), 177.92 (NCN), 198.23 (CO), 200.42 (CO), 219.81 (CO) ppm. ²⁹Si{¹H} NMR (99.36 MHz, C₆D₆, 25 °C): δ 40.32(s), 47.38(s) ppm. EI-MS: *m/z* 1100 [M – 2CO]⁺, 1065 [M – 2CO – Cl]⁺, 1037 [M – 3CO – Cl]⁺. FT-IR (Nujol, cm⁻¹): ν 2101 (s), 2070 (s), 2033 (s), 2013 (s), 1992 (s), 1959 (sh), 1941 (s), 1901 (m) (CO).

Crystal Structure Determination. Suitable single crystals for X-ray structural analysis of **1** and **2** were mounted at low temperatures in inert oil under an argon atmosphere by applying the X-Temp2 device.¹¹ The diffraction data were collected at 100 K on a Bruker D8 three circle diffractometer equipped with a SMART APEX II CCD detector and an INCOATEC Mo microsource with INCOATEC Quazar mirror optics ($\lambda = 0.71073$ Å).¹² The data were integrated with SAINT,¹³ and an empirical absorption correction with SADABS¹⁴ was applied. The structures were solved by direct methods (SHELXS-97) and refined against all data by full-matrix least-squares methods on *F*² (SHELXL-97).¹⁵ 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*_{iso} values constrained to 1.5 *U*_{eq} of their pivot atoms for terminal sp³ carbon atoms and 1.2 times for all other carbon atoms.

ASSOCIATED CONTENT

S Supporting Information. CIF files for **1** and **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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