The group 7 metal carbonyl complexes from a stable heteroleptic silylene $\text{PhC}(\text{NtBu})_2\text{SiNPh}_2^{\dagger}$

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Received 16th July 2012, Accepted 10th August 2012

DOI: 10.1039/c2dt31578e

Two silylene transition metal complexes were prepared by reacting stable N-heterocyclic silylene **L** ($\text{L} = \text{PhC}(\text{NtBu})_2\text{SiNPh}_2$) with $\text{Mn}_2(\text{CO})_{10}$ and $\text{Re}_2(\text{CO})_{10}$ respectively in a 2 : 1 ratio to yield $[\text{L}_2\text{Mn}(\text{CO})_4]^+[\text{Mn}(\text{CO})_5]^-$ (**1**) and $[\text{L}_2\text{Re}(\text{CO})_4]^+[\text{Re}(\text{CO})_5]^-$ (**2**). Both complexes **1** and **2** were characterized by NMR spectroscopy, EI-MS spectrometry and elemental analysis. The molecular structures of complexes **1** and **2** were established by single crystal X-ray analysis.

Introduction

In the past two decades, there has been increasing interest in the chemistry of N-heterocyclic carbenes (NHCs).^{1,2} The fascinating discovery of stable N-heterocyclic carbenes by Arduengo *et al.*³ led to burgeoning research activity. Since then, NHCs have been utilized as strong donor ligands for transition metals. On the one hand, many highly reactive species with low valent and zero valent elements stabilized by NHCs have been documented.⁴ On the other hand, the congeners of group 14 N-heterocyclic carbenes (N-heterocyclic silylenes,^{5,6} N-heterocyclic germylenes,⁷ N-heterocyclic stannyls,⁸ and N-heterocyclic plumbylenes⁹) are less developed as σ -donor ligands for transition metals when compared with those of NHCs. In view of the importance of NHC-transition metal complexes for catalysis, the analogous derivatives of N-heterocyclic silylenes (NHSis) with transition metals^{5,6} are still less explored. Currently we are interested in the chemistry of silylenes.^{5a-f,10,11} A synthetic challenge for the preparation of NHSis involves the use of strong reducing agents such as potassium or potassium graphite. These reducing agents and harsh conditions often lower the yields. Recently, we reported the high yield synthesis of stable N-heterocyclic chlorosilylene $\text{PhC}(\text{NtBu})_2\text{SiCl}$ using lithium bis(trimethylsilyl)amide as a dehydrochlorinating agent.¹² Further we reported on the facile synthesis of functionalized silylenes by treating monochlorosilylene $\text{PhC}(\text{NtBu})_2\text{SiCl}$ with alkali metal amides, phosphide, alkoxide and organo-alkyl reagents.¹³ In order to gain further insight into the reactivity of N-heterocyclic silylene towards transition metals and to investigate the presence of a bulky substituent on the silicon atom, we carried out the reaction of **L** ($\text{L} = \text{PhC}(\text{NtBu})_2\text{SiNPh}_2$) with group 7 metal carbonyls $\text{Mn}_2(\text{CO})_{10}$ and $\text{Re}_2(\text{CO})_{10}$. The group 7 carbonyl complexes have been

utilized for the formation of C–H and C–C bond reactions which have been considered as crucial steps in homogeneously catalyzed conversion of syngas to higher alkanes.¹⁴ The latter metal carbonyls were used for the preparation of complexes of composition $[\text{L}_2\text{Mn}(\text{CO})_4]^+[\text{Mn}(\text{CO})_5]^-$ (**1**) and $[\text{L}_2\text{Re}(\text{CO})_4]^+[\text{Re}(\text{CO})_5]^-$ (**2**) with **L**. The reaction of $\text{Re}_2(\text{CO})_{10}$ with $\text{PhC}(\text{NtBu})_2\text{SiNPh}_2$ shows a different reactivity pattern when compared with that of $\text{PhC}(\text{NtBu})_2\text{SiCl}$, which resulted in the product $[(\text{PhC}(\text{NtBu})_2\text{SiCl})_3\text{Re}(\text{CO})_3]^+[\text{Re}(\text{CO})_5]^-$ under elimination of two carbonyl groups.^{5b}

Results and discussion

Complexes **1** and **2** were obtained in good yields by the facile reactions of **L** with $\text{Mn}_2(\text{CO})_{10}$ and $\text{Re}_2(\text{CO})_{10}$ respectively in a 2 : 1 ratio (Scheme 1). The reaction of **L** with $\text{Re}_2(\text{CO})_{10}$ resulted in the product $[\text{L}_2\text{Re}(\text{CO})_4]^+[\text{Re}(\text{CO})_5]^-$ with elimination of one carbonyl group. The difference in the reactivity when compared with that of $\text{PhC}(\text{NtBu})_2\text{SiCl}$ might be due to the presence of the bulky NPh_2 group on the silicon(II) center.

Complexes **1** and **2** are soluble in common organic solvents and are stable both in solution and the solid state for a long

Scheme 1 Synthesis of **1** and **2**.

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[†] CCDC 886498 (**1**) and 886499 (**2**). For crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt31578e

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

Parameters	1 ·toluene	2 ·toluene
Empirical formula	C ₅₈ H ₆₆ MnN ₆ O ₄ Si ₂ , MnC ₅ O ₅ , C ₇ H ₈	C ₅₈ H ₆₆ N ₆ O ₄ ReSi ₂ , ReC ₅ O ₅ , C ₇ H ₈
Formula weight	1309.41	1571.93
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
Unit cell dimensions	<i>a</i> = 13.2094(3) Å <i>b</i> = 24.2295(5) Å <i>c</i> = 20.6981(5) Å β = 96.495(1)°	<i>a</i> = 13.3137(3) Å <i>b</i> = 24.3365(5) Å <i>c</i> = 20.8196(4) Å β = 95.935(1)°
Volume, <i>Z</i>	6582.1(3) Å ³ , 4	6709.6(2) Å ³ , 4
Density (calcd)	1.321 g cm ⁻³	1.556 g cm ⁻³
Absorption coefficient	3.966 mm ⁻¹	7.777 mm ⁻¹
<i>F</i> (000)	2744	3144
Crystal size	0.11 × 0.08 × 0.07 mm ³	0.09 × 0.07 × 0.04 mm ³
θ range for data collection	2.8 to 73.4°	2.8 to 73.5°
Limiting indices	−13 ≤ <i>h</i> ≤ 16, −30 ≤ <i>k</i> ≤ 30, −23 ≤ <i>l</i> ≤ 25	−16 ≤ <i>h</i> ≤ 15, −30 ≤ <i>k</i> ≤ 30, −25 ≤ <i>l</i> ≤ 25
Reflections collected	157 636	212 339
Independent reflections	11 793 (<i>R</i> _{int} = 0.059)	13 369 (<i>R</i> _{int} = 0.036)
Completeness to θ	99.1% (θ = 73.4°)	98.9% (θ = 73.5°)
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	13 133/77/825	13 369/78/825
Goodness-of-fit on <i>F</i> ²	1.054	1.241
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0479, <i>wR</i> ₂ = 0.1154	<i>R</i> ₁ = 0.0460, <i>wR</i> ₂ = 0.1413
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0539, <i>wR</i> ₂ = 0.1188	<i>R</i> ₁ = 0.0463, <i>wR</i> ₂ = 0.1415
Largest diff. peak and hole	0.556 and −0.517 e Å ⁻³	2.139 and −1.562 e Å ⁻³

period of time without any decomposition under an inert gas atmosphere. Complexes **1** and **2** were fully characterized by NMR spectroscopy, EI-MS spectrometry, elemental analysis and single crystal X-ray structural analysis.

Complex **1** shows a single resonance at δ 61.11 ppm in its ²⁹Si NMR spectrum which is downfield shifted compared to **L** (δ −20.5 ppm). This is similar to the trend observed for other silylene transition metal complexes.⁵ The *t*Bu protons show a broad singlet at δ 1.10 ppm for complex **1** in its ¹H NMR spectrum. The ¹³C NMR spectrum reveals the presence of carbonyl groups which resonate at 218.41 and 239.66 ppm. Moreover **1** displays its fragment ions for [L₂Mn(CO)₃]⁺, [L₂Mn(CO)]⁺ and [L₂Mn]⁺ in its mass spectrum at *m/z* 993, 937 and 909 respectively.

Complex **1** crystallizes in the monoclinic space group *P*2₁/*c* (Table 1). The molecular structure of **1** is shown in Fig. 1. In **1** both silicon atoms are tetra-coordinate and in a distorted tetrahedral geometry comprising three nitrogen atoms (two from the supporting amidinato ligand, one from the NPh₂ moiety) and one manganese atom. Two manganese atoms are present in the molecular structure, one atom as the central atom in the cation and the other in the anion. The manganese atom present in the cationic part is hexacoordinate (derived from two silicon and four carbon atoms of the carbonyl groups) and features a distorted octahedral geometry. The environment of manganese in the cationic part of the *trans* isomer [L₂Mn(CO)₄]⁺ is depicted in Fig. 1. The silylene ligands are located in *trans* positions and the Si2–Mn1–Si1 bond angle is 165.80(3)°. The Si–Mn bond distances in **1** are 2.3521(6) and 2.3571(7) Å, which are longer when compared with the average Si–Mn distance of 2.2802(8) Å in [(PhC(*Nt*Bu)₂SiCl)₂Mn(CO)₄]⁺[Mn(CO)₅][−].^{5b} The average manganese carbonyl bond length in the cation is 1.835(3) Å. The manganese atom present in the anion is pentacoordinate with a τ value of 0.48. The structural index τ defines the extent of deviation from trigonal bipyramidal to square pyramidal

Fig. 1 Cationic part of complex **1**. Selected bond lengths [Å] and angles [°]: Mn1–Si1 2.3521(7), Mn1–Si2 2.3571(7), Si1–N1 1.7370(19), Si2–N31 1.7376(19); Si1–Mn1–Si2 165.80(3), N2–Si1–N4 70.90(8), N32–Si2–N34 70.91(8).

geometry (τ = 1 for perfect trigonal bipyramidal; τ = 0 for perfect square based pyramidal).¹⁵ These Mn–CO bond lengths are quite comparable with those of the literature values.¹⁶ The average Si–N (from the NPh₂ moiety) bond length in **1** is 1.7373(19) Å and the bite angles (N–Si–N) are 70.90(8)° and 70.91(8)°.

Like in **1**, complex **2** shows a single resonance at δ 22.23 ppm in its ²⁹Si NMR spectrum. The *t*Bu protons for complex **2** in the ¹H NMR spectrum exhibit a singlet (δ 1.22 ppm). The ¹³C NMR spectrum of **2** shows carbonyl resonances at 193.11 and 219.60 ppm. Moreover complex **2** exhibits its fragment ions for [L₂Re(CO)₃]⁺, [L₂Re(CO)₂]⁺, [L₂Re(CO)]⁺ and [L₂Re]⁺ in its mass spectrum at *m/z* 1124, 1096, 1068 and 1040 respectively.

Fig. 2 Cationic part of complex **2**. Selected bond lengths [Å] and angles [°]: Re1–Si1 2.4816(17), Re1–Si2 2.4851(17), Si1–N1 1.732(6), Si2–N31 1.724(6); Si1–Re1–Si2 165.95(6), N2–Si1–N4 70.9(3), N32–Si2–N34 70.9(3).

Like **1**, complex **2** also crystallizes in the monoclinic space group $P2_1/c$ (Table 1) and its molecular structure is shown in Fig. 2. The molecular structure of **2** is isostructural to that of **1**. The silylene ligands are located in *trans* positions and the Si2–Re1–Si1 bond angle is 165.95(6)°. The Si–Re bond distances in **2** are 2.4816(17) and 2.4851(17) Å, which are comparable to the two Si–Re bond distances reported in $[(\text{PhC}(\text{NtBu})_2\text{SiCl})_3\text{Re}(\text{CO})_3]^+[\text{Re}(\text{CO})_5]^-$ (shorter one: 2.4384(18) and 2.4354(17) Å, and longer one: 2.4928(17) Å).^{5b} The average rhenium carbonyl bond length in the cation is 1.982(7) Å. The rhenium atom in the anionic part is pentacoordinate ($\tau = 0.34$). The data of the Re–CO bond lengths are comparable to the literature values.¹⁷ The average Si–N (from the NPh_2 moiety) bond length in **2** is 1.728(6) Å and the bite angles are in both cases 70.9(3)°.

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 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.^{13b} ^1H , ^{13}C and ^{29}Si NMR spectra were recorded with a Bruker Avance DRX 300, or a Bruker Avance DRX 500 spectrometer, using THF-d_8 as a solvent. Chemical shifts δ are given relative to SiMe_4 . The IR spectra were recorded on a Bio-Rad Digilab FTS7 spectrometer in the range of 4000–400 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.

Synthesis of 1

Toluene (60 mL) was added to a 100 mL Schlenk flask containing **L** (0.50 g, 1.17 mmol) and $\text{Mn}_2(\text{CO})_{10}$ (0.23 g, 0.59 mmol).

The reaction mixture was stirred at room temperature overnight. The solution was filtered and the solvent from the filtrate was reduced *in vacuo* to 20 mL and stored in a freezer at -27°C for 2 days to obtain pale yellow single crystals (0.62 g, 87%). For elemental analysis, **1**·toluene was treated under vacuum for six hours to remove the toluene molecules. Elemental analysis (%) calcd for $\text{C}_{63}\text{H}_{66}\text{Mn}_2\text{N}_6\text{O}_9\text{Si}_2$ (1217.28): C, 62.16; H, 5.46; N, 6.90. Found: C, 62.05; H, 5.41; N, 6.83. ^1H NMR (500 MHz, THF-d_8 , 25°C): δ 1.10 (s(br), 36H, $\text{C}(\text{CH}_3)_3$), 6.78–7.48 (br, *Ar*) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (125.75 MHz, THF-d_8 , 25°C): δ 31.12 $\text{C}(\text{CH}_3)_3$, 56.18 ($\text{C}(\text{CH}_3)_3$), 117.96, 120.64, 125.50, 127.36, 128.27, 128.38, 129.08, 129.25, 129.70, 130.57, 132.60, 141.53, 144.84, 149.10, 153.98 (*Ar*), 175.50 (NCN), 218.41 (CO), 239.66 (CO) ppm; $^{29}\text{Si}\{^1\text{H}\}$ NMR (99.36 MHz, THF-d_8 , 25°C): δ 61.11 ppm. FT-IR (Nujol, cm^{-1}): 2023 (s), 1999 (s), 1955 (sh), 1925 (br) (CO). EI-MS: m/z : 993 $[\text{L}_2\text{Mn}(\text{CO})_3]^+$, 937 $[\text{L}_2\text{Mn}(\text{CO})]^+$, 909 $[\text{L}_2\text{Mn}]^+$.

Synthesis of 2

Toluene (60 mL) was added to a 100 mL Schlenk flask containing **L** (0.28 g, 0.65 mmol) and $\text{Re}_2(\text{CO})_{10}$ (0.21 g, 0.32 mmol). The reaction mixture was stirred at room temperature overnight. The solution was filtered and the solvent from the filtrate was reduced *in vacuo* to 15 mL and stored in a freezer at -27°C overnight to obtain yellow colored single crystals (0.38 g, 79%). For elemental analysis, **2**·toluene was treated under vacuum for six hours to remove the toluene molecule. Elemental analysis (%) calcd for $\text{C}_{63}\text{H}_{66}\text{N}_6\text{O}_9\text{Re}_2\text{Si}_2$ (1479.82): C, 51.13; H, 4.50; N, 5.68. Found: C, 51.04; H, 4.42; N, 5.56. ^1H NMR (300 MHz, THF-d_8 , 25°C): δ 1.22 (s(br), 36H, $\text{C}(\text{CH}_3)_3$), 6.81–7.52 (br, *Ar*) ppm; $^{13}\text{C}\{^1\text{H}\}$ NMR (75.47 MHz, THF-d_8 , 25°C): δ 31.20 $\text{C}(\text{CH}_3)_3$, 55.84 $\text{C}(\text{CH}_3)_3$, 125.60, 127.10, 128.55, 128.71, 129.03, 129.36, 129.47, 129.54, 129.87, 130.28, 130.50, 130.57, 130.82, 132.46, 134.65, 149.17 (*Ar*), 175.82 (NCN), 193.11 (CO), 219.60 (CO) ppm; $^{29}\text{Si}\{^1\text{H}\}$ NMR (59.63 MHz, THF-d_8 , 25°C): δ 22.23(s) ppm. FT-IR (Nujol, cm^{-1}): 2075 (s), 2022 (s), 2008 (s), 1992 (s), 1957 (br), 1902 (br) (CO). EI-MS: m/z : 1124 $[\text{L}_2\text{Re}(\text{CO})_3]^+$, 1096 $[\text{L}_2\text{Re}(\text{CO})_2]^+$, 1068 $[\text{L}_2\text{Re}(\text{CO})]^+$, 1040 $[\text{L}_2\text{Re}]^+$.

Crystal structure determination

Suitable single crystals for X-ray structural analysis of **1** and **2** were obtained by storing their corresponding toluene solutions at -27°C and the crystals were taken out of the mother liquor under an argon atmosphere using NVH oil. The diffraction data were collected at 100 K on a Bruker three circle diffractometer equipped with a SMART 6000 CCD area detector and a $\text{CuK}\alpha$ rotating anode. Due to good crystal quality both datasets were collected to the edge of the Ewald sphere with high completeness and high multiplicity. The raw data were integrated with SAINT¹⁸ and an empirical absorption correction with SADABS¹⁹ 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).²⁰ SHELXLE²¹ was used as refinement GUI. All non-hydrogen-atoms were refined with anisotropic displacement parameters.

The rigid body restraint DELU was applied for carbon, nitrogen and oxygen atoms. Hydrogen atoms were constrained using suitable HFIX commands.

Conclusions

Like N-heterocyclic chlorosilylene $\text{PhC}(\text{NtBu})_2\text{SiCl}$, the functionalized silylene **L** can be also used as a ligand for the synthesis of silylene transition metal complexes. The reaction of **L** with $\text{Mn}_2(\text{CO})_{10}$ and $\text{Re}_2(\text{CO})_{10}$ forms complexes of composition $[\text{L}_2\text{Mn}(\text{CO})_4]^+[\text{Mn}(\text{CO})_5]^-$ (**1**) and $[\text{L}_2\text{Re}(\text{CO})_4]^+[\text{Re}(\text{CO})_5]^-$ (**2**). Due to the presence of the bulky NPh_2 moiety at the silycon(II) center, the reaction of **L** shows a different reactivity pattern with $\text{Re}_2(\text{CO})_{10}$ compared to that of $\text{PhC}(\text{NtBu})_2\text{SiCl}$.

Acknowledgements

We are thankful to the Deutsche Forschungsgemeinschaft for supporting this work. R. A. is thankful to the Alexander von Humboldt Stiftung for a research fellowship.

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