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The first metal complexes of bis(diisopropylamino)carbene: synthesis, structure and ligand properties[☆]

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Abstract

The synthesis of rhodium(I) and iridium(I) complexes of the bis(diisopropylamino)carbene is described for the first time. The formamidinium chloride and the free bis(diisopropylamino)carbene (L) were used as consecutive precursor compounds to form the metal complexes. Spectroscopic and, for LRh(cod)Cl, crystallographic data are presented for the complexes LRh(cod)Cl and LIr(cod)Cl (L = bis(diisopropylamino)carbene). The ligand properties of the acyclic bis(diisopropylamino)carbene are compared with imidazolin-2-ylidenes and imidazolidin-2-ylidenes as ligands in related rhodium(I) carbonyl complexes. Bis(diisopropylamino)carbene is the most basic known carbene ligand to date.

Keywords: *N*-Heterocyclic carbenes; Carbene complexes; Rhodium complexes; Iridium complexes

1. Introduction

The discovery of transition metal complexes of *N*-heterocyclic carbenes by Öfele [1] and Wanzlick and Schönherr [2] in 1968 and the isolation of stable free carbenes by Arduengo et al. in 1991 [3] were landmarks for a large number of applications in synthesis and catalysis [4]. For example, it has been shown that substitution of phosphane ligands by imidazolin-2-ylidene ligands can increase the activity of well-known catalyst systems [5]. The use of CC-saturated imidazolidin-2-ylidene ligands results in even higher catalytic activity in olefin metathesis, very likely due to the increased basicity of the ligand system [6]. The acyclic analogue bis(diisopropylamino)carbene published in 1996 by Alder et al. [7] is supposed to show an even higher proton affinity. Here we present the first complexes of this ligand. By comparison of these Rh(I) and Ir(I) complexes, the ligand properties of different carbenes were examined.

2. Synthesis and structure

2.1. Bis(diisopropylamino)carbene

The synthesis of the new metal complexes followed established procedures for the preparation of monocarbene complexes of Rh(I) and Ir(I) with imidazolin-2-ylidene ligands from the chloro-bridged dimer $[M(cod)Cl]_2$ [8,9] (Scheme 1).

The reaction of the complex $[Rh(cod)Cl]_2$ with free bis(diisopropylamino)carbene in THF yields the metal complex **1** as a yellow solid. The analogous reaction with $[Ir(cod)Cl]_2$ gave **2** as an orange solid. The pure compounds were obtained readily by washing with cold diethylether. Both compounds are soluble in polar organic solvents such as methylene chloride, chloroform and THF.

Alternatively, both complexes can be obtained by *in situ*-deprotonation of the formamidinium chloride. Substituting the chloro bridge in the precursor dimer by an ethoxy bridge, this internal base deprotonates the formamidinium chloride in situ, leading the reaction to the desired complexes **1** and **2**.

The reaction of an alcoholate adduct of the formamidinium salt **3** with the precursor dimer $[M(cod)Cl]_2$ is a third route to obtain complexes **1** and **2**. It is also possible to synthesize the mixed substituted carbene/

[☆] *N*-Heterocyclic carbenes, Part 28, for Part 27 see Ref. [1].

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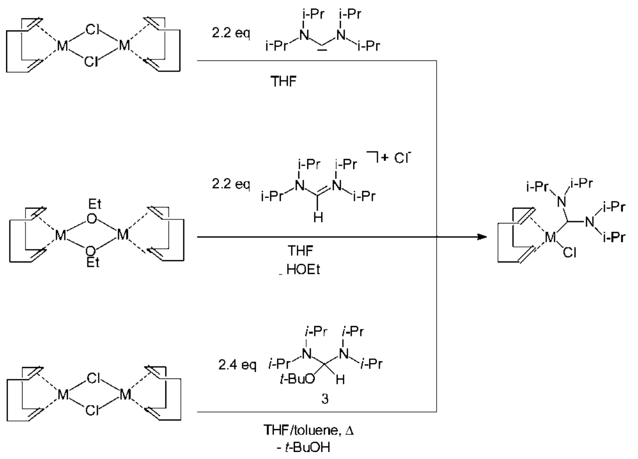


Scheme 1. Synthesis of **1** (M = Rh) and **2** (M = Ir).

phosphane ruthenium alkyidene systems with imidazolin-2-ylidene and imidazolidin-2-ylidene ligands in this way [5d,6]. The reaction of an alcoholate like K(O*t*-Bu) or Na(OMe) results in the formation of neutral adducts **3**. These preformed adducts **3** react with the chloro-bridged precursor [M(cod)Cl]$_2$ in THF/toluene at elevated temperature eliminating the corresponding alcohol and resulting in the complexes **1** or **2**.

The X-ray single crystal diffraction study of **1** (Fig. 1) and the spectroscopic data reveal the expected square-planar arrangement of the ligands. The angle between the NCN-plane and the coordination plane is 79°. The distance between rhodium and the carbene carbon in **1** is similar to that found in analogous rhodium complexes with CC-saturated heterocyclic (2.003 Å) [10] and CC-unsaturated heterocyclic carbene ligands (2.023 Å) [8]. The coordination of the COD-double bond *trans* to the carbene ligand is similar in **1** and the heterocyclic systems. The Rh–C$_{cod}$ distances in heterocyclic CC-saturated (2.205–2.227 Å) and CC-unsaturated (2.175–2.205 Å) systems are quite similar to those in **1**. The length of the *trans* C=C$_{cod}$ double bond is in the same range (1.354 Å in CC-saturated heterocyclic systems and 1.3682 Å in **1**) (Table 1).

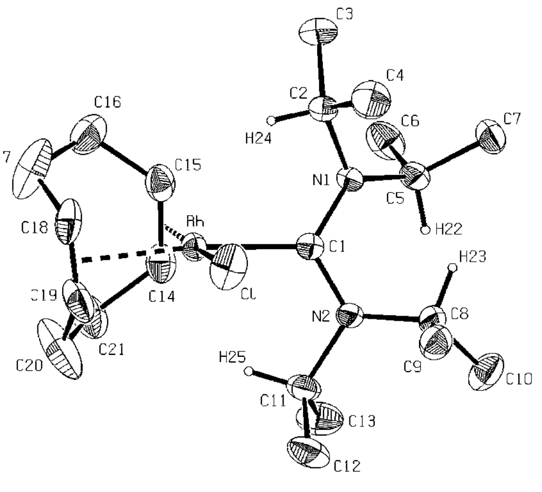
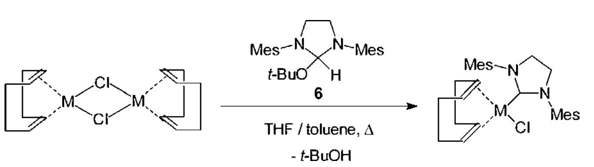


Fig. 1. PLATON plot of the solid state structure of the rhodium complex **1** [21]. Thermal ellipsoids were drawn at the 50% probability level; except for H22 and H25 all hydrogen atoms are omitted for clarity.

Table 1
Selected bond lengths (Å) and bond angles (°)

Bond lengths			
Rh–Cl	2.3790(6)	Rh–C14	2.120(2)
Rh–C1	2.041(2)	Rh–C15	2.108(2)
Rh–C18	2.247(2)	N1–C1	1.362(3)
Rh–C19	2.203(2)	N2–C1	1.358(3)
Bond angles			
C1–Rh–Cl	89.33(6)	N2–C1–N1	117.99(18)



Scheme 2. Synthesis of **4** (M = Rh) and **5** (M = Ir).

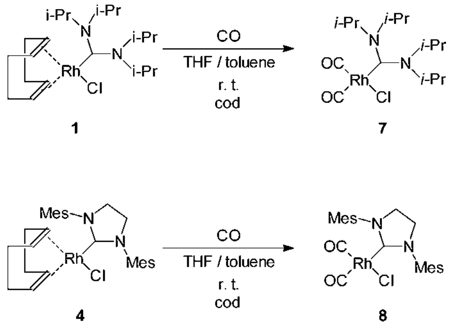
In the ^{13}C-NMR of the characterized mono(carbene)chloro complexes the signal for the carbene carbon is at $\delta = 211.9$ ($J_{C-Rh} = 47$ Hz) for a CC-saturated NHC system [10], $\delta = 195.9$ ($J_{C-Rh} = 50$ Hz) for a benzimidazolin system [11] and at $\delta = 182.6$ ($J_{C-Rh} = 51$ Hz) for an CC-unsaturated NHC system, the corresponding resonance for **1** occurs at $\delta = 233.79$ ($J_{C-Rh} = 67.8$ Hz). In the ^{13}C-NMR spectrum of **2**, the carbene C signal is at $\delta = 225.1$. This downfield shift is probably due to the increasing σ-donor abilities and Brønsted basicity of the carbene ligands

Even though the free bis(diisopropylamino)carbene is much less stable than the heterocyclic analogues the stability of the complexes **1** and **2** to air and moisture is similar to the complexes with *N*-heterocyclic carbene ligands.

2.2. *Dimesitylimidazolin-2-ylidene*

Complexes **4** and **5** were synthesized by reacting the alcoholate adduct of the corresponding imidazolidinium chloride **6** with the chloro bridged Rh and Ir-precursor [M(cod)Cl]$_2$, respectively (Scheme 2).

The reaction of the Rh(I)-complex [Rh(cod)Cl]$_2$ with the *tert*-butanolate adduct of *N*,*N*-dimesityl-imidazolinium chloride **6** in THF/toluene yields the metal complex **4** as a yellow solid. The analogous reaction with the iridium complex [Ir(cod)Cl]$_2$ gives **5** as a light orange solid. As mentioned above the pure compounds **4** and **5** were obtained by washing the crude products with cold diethylether. In the ^{13}C-NMR of **4** the signal for the carbene C is at $\delta = 212.1$ ($J_{C-Rh} = 48.1$ Hz). The corresponding resonance for **5** occurs at $\delta = 207.0$.



Scheme 3. Synthesis of **7** and **8**.

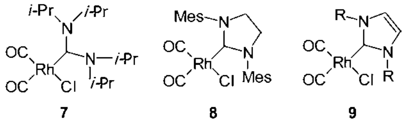


Fig. 2. Comparison of complexes **7** and **8** with known mono(carbene)bis(carbonyl)chloro complexes **9** [8].

Table 2
Carbonyl stretching frequencies in IR for mono(carbene)-bis(carbonyl)chloro complexes **7**–**9** [8]

Compound	ν(CO) I (cm^{-1})	ν(CO) II (cm^{-1})
7	2057	1984
8	2081	1996
9	2076	2006

3. Discussion

The pronounced basicity of *N*-heterocyclic carbene ligands is well documented. For example, 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene shows a pK_a value of 24 in DMSO-d_6 and is therefore one of the strongest neutral bases known [12]. A simple way to evaluate the basicity of a carbene ligand is to compare the IR data of carbon monoxide ligands in corresponding carbene(carbonyl) complexes. The wavenumber of the CO-stretching frequencies is directly proportional to the back-donation from the metal center. A very basic ligand should result in a relatively low wavenumber inducted by a strong σ-donation of the carbon atom to the metal and little π-back-donation from the metal center to the ligand. In order to examine the ligand properties of the bis(diisopropylamino)carbene, dicarbonyl complexes **7** and **8** were synthesized (Scheme 3).

The rhodium complexes **7** and **8** were obtained by passing carbon monoxide through a solution of complexes **1** and **4** in toluene/THF at room temperature, respectively (Scheme 3). The products **7** and **8** were formed within minutes as air and moisture sensitive pale brown solids. Due to the strong donor capability of the carbene ligands the cyclooctadiene ligand can be totally substituted by the stronger acceptor ligand, carbon monoxide [8]. This is proven by IR and NMR studies.

Compared with IR data for the known mono(carbene)(dicarbonyl)chloro complexes (Fig. 2), complexes **7** and **8** show stronger backdonation from the metal center than the unsaturated analogues ($\nu(CO) = 2056$ and 1984 cm^{-1}) (Table 2).

This result demonstrates that the acyclic bis(diisopropylamino)carbene ligand and the CC-saturated dimesitylimidazolidin-2-ylidene induce higher electron density at the metal atom than the CC-unsaturated *N*,*N*-di-(*R*)-imidazolin-2-ylidenes. Especially the acyclic carbene ligand is the most basic known carbene ligand to date. Further work is in progress.

4. Experimental

4.1. General comments

All reactions were performed by standard Schlenk techniques in an oxygen free Ar or nitrogen atmosphere. Solvents were dried by standard methods and distilled under nitrogen. Infrared spectra were recorded in a Perkin–Elmer 1600 series FT-IR spectrometer, and the ^{1}H- and ^{13}C-NMR spectra at 400 and 100.54 MHz, respectively, in a FT JEOL GX 400 instrument. Elemental analyses were performed in the microanalytical laboratory of the TU München. Mass spectra were obtained with Finnigan MAT 311A and MAT 90 spectrometers. Bis[μ-chloro(1,5-cyclooctadiene)-rhodium(I)] and bis[μ-chloro(1,5-cyclooctadiene)-iridium(I)] were prepared as reported in Ref. [13]. Bis(diisopropylamino)formamidinium chloride and the corresponding bis(diisopropylamino)carbene were prepared as reported in Ref. [7], 1,3-dimesitylimidazolidinium chloride was prepared as reported in Ref. [14].

4.2. Chloro(η^4-1,5-cyclooctadiene)-(bis(diisopropylaminocarbene)rhodium(I) (**1**)

4.2.1. Synthesis via free bis(diisopropylamino)carbene

A solution of bis(diisopropylamino)carbene prepared according to Ref. [7] (340 mg, 1.71 mmol, 2.0 equivalents) in THF (20 ml) was added dropwise to a stirred solution of bis[μ-chloro(1,5-cyclooctadiene)-rhodium(I)] (421 mg, 0.85 mmol, 1.0 equivalent) in THF (40 ml). Immediately a color change was observed from light to dark yellow. After stirring the reaction mixture for 30 min at room temperature, the solvent was removed in vacuo. The precipitate was washed with ice cold Et_2O (2 × 10 ml) and dried in vacuo. The compound is most soluble in $CHCl_3$, CH_2Cl_2 and THF and less soluble in Et_2O, *n*-pentane and *n*-hexane.

Yield: 533 mg, 1.21 mmol, 71%. ^{1}H-NMR (400 MHz, $CDCl_3$, 20 °C): $\delta = 5.16$ (2H, cod_{vinyl}), 4.73 (1H, cod_{vinyl}), 4.09 (4H, NCH), 3.09 (1H, cod_{vinyl}), 2.35 (4H, cod_{allyl}), 1.74–1.17 (m, 28H, cod_{allyl}, CH_3). $^{13}C\{^1H\}$-NMR (100.1 MHz, $CDCl_3$, 20 °C): $\delta = 233.6$ (NCN, d, $^1J(C–Rh) = 67.8$ Hz), 97.5, 67.3, 32.5, 30.9, 28.6 (cod), 56.4 (NCH), 23.8 (CH_3). CIMS; m/z: 458 ([M^+], correct isotope pattern), 423 (M − Cl, correct isotope pattern), 314 (M − Cl − cod, correct isotope pattern). Elemental analysis: Calc. for $C_{21}H_{40}ClN_2Rh$ (458.92): C, 54.96; H, 8.78; N, 6.10. Found: C, 54.90; H, 8.81; N, 6.17%.

4.2.2. Synthesis via in situ deprotonation

A 1 M solution of sodiumethanolate (2.48 ml) was added dropwise to a stirred suspension of bis[μ-chloro(1,5-cyclooctadiene)-rhodium(I)] (300 mg, 0.61 mmol, 1.0 equivalent) in EtOH (30 ml). Within 5 min a color change from yellow to lemon yellow was observed due to the formation of bis[μ-ethoxy(1,5-cyclooctadiene)-rhodium(I)]. After stirring the reaction mixture for another 10 min at r.t. bis(diisopropyl)formamidinium chloride (400 mg, 1.22 mmol, 2.0 equivalents) was added. Again a color change to dark yellow was observed. The reaction mixture was stirred for another 30 min at r.t. After removing the volatiles in vacuo the crude product was washed with ice cold Et_2O (2 × 10 ml) and dried in vacuo.

Yield: 531 mg, 1.16 mmol, 68%.

4.2.3. Synthesis via alcoholate adduct

A solution of KO*t*-Bu (191 mg, 1.70 mmol, 2.8 equivalents) in THF (20 ml) was added dropwise to a stirred suspension of bis(diisopropyl)formamidinium chloride (280 mg, 1.70 mmol, 2.8 equivalents) in THF (30 ml) at r.t. The formamidinium chloride was slowly solved and the color of the reaction mixture turned to light yellow. After stirring the mixture for 30 min at r.t., bis[μ-chloro(1,5-cyclooctadiene)-rhodium(I)] (300 mg, 0.61 mmol, 1.0 equivalent) and toluene (30 ml) were added. The reaction mixture was stirred at 80 °C for 1 h. After removing the volatiles in vacuo the product was extracted with hexane (60 ml) and dried in vacuo.

Yield: 570 mg, 1.24 mmol, 73%.

4.3. Chloro(η^4-1,5-cyclooctadiene)-(bisdiisopropylaminocarbene)iridium(I) (**2**)

4.3.1. Synthesis via free bis(diisopropylamino)carbene

Following the procedure outlined in Section 4.2.1, the reaction of bis[μ-chloro(1,5-cyclooctadiene)-iridium(I)] (340 mg, 1.00 mmol, 1.0 equivalent) and bis(diisopropylamino)carbene, prepared as described in Ref. [7] (200 mg, 1.00 mmol, 2.0 equivalents) gave complex **2.**

Yield: 746 mg, 1.36 mmol, 68%. ^{1}H-NMR (400 MHz, $CDCl_3$, 20 °C): $\delta = 5.13$ (2 H, cod_{vinyl}), 4.73 (2H, cod_{vinyl}), 3.85 (4H, NCH), 2.95 (4H, cod_{allyl}), 2.11 (m, 4H, cod_{allyl}), 1.58–1.17 (m, 24H, CH_3). $^{13}C\{^1H\}$-NMR (100.1 MHz, $CDCl_3$, 20 °C): $\delta = 225.6$ (NCN), 82.1, 67.9, 33.2, 31.9, 29.2 (cod), 51.1 (NCH), 23.8 (CH_3). CIMS; m/z: 548 ([M^+], correct isotope pattern). Elemental analysis: Calc. for $C_{21}H_{40}ClN_2Ir$ (548.23): C, 46.01; H, 7.35; N, 5.11. Found: C, 46.09; H, 7.41; N, 5.07%.

4.3.2. Synthesis via in situ deprotonation

Following the procedure in Section 4.2.2, the reaction of bis[μ-chloro(1,5-cyclooctadiene)-iridium(I)] (333 mg, 0.61 mmol, 1.0 equivalent), 1 M sodiumethanolate solution (2.48 ml), and bis(diisopropyl)formamidinium chloride (400 mg, 1.22 mmol, 2.0 equivalents) gave complex **2**.

Yield: 778 mg, 1.42 mmol, 71%.

4.3.3. Synthesis via alcoholate adduct

Following procedure in Section 4.2.3, the reaction of bis[μ-chloro(1,5-cyclooctadiene)-iridium(I)] (333 mg, 0.61 mmol, 1.0 equivalent), KO*t*-Bu (191 mg, 1.70 mmol, 2.8 equivalents) and bis(diisopropyl)formamidinium chloride (280 mg, 1.70 mmol, 2.8 equivalents) gave complex **2**.

Yield: 723 mg, 1.32 mmol, 66%.

4.4. Chloro(η^4-1,5-cyclooctadiene)-(1,3-dimesitylimidazolidin-2-ylidene)rhodium(I) (**4**)

A solution of KO*t*-Bu (314 mg, 2.80 mmol, 2.8 equivalents) in THF (20 ml) was added dropwise to a stirred suspension of 1,3-dimesitylimidazolidinium chloride (956 mg, 2.80 mmol, 2.8 equivalents) in THF (50 ml) at r.t. The 1,3-dimesitylimidazolidinium chloride was slowly dissolved and the color of the reaction mixture turned to light yellow. After stirring the mixture for 30 min at r.t., bis[μ-chloro(1,5-cyclooctadiene)rhodium(I)] (493 mg, 1.00 mmol, 1.0 equivalent) and toluene (30 ml) were added. The reaction mixture was stirred at 80 °C for 1 h. After removing the volatiles in vacuo the product was extracted with hexane (30 ml) and dried in vacuo.

Yield: 822 mg, 1.46 mmol, 73%. ^{1}H-NMR (400 MHz, $CDCl_3$, 20 °C): $\delta = 7.86$ (4 H, NCH_2CH_2N), 6.85 (4H, s, Mes–H), 4.31 (2 H, cod_{vinyl}), 3.76 (2H, cod_{vinyl}), 3.28 (4H, cod_{allyl}), 2.41–1.63 (m, 22H, cod_{allyl}, CH_3). $^{13}C\{^1H\}$-NMR (100.1 MHz, $CDCl_3$, 20 °C): $\delta = 212.0$ (d, $^1J(C–Rh) = 48.1$ Hz, NCN), 137.6 (*p*-C), 136.9 (*o*-C), 135.9 (R_2NC), 134.6 (*m*-C), 129.2 (NCH_2), 127.8 (NCH_2), 96.2, 99.9, 66.8, 32.0, 30.2, 27.5 (cod), 19.3 (*o*-CH_3), 17.7 (*p*-CH_3). CIMS; m/z: 563 ([M^+], correct isotope pattern). Elemental analysis: Calc. for

$C_{29}H_{48}ClN_2Rh$ (563.07): C, 61.86; H, 8.59; N, 4.97. Found: C, 61.79; H, 8.63; N, 5.02%.

4.5. Chloro(η^4-1,5-cyclooctadiene)-(1,3-dimesitylimidazolidin-2-ylidene)iridium(I) (**5**)

Following procedure in Section 4.4, the reaction between bis[μ-chloro(1,5-cyclooctadiene)-iridium(1)] (300 mg, 0.45 mmol, 1.0 equivalent), KO*t*-Bu (141 mg, 1.26 mmol, 2.8 equivalents) and 1,3-dimesitylimidazolidinium chloride (432.05 mg, 1.26 mmol, 2.8 equivalents) gave complex **5**.

Yield: 398 mg, 0.621 mmol, 69%. ^{1}H-NMR (400 MHz, $CDCl_3$, 20 °C): $\delta = 7.56$ (4H, NCH_2CH_2N), 7.26 (4H, s, Mes–H), 4.38 (4H, cod_{vinyl}), 4.20 (4H, cod_{allyl}), 3.42 (4H, cod_{allyl}), 2.84 (4H, cod_{allyl}), 2.66–2.50 (18H, CH_3). $^{13}C\{^1H\}$-NMR (100.1 MHz, $CDCl_3$, 20 °C): $\delta = 207.0$ (NCN), 137.8 (*p*-C), 137.5 (*o*-C), 135.1 (R_2NC), 135.0 (*m*-C), 129.6 (NCH_2), 83.73, 67.8, 33.2, 28.5 (cod), 20.2 (*o*-CH_3), 19.7 (*p*-CH_3). CIMS; m/z: 642 ([M^+], correct isotope pattern), 607 (M − Cl, correct isotope pattern), 496 (M − Cl − cod, correct isotope pattern). Elemental analysis: Calc. for $C_{29}H_{48}ClN_2Ir$ (642.39): C, 53.40; H, 7.42; N, 4.29. Found: C, 53.33; H, 7.48; N, 4.33%.

4.6. Dicarbonylchloro(bis(diisopropylamino)carbene)-rhodium(I) (**7**)

Carbon monoxide was bubbled (30 min) through a yellow solution of chloro(η^4-1,5-cyclooctadiene)(bis-(diisopropylaminocarbene)rhodium(I) (**1**) (300 mg, 0.65 mmol) in a 1:1 mixture of THF and toluene (35 ml). After the color had changed to pale brown, the solvent was removed in vacuo and the crude product was washed with *n*-pentane (2 × 5 ml). The compound is soluble in $CHCl_3$, CH_2Cl_2, toluene and THF and not so soluble in Et_2O and *n*-pentane.

Yield: 180 mg, 0.442 mmol, 68%. ^{1}H-NMR (400 MHz, $CDCl_3$, 20 °C): $\delta = 4.11$ (4H, NCH), 1.36 (24H, CH_3). $^{13}C\{^1H\}$-NMR (100.1 MHz, $CDCl_3$, 20 °C): $\delta =$ 221.7 (NCN, d, ^1J(C–Rh) = 64 Hz), 186.9 (CO, d, ^1J(C–Rh) = 74 Hz), 56.1 (NCH), 23.5 (CH_3). CIMS; m/z: 406 ([M^+], correct isotope pattern). IR (KBr, cm^{-1}): ν 2056 (s, CO), 1985 (s, CO). Elemental analysis: Calc. for $C_{15}H_{28}ClN_2O_2Rh$ (406.76): C, 44.29; H, 6.93; N, 6.88. Found: C, 44.32; H, 6.89; N, 6.91%.

4.7. Dicarbonylchloro(1,3-dimesitylimidazolidin-2-ylidene)rhodium(I) (**8**)

Following procedure in Section 4.6, the reaction of chloro(η^4 - 1,5 - cyclooctadiene)(1,3 - dimesitylimidazolidin-2-ylidene)rhodium(I) (**4**) (330 mg, 0.59 mmol) and carbon monoxide gives complex **8**.

Yield: 230 mg, 0.46 mmol, 78%. ^{1}H-NMR (400 MHz, $CDCl_3$, 20 °C): $\delta = 7.24$ (4H, NCH_2CH_2N), 6.99 (4H, s, Mes–H), 2.40 (s, 18H, CH_3). $^{13}C\{^1H\}$-NMR (100.1 MHz, $CDCl_3$, 20 °C): $\delta = 205.7$ (NCN, d, ^1J(C–Rh) = 41 Hz), 185.2 (CO), 183.4 (CO), 138.5 (*p*-C), 136.2 (*o*-C), 135.6 (R_2NC), 134.9 (*m*-C), 129.5 (NCH_2), 21.1 (*o*-CH_3), 20.9 (*p*-CH_3). CIMS; m/z: 500 ([M^+], correct isotope pattern). IR (KBr, cm^{-1}): ν 2081 (s, CO), 1997 (vs, CO). Elemental analysis: Calc. for $C_{23}H_{26}ClN_2O_2Rh$ (500.83): C, 55.16; H, 5.23; N, 5.59. Found: C, 55.21; H, 5.19; N, 5.52%.

4.8. X-ray crystal structure determination of **1**

Suitable single crystals for the X-ray diffraction study were grown by standard techniques from a saturated solution of **1** in THF at 25 °C. Crystal color, shape, and size were yellow, plate, and 0.58 × 0.41 × 0.18 mm, respectively. X-ray data were collected on a Kappa-CCD area detecting diffraction system from Nonius equipped with a rotating anode (Nonius FR591) and Mo–K_α radiation using both φ- and ω-scans with $\Delta\varphi = \Delta\omega = 1°$ [15]. The unit cell was determined from 35 734 reflections. The intensities were first corrected for beam inhomogeneity, crystal decay, Lorentz and polarization effects and anomalous dispersion by the program SCALEPACK [16] using a tight scale restraint (0.002). An empirical absorption correction was then applied ($T_{min} = 0.6312$, $T_{max} = 0.8586$) and symmetry equivalent and multiply measured reflections were averaged with the program SORTAV [17]. A total of 35 734 reflections was collected at a detector distance of 40 mm [$4.0 < 2\Theta < 52.8$; h (−12/13), k (−17/19), l (−35/34)] and merged [$R_{int}(F_o^2) = 0.030$] to give 4585 unique reflections [3760 observed reflections with $I > 2\sigma(I)$]. The structure was solved by a combination of direct methods (SIR92 [18]) and difference-Fourier syntheses (SHELXL-97 [19]). Full-matrix least-squares refinements were carried out by minimizing $\Sigma w(F_o^2 - F_c^2)^2$ with SHELXL-97 weighting scheme and stopped at shift/error < 0.001. The non-hydrogen atoms of the asymmetric unit were refined anisotropically. Except H22–H25 all hydrogen atoms were placed in calculated positions and included in the structure factor calculations but not refined. H22–H25 were found in the difference map and refined isotropically. Scattering factors and anomalous dispersion corrections were taken from Ref. [20]. All calculations were performed on a Linux-PC. A summary of the crystal and experimental data is reported in Table 3.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic

Table 3
Crystal data and structure refinement parameters for complex **1**

Empirical formula	$C_{21}H_{40}ClN_2Rh$
Formula weight	458.91
Crystal system	Orthorhombic
Space group	*Pbca* (No. 61)
Unit cell dimensions	
a (Å)	10.6176(1)
b (Å)	15.2100(2)
c (Å)	28.2000(3)
V (Å^3)	4554.12(9)
Z	8
ρ_{calc} (g cm^{-3})	1.339
Radiation; λ (Å)	Mo–K$_\alpha$; 0.71073
F(000)	1936
μ (mm^{-1})	0.874
T (K)	183(1)
Number of independent reflections ($I>2\sigma(I)$; all data)	3760; 4585
Number of variables	242
R_1 [a] ($I>2\sigma(I)$; all data)	0.0281; 0.0377
wR_2 [b]($I>2\sigma(I)$; all data)	0.0693; 0.0722
Goodness-of-fit (GOF) [c]	1.047
$\Delta/\rho_{min;\ max}$ (e Å^{-3})	−0.617; 0.852

[a] $R_1=\Sigma(||F_o|-|F_c||)/\Sigma|F_o|$.

[b] $wR_2=[\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w=1/[\sigma^2(F_o^2)+(0.0000P)^2+2.2351P]$ where $P=(F_o^2+2F_c^2)/3$.

[c] $GOF=[\Sigma w(F_o^2-F_c^2)^2/(n_{data}-n_{variables})]^{1/2}$.

Data Centre, CCDC No. 178636 for **1**. Copies of this onformation may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-366-033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.ukl).

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