N-Heterocyclic Carbenes[+]: Generation under Mild Conditions and Formation of Group 8–10 Transition Metal Complexes Relevant to Catalysis**

Wolfgang A. Herrmann,* Martina Elison, Jakob Fischer, Christian Köcher and Georg R. J. Artus

Dedicated to Professor Max Herberhold on the occasion of his 60th birthday

Abstract: Stable mono- and dicarbene adducts of late transition metals are readily accessible either by reaction of imidazolium salts with metal complexes bearing basic ligands, or by the cleavage of chloro- and acetato-bridged dinuclear metal complexes with the free carbenes (e.g., 1,3-dimethylimidazoline-2-ylidene). A general novel method for the deprotonation of N-substituted azolium salts in liquid ammonia—the liquid ammonia route—is described. This method yields not only the known free monomeric 1,3-dimethylimidazoline-2-ylidene in quantitative yield, but also otherwise hardly accessible derivatives. For example, imidazoline-2-ylidenes with linear, branched, cyclic, heteroatom-substituted and even chiral hydrocarbon residues can be obtained. The nucleophilic behaviour of 1,3-dimethylimidazoline-2-ylidene is reported and compared with that of other donor ligands. Novel carbene complexes of $\mathrm{Ru^{II}}$, $\mathrm{Rh^{I}}$, $\mathrm{Pd^{II}}$, $\mathrm{Os^{II}}$ and $\mathrm{Ir^{I}}$ are presented. Reaction of the potentially chelating ligand 1,1′-(1,2-ethylene)-3,3′-dimethyldiimidazoline-2,2′-diylidene with $[(\mathrm{COD})\mathrm{RhCl}]_2$ yields a dinuclear complex, in which two rhodium centres are linked by the dicarbene bridge. Four single-crystal X-ray diffraction structures of *new* metal–carbene complexes (Rh, Os) are reported. N-Heterocyclic carbene complexes of Group 8–10 transition metals are both thermally and chemically very stable. They do not show the typical reactivity of metal–carbon double bonds. For a number of reasons, these complexes must be regarded as donor adducts of the Lewis-*basic* imidazoline-2-ylidene ligand and the Lewis-*acidic* organometallic fragment.

Keywords
chelate ligands · intermolecular interactions · reductions · ruthenium complexes · semiconductors

Introduction

The discovery of metal carbenes by Fischer and Maasböl in 1964[1] revolutionized organometallic chemistry and has led to a huge number of applications in synthesis and catalysis.[2] For example, in olefin metathesis and the cyclopropanation of olefins, both of which are employed in industry, metal carbenes are involved as the reactive intermediates.[3]

One class of metal carbenes has long remained in the shadow of this development: as early as 1968 Wanzlick and Öfele reported that heterocyclic carbenes derived from imidazolium and pyrazolium salts form extraordinarily stable complexes with certain transition metals. The syntheses of the mercury complex **A** and chromium complex **B** are landmarks in this discovery (Scheme 1).[4, 5]

In the complexation reactions of imidazolium salts with, for example, mercury acetate or the nucleophilic carbonylchromate $[\mathrm{Cr(CO)_5H}]^-$, Wanzlick and Öfele made use of the acidic proton in the precursor ligands. It was Wanzlick who first attempted to use strong bases, such as potassium *tert*-butoxide, in the synthesis of metal–carbene complexes,[4] but he did not isolate the free carbene. In 1991 Arduengo et al. were the first to report remarkably stable free carbenes.[6] They have been used to prepare metal complexes ever since.[7]

In our research group it has been shown that the standard imidazoline-2-ylidene ligand, 1,3-dimethylimidazoline-2-ylidene, coordinates to transition metals of low and high oxidation states,[7a, 8] such as zerovalent iron (reaction with pentacarbonyl iron), tetravalent titanium and heptavalent rhenium. Furthermore, the extraordinarily small beryllium cation $\mathrm{Be^{2+}}$ forms the ionic complex **C** (Scheme 1) upon treatment of beryllium dichloride with an excess of free carbene.[8b] This example shows that the strictly planar, five-membered cyclic carbenes are not very sterically demanding, in contrast to the bulky phosphines commonly exploited in coordination chemistry and homogeneous catalysis.[9a]

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[**] Heterocyclic Carbenes, Part 5. Part 4: see ref. [20].

[+] Carbenes may be defined as "divalent" carbon compounds. More precisely, the carbene carbon is linked to two adjacent groups by covalent bonds and possesses two nonbonding electrons, which may have antiparallel spins (singlet state) or parallel spins (triplet state). In other compounds with formally "divalent" carbons (e.g., carbon monoxide, isocyanides), resonance stabilization of the "divalent" carbon by neighbouring groups is extremely strong. The term carbene, conceived by Doering, Winstein and Woodward, seems well suited to describe the class of compounds under discussion, but the carbene nomenclature conflicts with established rules of the International Union of Pure and Applied Chemistry (IUPAC). The nomenclature for metal–carbene complexes was introduced by E. O. Fischer [2a–d] and became common in the organometallic literature.

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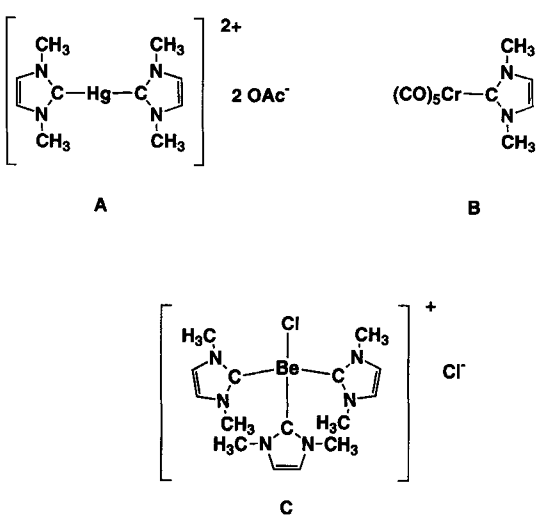


Scheme 1. The mercury (Wanzlick [4]), chromium (Öfele [5]) and berylium (Herrmann [8 b]) complexes of heterocyclic carbenes.

It is now generally accepted that π-backbonding is of litte or no importance in the coordination chemistry of N-heterocyclic carbene ligands. The oxidation state of the metal does not seem to influence the stability of the metal–carbene bond to any great extent, although the carbene complexes with Group 8–10 transition metals described in this paper are more stable than those with metals of oxidation states IV–VII reported earlier. The recent discovery that the former class of complex can catalyse a number of homogenous reactions, such as C–C coupling reactions,[9a–d] means that this chemistry might be expected to have a great impact on future synthetic methods.

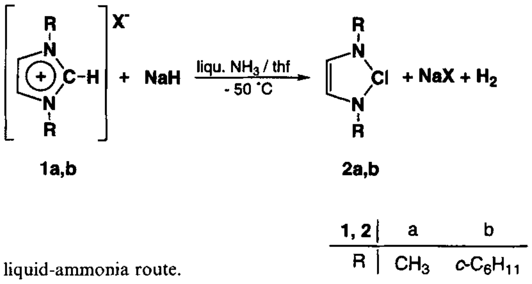
The present paper reports a number of new complexes of Group 8–10 transition metals with carbenes derived from imidazolium salts. We also describe a new general method of generating the free carbenes under mild conditions.

Results and Discussion

1. Ligand synthesis—the liquid-ammonia route: Imidazolium salts are readily available from inexpensive starting materials (e.g., imidazole). According to Arduengo et al., the free carbenes can be generated from the ionic imidazolium precursors by treatment with sodium hydride/potassium *tert*-butylate at ambient temperatures in THF.[6] This procedure is only satisfactory for carbenes that are relatively thermally robust and can survive rather prolonged reaction times (normally 3–4 h). Kuhn et al. described an alternative access to 1,3-dialkylimidazoline-2-ylidenes by desulfurization of the corresponding cyclic thiourea derivatives, which are readily available.[10] However, this technique also has its drawbacks: 24 hours in refluxing THF are required for the carbene to be formed in sufficient yields. This excludes the preparation of heat-sensitive carbenes.

We therefore set ourselves the task of finding a more general route for the synthesis of carbenes, and we were successful in developing the "liquid-ammonia route": an azolium salt is dissolved or suspended in a mixture (ca. 5:1) of liquid ammonia and a polar, aprotic solvent (typically THF) and is then treated with sodium hydride. Depending on the solvent, the deprotonation reaction occurs between −80 and −30 °C. The deprotonating agent is sodium hydride or sodium amide (formed by solvolysis).

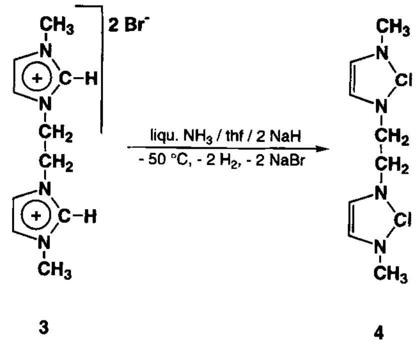
In a typical procedure (Scheme 2), a 1,3-dialkylimidazolium halide (e.g., 1,3-dimethylimidazolium iodide (**1a**), 1,3-dicyclohexylimidazolium chloride (**1b**) or 1,1′-(1,2-ethylene)-3,3′-dimethyldiimidazolium dibromide (**3**)) is deprotonated in liquid ammonia/THF by sodium hydride at about −30 °C. The reaction goes to completion within *minutes*. The generated carbenes are completely soluble in ammonia/THF, whereas the solubility of the carbenes in pure THF is limited at very low temperatures. The *free* monomeric carbene of high purity is thus obtained as a *colourless* solution in ammonia/THF or in THF after removal of the ammonia by freeze–pump techniques. The sodium halide formed during the generation of the free carbene is removed by extracting the carbene with nonpolar solvents such as hexene and filtration. Yields of greater than 95% are typically obtained.



Scheme 2. The liquid-ammonia route.

The key advantage of the liquid-ammonia route is that the deprotonation proceeds rapidly and smoothly at low temperatures. Ammonia seems to have an activating effect on the acidic proton of the azolium salt. Temperatures can be kept below −30 °C throughout the procedure. Furthermore, imidazolium salts are much more soluble in mixtures containing liquid ammonia than in pure aprotic organic solvents. This is of particular importance in the synthesis of carbenes derived from imidazolium salts.

2. The first free N-heterocyclic dicarbene generated by the liquid ammonia route: Öfele et al. showed that bridged dicarbenes derived from N-heterocycles can act as chelating ligands with transition metals.[11] However, we were the first group to synthesize a free dicarbene: **4** was obtained in over 95% yield by our new liquid-ammonia route (Scheme 3). Low yields are obtained with potassium *tert*-butylate in anhydrous THF *without* liquid ammonia at −40/ − 20 °C. The free carbene **4** is sensitive to temperature and moisture. The identity of the *free* monomeric dicarbene was established by means of its NMR spectra (and by the formation of complex **15**): in the ^{13}C NMR spectrum (THF/[D$_8$]THF, 20 °C, singlet in the off-resonance decoupled spectrum), the resonance of the carbene carbon at $\delta = 216$ is typical of a free carbene; the *C*H resonance of the corresponding imidazolium salt is at $\delta = 137$ ($CDCl_3$, 20 °C).

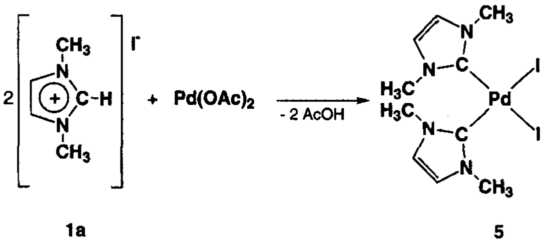


Scheme 3. Synthesis of the free dicarbene **4**.

3. Scope of the liquid-ammonia route—functionalized carbenes and other N-heterocyclic carbenes: The liquid-ammonia route is not restricted to imidazolium salts. Carbenes derived from other azolium salts can be generated, and there is no reason to assume that other CH-acidic heterocycles will not react in the same way. Numerous new carbenes have been generated according to Schemes 2 and 3, normally in quantitative yields. In most cases, in addition to isolation of the free carbenes, we were aiming at the synthesis of their metal complexes. Furthermore, carbene complexes with functionalized side chains (e.g., with O-, N- or P-heteroatoms) and chiral, water-soluble and polymer-supported carbenes have been prepared. These carbenes, and the properties and applications of their complexes will be the subject of another paper.[12]

4. Metal complexes: The carbene complexes described below all derive from the free ligand 1,3-dimethylimidazoline-2-ylidene (**2a**) or its azolium precursor **1a**, or from the free dicarbene (**4**).

Palladium: Imidazolium salt **1a** reacted with palladium(II) acetate in refluxing THF to yield the palladium carbene complex **5** in greater than 70% yield (Scheme 4). Yellow needles of **5** separated from the THF solution when it was cooled to 20 °C. Alternatively, the imidazolium salt and palladium(II) acetate were heated *without solvent* in vacuo at about 140 °C; the success of this reaction shows the high thermostability of the resulting carbene complex **5** (it melts at 299 °C). In addition, it is remarkably stable towards moisture and air.



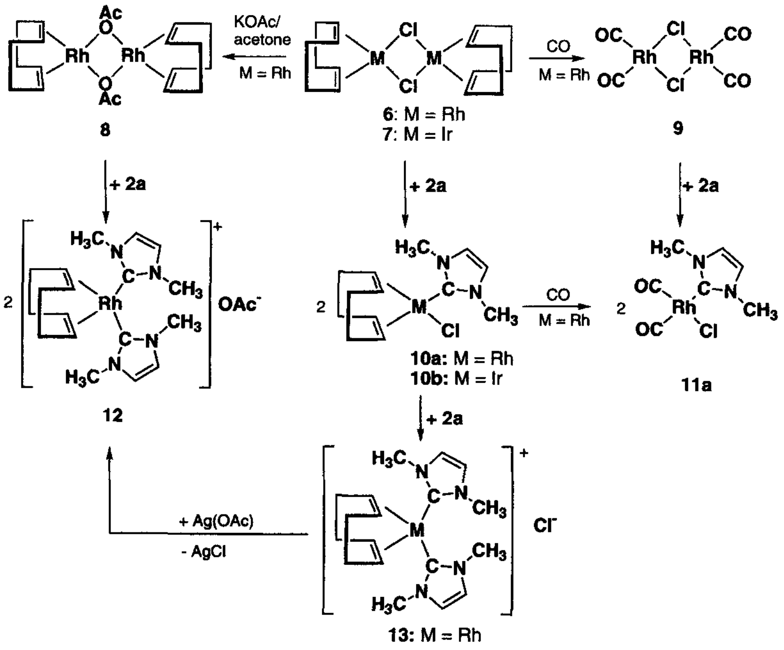
Scheme 4. Synthesis of palladium complex **5**.

The crystal and molecular structures of **5** was determined by means of a single-crystal X-ray diffraction analysis (Fig. 1).[9b]

Apart from the expected square-planar coordination of the divalent metal, this study revealed that **5** has a *cis* configuration and that the two planar, five-membered carbene ligands are twisted relative to the plane of coordination by ca. 70°. The I-Pd-I angle is 93.590(9)°, and the C-Pd-C angle is 90.2(1)°.

Complex **5** is relatively inert to carbene substitution. For example, triphenylphosphine does not displace the carbene ligand in a smooth reaction. The palladium complex **5** proved to be both highly active and stable in Heck-type reactions. These results have been published elsewhere.[9]

Rhodium and iridium: The reaction of rhodium(I) complex **6** with **2a** in THF yielded the metal complex **10a** as a yellow solid (Scheme 5). The analogous reaction with iridium(I) complex **7** gave **10b** as an orange solid. The pure compounds were readily obtained in excellent yields by recrystallization from methylene chloride/*n*-pentane. Both compounds are soluble in polar organic solvents (e.g., methylene chloride, chloroform and nitromethane). The X-ray single-crystal diffraction study of **10a** (Fig. 2) and the



Scheme 5. Carbene complexes of rhodium and iridium.

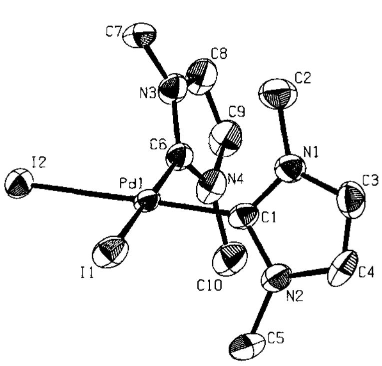


Fig. 1. PLATON [22] plot of the solid-state structure of the palladium complex **5**. Thermal ellipsoids were drawn at the 50% probability level. Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): Pd1-I1 = 2.6479(3), Pd1-I2 = 2.6572(3), Pd1-C1 = 1.990(3), Pd1-C6 = 1.997(3), N1-C1 = 1.347(4), N2-C1 = 1.363(4), N3-C6 = 1.357(4), N4-C6 = 1.336(4); I2-Pd1-I1 = 93.590(9), C1-Pd1-I1 = 87.32(8), C1-Pd1-I2 = 178.08(8), C6-Pd1-I1 = 175.52(9), C6-Pd1-I2 = 88.97(8), C6-Pd1-C1 = 90.2(1).

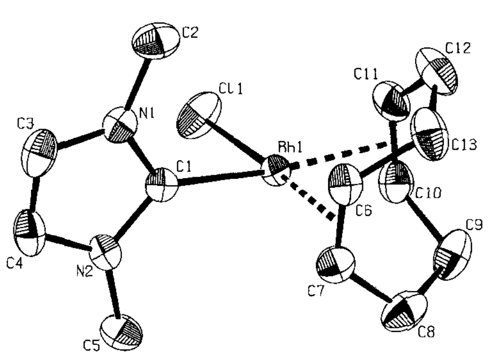


Fig. 2. PLATON [22] plot of the solid-state structure of the rhodium complex **10a**. Thermal ellipsoids were drawn at the 50% probability level. Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): Rh1-Cl1 = 2.3767(6), Rh1-C1 = 2.023(2), Rh1-C6 = 2.114(2), Rh1-C7 = 2.095(2), Rh1-C10 = 2.205(2), Rh1-C11 = 2.175(2), N1-C1 = 1.349(2), N1-C3 = 1.384(2), N2-C1 = 1.355(2), N2-C4 = 1.386(3), C3-C4 = 1.332(3), C1-Rh1-Cl1 = 88.04(5), N2-C1-N1 = 104.0(1).

spectroscopic data revealed the expected square-planar arrangement of the ligands.

The angle between the carbene heterocycle and the coordination plane is 88.8°. The distance between rhodium and the carbene carbon in **10a** is similar to those found in analogous rhodium complexes with CC-saturated heterocyclic carbene ligands (2.003(5)–2.004(4) Å).[14] The bonding of the COD (1,5-cyclooctadiene) double bond *trans* to the carbene is also similar in **10a** and the CC-saturated systems: the $Rh-C_{COD}$ (2.205(no esd given)–2.227(6) Å) and $C{=}C_{COD}$ (1.354(no esd given)–1.386(9) Å) distances in the CC-saturated systems are quite similar to those in **10a**. The double bond *trans* to ligand X in the system (COD)ClRh–X serves as an indicator for the donor characteristics of X. If X is nitrogen, mean distances of $d(Rh-C_{COD}) = 2.13$ Å and $d(C{=}C) = 1.38$ Å are found.[15] If X is phosphorous,[16] the mean distances $Rh-C_{COD} = 2.23$ Å and $C{=}C = 1.37$ Å; these values are quite similar to those observed in **10a** (X = C).

The free CC-unsatured carbene **2a** shows a different reactivity to the corresponding electron-rich olefin:[17] to obtain a monorhodium complex from the electron-rich olefin, a xylene solution must be heated at 140 °C for one hour. The reaction mechanism clearly involves attack of the nitrogen at the metal centre, followed by cleavage of the C–C double bond. In similar reactions with the free monomeric carbene ligand heating is not necessary, as the nucleophilicity of the carbene C is strong enough to cleave the chloro bridge of the dimeric starting material. In the ^{13}C NMR spectrum of the only characterized mono(carbene)(chloro)rhodium complex with benzimidazole as the carbene ligand, the signal for the carbene carbon is at $\delta = 195.9$ with $J_{C-Rh} = 50$ Hz;[18] the corresponding resonance for **10a** occurs at $\delta = 182.6$ with $J_{C-Rh} = 51$ Hz.

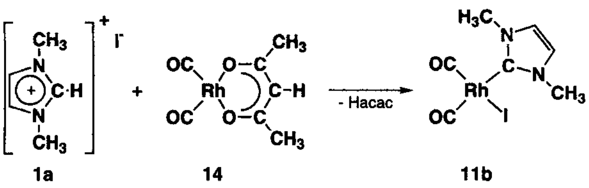
In the ^{13}C NMR spectrum of **10b**, the carbene C signal is at $\delta = 176.6$. Complexes **10a** and **10b** are stable to air and moisture, and **10a** can even be refluxed in toluene under an atmosphere of oxygen for days without any decomposition.

Rhodium(I) complex **11a** could be prepared by passing carbon monoxide through a solution of **10a** in methylene chloride at ambient temperature. The product **11a** was formed within minutes in quantitative yield as a pale yellow solid (Scheme 5). The IR and NMR spectra inidicate complete displacement of 1,5-cyclooctadiene by carbon monoxide. In accordance with the strong donor capability of the carbene ligands, the cyclooctadiene ligand can be replaced by the better acceptor ligand, carbon monoxide. The IR data of **11a** ($\tilde{\nu}$(CO) = 2076 (s) and 2006 (vs) cm^{-1}) indicate strong backdonation from the metal centre. We conclude that carbene ligands induce high electron density at the metal atom.

Alternatively, complex **11a** could be obtained in quantitative yield by cleaving bis[(μ-chloro)dicarbonylrhodium(I)], available from **6** and CO, with carbene **2a** (Scheme 5). Complex **11a** was found to be more sensitive to moisture and air than **10a**.

The analogous iodo complex **11b** was obtained in high yields in a one-step reaction of **1a** with the acetylacetonate (acac) rhodium complex **14** (Scheme 6). This synthesis is based on the protonation of the acac ligand by the protic imidazolium salt and trapping of the resulting carbene by the $Rh(CO)_2$ fragment. The iodide counterion coordinates to the rhodium centre at the same time.

The chloro ligand in **10a** could be replaced by an additional equivalent of carbene to give the cationic *cis* dicarbene–COD complex **13**, which precipitated nearly quantitatively as a yellow solid (Scheme 5). Complex **13** is almost insoluble in most common organic solvents (e.g., toluene, *n*-pentane, ether and THF), sparingly soluble in methylene chloride and soluble without decomposition in water or ethylene glycol methyl ether. Below the melting point of 150 °C it is stable in air. According to the X-ray single-crystal diffraction study, the Rh central atom resides in a square-planar environment (Fig. 3).



Scheme 6. Synthesis of the iodo analogue of **11a**.

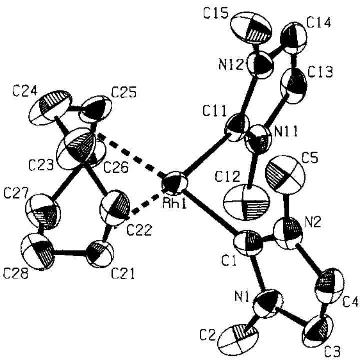


Fig. 3. PLATON [22] plot of the solid-state structure of the rhodium complex **13**. Thermal ellipsoids were drawn at the 50% probability level. Hydrogen atoms, solvent molecules and anions were omitted for clarity. Only one of the two independent molecules is shown. Selected bond lengths (Å) and angles (°) [values given in brackets refer to the second independent molecule in the asymmetric unit]: Rh1–C1 = 2.026(8) (2.053(8)), Rh1–C11 = 2.049(8) (2.059(8)), Rh1–C21 = 2.203(9), Rh1–C22 = 2.181(9), Rh1–C25 = 2.195(9), Rh1–C26 = 2.178(9), N1–C1 = 1.35(1), N1–C3 = 1.39(1), N2–C1 = 1.36(1), N2–C4 = 1.38(1), N11–C11 = 1.38(1), N11–C13 = 1.37(1), N12–C11 = 1.36(1), N12–C14 = 1.38(1), C3–C4 = 1.33(1), C13–C14 = 1.34(1), C11–Rh1-C1 = 94.4(3), N2-C1-N1 = 102.9(7), N12-C11-N11 = 103.2(7).

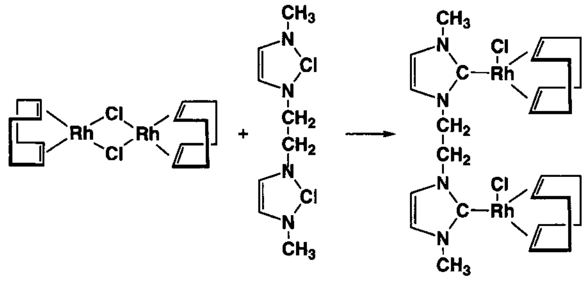
The asymmetric part of the unit cell contains two independent molecules. In order to compensate the different sizes of anion and cation, two water molecules and one methylene chloride molecule cocrystallize with two ion pairs of the rhodium chloride complex. The angles between the least-squares planes through the carbene rings and the plane of the coordination sphere are larger than 81.8°. The rhodium–olefin distances are the same as in **10a**; the averaged rhodium–carbene bond lengths are slightly longer. The separation between rhodium and olefin in **13** is slightly shorter than in ionic COD–bisphosphine rhodium complexes.[19] Owing to the larger standard deviations of the calculated coordinates of **13**, a comparison of angles and distances in the carbene ligands with those of **10a** and the dinuclear rhodium complex **15** does not seem meaningful.

Even at high temperatures no dissociation equilibrium is observed, and the carbene ligands are not displaced by phosphines under mild conditions. We conclude that carbene **2a** is a strong nucleophile, similar to trialkylphosphines.[7a] Triphenylphosphine–rhodium complexes are involved in a rapid ligand exchange process, which can be observed by ^{31}P NMR. At ambient temperature only the signal of the free phosphine is observed. At −30 °C the signal sharpens at about $\delta = 30$, and the $^{1}J_{P-Rh}$ coupling is then about 150 Hz. However, the analogous carbene–rhodium complexes show coupling between carbene C and Rh at all temperatures between −30 and

+70 °C, and no signals corresponding to the free ligand are observed. Additionally, **13** does not react with **6** at temperatures between −30 and 110 °C, and the expected product **10a** cannot be detected by spectroscopic methods (^{1}H, ^{13}C NMR spectrum).

Apart from the chloro compounds, many other μ-bridged two-centred structures undergo ready cleavage by carbenes. For example, the acetate-bridged rhodium complex **8** gave the carbene complex **12** upon treatment with two mol equivalents of **2a** in THF (Scheme 5). The product precipitated immediately as a yellow-orange solid, which is stable to air and moisture. Biscarbene complex **12** is nearly insoluble in most common organic solvents (e.g., toluene, pentane, ether and THF) and sparingly soluble in methylene chloride. It is also soluble in water without (!) decomposition. A synthesis of **12** was first attempted by treating **13** with AgOAc in methylene chloride. However, the yields of **12** were rather low (<40%). In the ^{13}C NMR spectrum, the carbene signal is at $\delta = 180.25$ ($^1J_{C-Rh} = 50$ Hz). The IR spectrum (KBr) shows the presence of the acetate counterion ($\tilde{\nu}$(CO) = 1580 (br), 1423 (br) cm^{-1}).

When the chloro-bridged complex **6** was treated with **4** in THF (Scheme 7), the dinuclear complex **15** immediately precipitated as a yellow solid, which is stable to air and moisture and soluble in polar organic solvents, such as methylene chloride, chloroform and nitromethane.



6 4 15

Scheme 7. Synthesis of dinuclear complex **15**.

The X-ray single-crystal diffraction study and the spectroscopic data confirm a two-centred dimeric structure. Although several complexes between chelating carbenes and metals have been known since 1970 (mononuclear complexes of chelating carbene ligands with a methylene bridge have been structurally characterized[20i]), the free dicarbene **4** has not been characterized until now. The core geometry of **15** around the metal resembles that of **10a** in every respect. Within limits of error all bond lengths and angles are identical. Modelling of a mononuclear complex with ligand **4** reveals that a square-planar coordination at the metal centre within the seven-membered ring should be possible. But this type of coordination would imply a sterically unfavourable eclipsed conformation of the two carbene rings and the four hydrogen atoms in the ethylene bridge. In the dimeric structure obtained (Fig. 4) the carbene substituents adopt a synclinal conformation. In the crystal, the molecule lies on a twofold axis perpendicular to the ethylene bridge. Together with one methylene chloride solvent molecule, two independent halves of the binuclear complex reside in the asymmetric part of the unit cell.

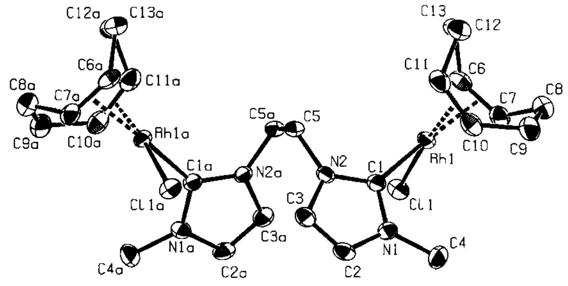
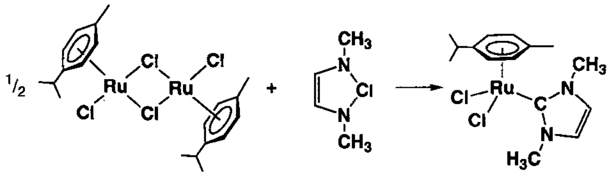


Fig. 4. PLATON [22] plot of the solid-state structure of the rhodium complex **15**. Thermal ellipsoids were drawn at the 50% probability level. Hydrogen atoms and solvent molecules were omitted for clarity. Only one of the two independent molecules is shown. Selected bond lengths (Å) and angles (°) [values given in brackets refer to the second independent molecule in the asymmetric unit]: Rh1−Cl1 = 2.3920(9) (2.387(1)), Rh1−C1 = 2.037(3) (2.027(4)), Rh1−C6 = 2.210(4), Rh1−C7 = 2.227(4), Rh1−C10 = 2.093(4), Rh1−C11 = 2.125(4), N1−C1 = 1.360(4), N1−C2 = 1.386(5), N2−C1 = 1.349(5), N2−C3 = 1.399(5), C3−C2 = 1.331(6), C1-Rh1-Cl1 = 88.4(1), N2-C1-N1 = 104.1(3).

In homogeneous catalysis with phosphine and phosphite ligands, the ligands not only protect low-valent metal centres from aggregation (stabilization effect), but also activate the metal at which the catalytic elementary steps occur. The new rhodium imidazoline-2-ylidene complexes have a number of advantageous properties for potential development: as a result of the exceptionally stable M−C bonds, they are of high thermal and hydrolytic stability; they are readily accessible; and there is no need for excess ligand to be added in possible catalytic reactions. Some further results regarding the use of these complexes in homogenous catalysis will be reported in the near future.

Ruthenium, Osmium: The dimeric precursor **16** (Scheme 8) was synthesized according to a literature procedure[21] in quantitative yield. It is soluble in most organic solvents; the analogous COD complex is polymeric, and the benzene complex is of poor solubility. Cleavage of the chloro bridges in **16** could be achieved with, for example, phosphines or even water. Another one or two equivalents of donor molecules generated a cationic compound with one or two chloride counterions. Using this principle, we were able to obtain the carbene−Ru complex **17** bearing an η^6 aromatic ligand by treatment of **16** with one molar equivalent of **2a** in THF (Scheme 8). The resulting red precipitate is air and moisture sensitive. It dissolves in chloroform, methylene chloride and THF, and is hardly soluble in ether and *n*-pentane. Traces of a biscarbene complex of Ru could be observed in the ^{13}C and ^{1}H NMR spectra.

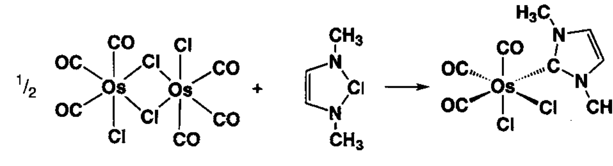


16 2a 17

Scheme 8. Synthesis of Ru^{II} complex **17** bearing an η^6 aromatic ligand.

The bis(dichloroosmium(II)) complex **18** was treated with two equivalents of **2a** to give a monocarbene complex of osmium(II), **19** (Scheme 9). This complex was characterized by NMR, IR, elemental analysis and X-ray single-crystal diffraction (Fig. 5).

Osmium resides in an octahedral environment. The three carbonyl ligands form one face of the octahedron, and the chloro ligands adopt a *cis* arrangement. The Os1−C1 bond length (2.136(7) Å) is comparable to that of an osmium−carbon single



18 **2a** **19**

Scheme 9. Synthesis of a monocarbene complex of Os^{II}.

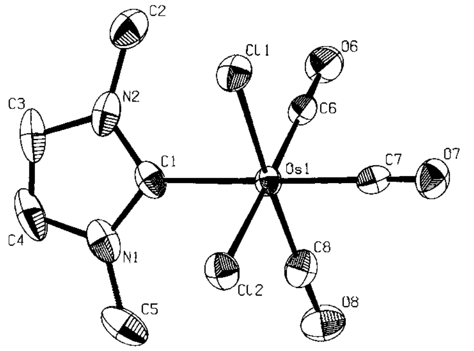


Fig. 5. PLATON [22] plot of the solid-state structure of the osmium complex **19**. Ellipsoids were drawn at the 50% probability level. Hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): Os1–Cl1 = 2.435(1), Os1–Cl2 = 2.440(2), Os1–C1 = 2.136(7), Os1–C6 = 1.864(7), Os1–C7 = 1.991(6), Os1–C8 = 1.886(7), O6–C6 = 1.150(8), O7–C7 = 1.107(8), O8–C8 = 1.149(8), N1–C1 = 1.333(8), N1–C4 = 1.38(1), N2–C1 = 1.373(9), N2–C3 = 1.367(9), C3–C4 = 1.33(1), N2-C1-N1 = 104.6(6).

bond. A clear difference in the bonding in the various carbonyl ligands can be observed. The bond Os–C7 (1.991(6) Å) is clearly longer than the bonds Os–(C6, C8) (1.864(7), 1.886(7) Å). Accordingly, the bond C7–O7 (1.107(8) Å) is shorter than the bonds C6–O6 and C8–O8 (1.150(8), 1.149(8) Å). Obviously the *trans* influence of the carbene ligand is much greater than that of the chloro ligand, that is, the bond to the carbonyl *trans* to the carbene ligand is weakened to a much greater extent.

5. Comparison of free and metal-bound N-heterocyclic carbenes: The interesting bond lengths and angles of the metal complexes presented here are collected in Table 1 together with the values for free carbenes. The widening of the N-$C_{carbene}$-N angle in the metal-coordinated ligands compared to the free carbene ligands is the most striking difference. The C=C double bond and the neighbouring C–N bonds do not change significantly in length. The angles C=C-N also vary very little. Thus, the geometry of the N-C=C-N ring fragment is the same in both complexed and uncomplexed ligands. A widening of the the N-$C_{carbene}$-N angle should therefore be accompanied by a shortening of the $C_{carbene}$–N bonds. The X-ray data suggest a trend towards a shortening of the $C_{carbene}$–N bonds in the carbene complexes. A shorter $C_{carbene}$–N bond in the metal complex would not be unexpected; however, bearing in mind that even threefold standard deviations are often an inadequate measure for the limits of error, the suggested trend cannot be regarded as proven. Theoretical calculations will be necessary if the bonding in N-heterocyclic carbenes is to be better understood.

Some ^{1}H and ^{13}C NMR data of the metal carbene complexes discussed in this paper are given in Table 2. A comparison of the spectra shows that the the metal fragment has no significant influence on the chemical shifts of the methyl groups or the ring carbons. Only the carbene carbon signals are influenced by the bonding environment of the carbene. The signal corresponding to the carbene centre lies in the range $\delta = 168.2$ (**5**) to 187.33 (**11b**); this shift indicates an increase in the carbocation character of the carbene carbon atom.

Table 2. NMR data for carbene complexes of Ru^{II}, Os^{II}, Rh^{I}, Ir^{I} and Pd^{II}.

	^{13}C NMR ($CDCl_3$)		^{1}H NMR ($CDCl_3$)	
	$\delta(C_{carbene})$	δ(C=C)	δ(NCH)	$\delta(NCH_3)$
10a	182.6 (d) [a]	121.9	6.80	4.10
10b	176.6 (s)	122.83	6.79	3.67
11a	185.3 (d)	122.75	6.93	3.87
11b	187.3 (d)	123.20	7.14	4.00
13	180.5 (d)	123.1	7.00	4.00
12	180.3 (d)	123.1	6.96	3.85
15	181.3 (d)	123.85, 120.62	6.85, 6.47	4.01
5	168.2 (s)	122.3	7.24	3.92
17	173.2	123.71	6.97	3.96
19	171.54 [b]	125.70	7.23	4.14

[a] ^1J(C–Rh) = 51.1 Hz. [b] In CD_3NO_2.

Table 1. Minimum and maximum values of selected bond lengths (Å) and angles (°) for free carbenes and the presented metal complexes

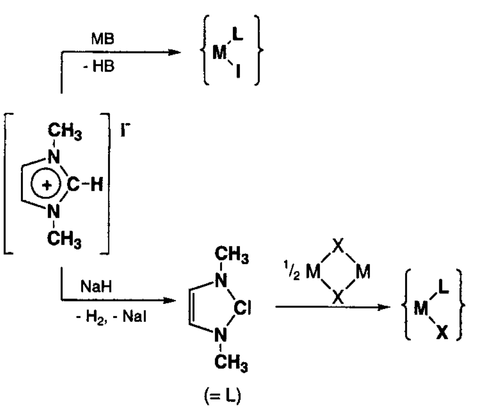
Compound	$C_{carbene}$–N	N–C	C=C	N-$C_{carbene}$-N	C=C-N
10a	1.349(2)	1.384(2)	1.332(3)	104.0(1)	106.4(2)
	1.355(2)	1.386(3)			107.1(2)
13	1.35(1)	1.37(1)	1.30(1)	102.9(7)	106.2(8)
	1.38(1)	1.40(1)	1.34(1)	104.6(7)	107.9(8)
15	1.349(5)	1.378(5)	1.331(6)	103.4(3)	106.2(3)
	1.364(5)	1.399(5)	1.332(6)	104.1(3)	107.4(3)
19	1.333(8)	1.367(9)	1.33(1)	104.6(6)	106.3(7)
	1.373(9)	1.38(1)			108.0(7)
5	1.336(4)	1.383(4)	1.337(6)	105.0(3)	105.9(3)
	1.363(4)	1.403(4)	1.344(5)	105.3(2)	107.2(3)
1,3,4,5-tetramethyl-iy [a]	1.363(1)	1.394(1)	1.352(2)	101.5(1)	105.78(5)
1,3-di(1-adamantyl)-iy [a]	1.367(2)	1.382(2)	1.338(3)	102.2(2)	106.2(2)
	1.373(2)	1.386(2)			107.2(2)
1,3-bis(2,4,6-trimethylphenyl)-iy [a]	1.365(4)	1.378(4)	1.331(5)	101.4(2)	106.5(3)
	1.371(4)	1.381(4)			106.5(3)
1,3-bis(4-methylphenyl)-iy [a]	1.371(2)	1.392(2)	1.334(2)	101.2(1)	106.2(1)
	1.375(2)	1.394(2)			106.6(2)
1,3-bis(*p*-chlorophenyl)-iy [a]	1.368(2)	1.391(2)	1.339(2)	101.7(1)	106.3(1)
	1.368(2)	1.392(2)			106.4(1)

[a] iy = imidazol-2-ylidene; data taken from ref. [6b].

Conclusion

Metal complexes of N-heterocyclic carbenes are available starting from azolium salts or the free carbenes. The former route depends on the metal-containing precursor compounds exhibiting sufficient basicity, either at the metal or at one of the ligands; the counterion of the azolium salt is normally attached to the metal in the course of the reaction (Scheme 10, upper part). The second route, the free-carbene route, does not have these limitations. The free carbene, as a highly nucleophilic molecule, can generate its own coordination site; this process works particularly well with halide- or acetate-bridged dinuclear complexes (Scheme 10, lower part).

In the imidazolium route, the introduction of an iodide ion in the resulting metal complex may be a drawback of an otherwise straightforward and elegant method. Imidazolium tetrafluoroborates or hexafluorophosphates can certainly be generated from the iodides, but this requires a second step (salt



Scheme 10. MB = metal complex containing a Lewis base B (e.g., $Pd(OAc)_2$); L = carbene ligand.

metathesis), which does not always proceed cleanly. Another limitation of this route is the fact that imidazolium salts other than halides are normally poorly soluble in common organic solvents, including THF.

The new liquid-ammonia route allows thermally labile free carbenes to be generated for the first time. The fact that substituted N-heterocyclic carbenes (including those with long alkyl chains), heteroatom-substituted and chiral derivatives, as well as immobilized free carbenes and their metal complexes[12] can be synthesized demonstrates that a significant development in organometallic chemistry and catalysis has been achieved.

Experimental Section

All reactions were performed with standard Schlenck techniques in an oxygen-free nitrogen atmosphere. Solvents were dried by standard methods and distilled under N_2. Infrared spectra were recorded on a Perkin-Elmer 1600 series FT-IR spectrometer, and the ^1H and ^{13}C NMR spectra at 400 and 100.54 MHz, respectively, on an FT Jeol GX400 instrument. Elemental analyses were performed in the microanalytical laboratory of our institute. Mass spectra were obtained with Finnigan MAT311A and MAT90 spectrometers. Bis[μ-chloro(1,5-cyclooctadiene)-rhodium(I)] (**6**), bis[μ-chloro(1,5-cyclooctadiene)iridium(I)] (**7**) and bis{μ-chloro-(chloro)[η^6-(1-isopropyl)(4-methyl)benzene]ruthenium(II)} (**16**) were prepared as reported in ref. [21].

1. General procedure for the liquid-ammonia route: synthesis of 1,3-dimethylimidazoline-2-ylidene (2a), 1,3-dicyclohexylimidazoline-2-ylidene (2b) and 1,1′-(1,2-ethylene)-3,3′-dimethyldiimidazoline-2,2′-diylidene (4): In an evacuated apparatus fitted with an oil-charged NORMAG® bubbler, ammonia (75 mL of grade 2.8) was condensed onto potassium (2 g), to ensure complete dryness. A 250 mL three-necked round-bottom flask was fitted with a solid funnel and a reflux condenser. The 1,3-dialkylimidazolium halide (10 mmol) was added to the flask and suspended in THF (15 mL); the solid funnel was charged with NaH (265 mg, 11 mmol). The flask and condenser were cooled by acetone/dry ice (−65 °C), and the predried ammonia was then recondensed (1 h) into the flask. 1,3-Dimethylimidazolium iodide (**1a**) was completely soluble in the resulting mixture (ammonia/THF 5:1), whereas 1,3-dicyclohexylimidazolium chloride (**1b**) and 1,1′-(1,2-ethylene)-3,3′-dimethyldiimidazolium dibromide (**3**) were only partially soluble. NaH was then added in one portion and the cooling bath was removed after 15 min. The mixture was allowed to react for ca. 30 min under reflux. The ammonia was then allowed to evaporate (2 h) or was removed in vacuo. To remove traces of ammonia, the apparatus was evacuated and purged several times with argon. The colourless solution of the 1,3-dialkylimidazoline-2-ylidene was diluted to a total volume of 30 mL with pentane or toluene (to separate the sodium halide) and was then filtered. Aliquots can be used for subsequent reactions without further purification.
2b: $^{13}C\{^1H\}$ NMR (100.1 MHz, THF/[D$_8$]THF, 20 °C): $\delta = 210.1$ (s, carbene C), 115.7 (s, NCH), 59.6, 34.9 (s, cyclohexyl), 27–25 (m, cyclohexyl, THF).
4: $^{13}C\{^1H\}$ NMR (100.1 MHz, THF/[D$_8$]THF inlet, 20 °C, ppm): $\delta = 215.9$ (s, carbene C), 120.3, 119.7 (s, NCH), 52.7 (s, NCH_2), 37.7 (s, NCH_3).

2. Diiodobis(1,3-dimethylimidazoline-2-ylidene)palladium(II) (5): Iodide **1a** (4.20 g, 18.7 mmol) was added at room temperature to a stirred solution of palladium(II) acetate (2.00 g, 8.9 mmol) in anhydrous THF (150 mL). After the mixture had been refluxing for 2 min, a colour change from dark brown to yellow occurred. Stirring was continued for another 15 min at room temperature, and the solvent was then removed in vacuo. The precipitate was washed with ether (2 × 10 mL). The yellow product was recrystallized from methylene chloride (10 mL) and *n*-pentane (30 mL). After the solvent was decanted, the resulting yellow crystals were dried in vacuo. The compound was most soluble in chloroform and methylene chloride, and sparingly soluble in ether and *n*-pentane. Yield: 3.70 g (75%); ^1H NMR (400 MHz, $CDCl_3$, 20 °C): $\delta = 7.20$ (s, 4H; NCH), 3.92 (s, 12H; NCH_3); $^{13}C\{^1H\}$ NMR (100.1 MHz, $CDCl_3$, 20 °C): $\delta = 168.2$ (s, carbene C), 122.3 (NCH), 38.2 (NCH_3); $C_{10}H_{16}I_2N_4Pd$ (552.49): calcd C 21.73, H 2.92, N 10.14; found C 23.26, H 3.45, N 10.00.

3. Chloro(η^4-1,5-cyclooctadiene)(1,3-dimethylimidazoline-2-ylidene)rhodium(I) (10a): Ligand **2a** (96 mg, 1 mmol) was added at room temperature in portions to a stirred solution of **6** (247 mg, 0.5 mmol) in anhydrous THF (20 mL). A colour change was immediately observed from light to dark yellow. After the reaction mixture had been stirred for another 15 min at room temperature, the solvent was removed in vacuo. The precipitate was washed with ether (2 × 10 mL). The yellow product was recrystallized from methylene chloride (10 mL) and *n*-pentane (30 mL). After the solvent was decanted, the resulting yellow crystals were dried in vacuo. The compound was most soluble in chloroform and methylene chloride, relatively soluble in THF and toluene, and less soluble in ether and *n*-pentane. Yield: 310 mg (91%); ^1H NMR (400 MHz, $CDCl_3$, 20 °C): $\delta = 6.8$ (s, 2H; NCH), 4.1 (s, 6H; NCH_3), 5.0 (2H), 3.3 (2H), 2.4 (4H), 1.9 (4H; cyclooctadiene); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.1 MHz, 20 °C): $\delta = 182.6$ (d, $^1J(C-Rh) = 51.1$ Hz; carbene C), 121.9 (NCH), 37.6 (NCH_3), 98.5, 67.7, 33.0, 28.9 (COD); IR (KBr, cm^{-1}): $\tilde{\nu} = 3500$, 3154, 3103, 2931, 2875, 2828, 1652, 1507, 1456, 1378, 1328, 1228, 1115, 1079, 992, 957, 865, 816, 744, 694, 459; $C_{13}H_{20}ClN_2Rh$ (342.68): calcd C 45.57, H 5.88, N 8.17; found C 45.63, H 5.98, N 8.35.

4. Chloro(η^4-1,5-cyclooctadiene)(1,3-dimethylimidazoline-2-ylidene)iridium(I) (10b): Following procedure 3, the reaction between **7** (282 mg, 0.5 mmol) and **2a** (96 mg, 1 mmol) gave 340 mg (90%) of complex **10b**. ^1H NMR (400 MHz, $CDCl_3$, 20 °C): $\delta = 6.79$ (s, 2H; NCH), 3.67 (s, 6H; NCH_3), 5.23 (m, 2H), 4.2 (m, 2H), 1.50 (m, 4H), 1.89 (m, 4H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.1 MHz, 20 °C): $\delta = 176.62$ (carbene C), 122.83 (NCH), 37.77 (NCH_3), 83.64, 59.24, 31.06, 31.68 (COD); IR (KBr, cm^{-1}): $\tilde{\nu} = 3500$, 3158, 3104, 2919, 2876, 2828, 1652, 1575, 1456, 1386, 1324, 1229, 1115, 1081, 997, 872, 803, 745, 700, 466; MS(CI) *m*/*z*: 432 (M^+, correct isotope pattern), 397 ($M - Cl$, correct isotope pattern); $C_{13}H_{20}ClN_2Ir$ (431.99): calcd C 36.15, H 4.67, N 6.48; found C 36.00, H 4.52, N 6.50.

5. Dicarbonylchloro(1,3-dimethylimidazoline-2-ylidene)rhodium(I) (11a): Carbon monoxide was bubbled (10 min) through a yellow solution of **10a** (200 mg, 0.59 mmol) in methylene chloride (30 mL). After the colour had changed to pale yellow, the solvent was removed in vacuo, and the precipitate washed with *n*-pentane (10 mL). The product was recrystallized from methylene chloride (10 mL) and *n*-pentane (30 mL). The solvent was decanted, and the resulting yellow crystals were dried in vacuo. The compound was soluble in chloroform and methylene chloride, relatively soluble in toluene and THF and not so soluble in ether and *n*-pentane. Yield: 161 mg (94%); ^1H NMR (400 MHz, $CDCl_3$, 20 °C): $\delta = 6.93$ (s, 2H; NCH), 3.87 (s, 6H; NCH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.1 MHz, 20 °C): $\delta = 185.30$ (d, $^1J(C-Rh) = 53$ Hz; carbene C), 182.4 (d, $^1J(C-Rh) = 75$ Hz, CO), 122.75 (NCH), 38.27 (NCH_3); IR (KBr, cm^{-1}): $\tilde{\nu} = 2076$ (s, CO), 2006 (vs, CO); MS (CI) *m*/*z*: 290 (M^+, correct isotope pattern), 262 ($M - CO$, correct isotope pattern), 234 (262 − CO, correct isotope pattern), 199 (234 − Cl); $C_7H_8ClN_2O_2Rh$ (290.52): calcd C 28.94, H 2.78, N 9.64; found C 29.18, H 2.86, N 9.56.

6. Dicarbonyliodo(1,3-dimethylimidazoline-2-ylidene)rhodium(I) (11b): Iodide **1a** (173 mg, 0.77 mmol) was added at room temperature to a stirred solution of acetylacetonatodicarbonylrhodium(I) (**14**) (100 mg, 0.38 mmol) in anhydrous THF (20 mL). After refluxing for 2 h, the mixture changed colour from green to yellow. It was stirred for another 15 min at room temperature, before removing the solvent in vacuo. The precipitate was washed with ether (2 × 10 mL). The yellow product was recrystallized from methylene chloride (10 mL) and *n*-pentane (30 mL). After the solvent had been decanted, the resulting yellow crystals were dried in vacuo. The compound was most soluble in chloroform and methylene chloride, relatively soluble in THF and toluene, and less soluble in ether and *n*-pentane. Yield: 129 mg (89%); ^1H NMR (400 MHz, $CDCl_3$, 20 °C): $\delta = 7.14$ (s, 2H; NCH), 4.00 (s, 6H; NCH_3); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.1 MHz, 20 °C): $\delta = 187.3$ (d, carbene C, $^1J(C-Rh) = 53.44$ Hz), 181.15 (d, CO, $^1J(C-Rh) = 78.22$ Hz), 123.02 (NCH), 38.27 (NCH_3); IR (THF, cm^{-1}): $\tilde{\nu} = 2068.2$ (CO), 1994.6 (CO); $C_7H_8IN_2O_2Rh$ (381.96): calcd C 22.01, H 2.11, N 7.33; found C 22.40, H 2.48, N 8.07.

7. [(η^4-1,5-Cyclooctadiene)bis(1,3-dimethylimidazoline-2-ylidene)rhodium(I)]acetate (12): Ligand **2a** (0.55 mmol, 2 equiv) were added at room temperature in portions to a stirred solution of bis[μ-acetate-(η^4-1,5-cyclooctadiene)rhodium(I)] (**8**) (150 mg, 0.28 mmol) in anhydrous THF (10 mL). The mixture immediately changed colour from light to dark yellow. After another 15 min of stirring at room temperature, the solvent was removed in vacuo. The precipitate was washed with ether (2 × 10 mL). The yellow product was recrystallized from methylene chloride (10 mL) and *n*-pentane (30 mL). After the solvent was decanted, the resulting orange crystals were dried in vacuo. Yield: 101 mg (70%); ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$, 20 °C): $\delta = 6.96$ (s, 4H; NCH), 4.07 (m, 4H; cyclooctadiene, 3.85 (s, 12H; $\mathrm{NCH_3}$), 2.28 (m, 8H, $\mathrm{CH_2}$), 2.03 (s, 3H; Ac); ^{13}C{^{1}H} NMR ($\mathrm{CDCl_3}$, 100.1 MHz, 20 °C): $\delta = 180.3$ (d, ^1J(C–Rh) = 50 Hz, carbene C), 176.5 (d, CO), 123.1 (NCH), 38.8 ($\mathrm{NCH_3}$), 88.7 (s, olefinic COD CH), 30.5 (COD), 24.6 (s, $\mathrm{CH_3COO}$); IR (KBr, cm^{-1}): $\tilde{\nu} = 3500$, 3100, 2923, 2859, 2823, 1580, 1530, 1423, 1460, 1378, 1310, 1223, 1082, 1023, 956, 864, 743, 693.

8. [(η^4-1,5-Cyclooctadiene)bis(1,3-dimethylimidazoline-2-ylidene)rhodium(I)] chloride (13): Ligand **2a** (192 mg, 2 mmol, 2 equiv) was added at room temperature in portions to a stirred solution of **6** (247 mg, 0.5 mmol) in anhydrous THF (20 mL). The mixture underwent an immediate colour change from light to dark yellow. After another 15 min of stirring at room temperature, the solvent was removed in vacuo. The precipitate was washed with ether (2 × 10 mL). The yellow product was recrystallized from methylene chloride (10 mL) and *n*-pentane (30 mL). After the solvent was decanted, the resulting yellow crystals were dried in vacuo. The compound was soluble in water, chloroform and methylene chloride, but sparingly soluble in toluene, ether and *n*-pentane. Yield: 410 mg (93%); ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$, 20 °C): $\delta = 7.0$ (s, 4H; NCH), 4.0 (s, 12H; $\mathrm{NCH_3}$), 4.2 (4H), 2.3 (4H), 2.1 (4H) (COD); ^{13}C{^{1}H} NMR ($\mathrm{CDCl_3}$, 100.1 MHz, 20 °C): $\delta = 180.5$ (d, ^1J(C–Rh) = 52.4 Hz, carbene C), 123.1 (NCH), 38.3 ($\mathrm{NCH_3}$), 88.8, 30.4 (COD); IR (KBr, cm^{-1}): $\tilde{\nu} = 3450$, 3154, 3094, 2920, 2977, 2828, 1634, 1574, 1458, 1380, 1230, 1115, 1084, 991, 823, 744, 695, 668, 461; $\mathrm{C_{18}H_{28}ClN_4Rh}$ (438.81): calcd C 49.27, H 6.43, N 12.77; found C 50.26, H 6.44, N 12.66.

9. [1,1′-(1,2-Ethylene)-3,3′-dimethyldiimidazoline-2,2′-diylidene]bis[chloro(η^4-1,5-cyclooctadiene)rhodium(I)] (15): Ligand **4** (190 mg, 1 mmol) was added in portions to a stirred solution of **6** (247 mg, 0.5 mmol) in anhydrous THF (20 mL). After the mixture had been stirred for 3 h, the solvent was removed in vacuo, and the crude residue washed with diethyl ether (3 × 10 mL). The yellow product was recrystallized from methylene chloride (10 mL) and *n*-pentane (30 mL). After the solvent had been decanted, the resulting yellow crystals were dried in vacuo. The compound was most soluble in chloroform and methylene chloride, relatively soluble in THF and toluene, less soluble in ether and *n*-pentane. Yield: 80 mg (18%); ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$, 20 °C): $\delta = 6.85$ (d, 2H; $J = 1.9$ Hz), 6.47 (d, 2H; $J = 1.9$ Hz, NCH), 4.73 (m, 4H; $\mathrm{CH_2CH_2}$), 4.01 (s, 6H; $\mathrm{NCH_3}$); 3.34 (m, 4H), 3.22 (m, 4H), 2.44 (m, 4H), 2.00 (m, 4H), 5.17 (m, 4H), 4.98 (m, 4H; COD); ^{13}C{^{1}H} NMR ($\mathrm{CDCl_3}$, 100.1 MHz, 20 °C): $\delta = 181.30$ (d, ^1J(C–Rh) = 50.5 Hz, carbene C), 123.85, 120.62 (NCH), 37.76 ($\mathrm{NCH_3}$), 50.85 ($\mathrm{CH_2CH_2}$), 69.18 (d, ^1J(C–Rh) = 14.6 Hz), 67.75 (d, ^1J(C–Rh) = 14.5 Hz), 29.45, 28.39 (COD); $\mathrm{C_{26}H_{28}Cl_2N_4Rh_{2*}CH_2Cl_2}$ (768.28) calcd: C 42.21, H 5.25, N 7.29; found C 43.02, H 5.41, N 7.31.

10. Dichloro(1,3-dimethylimidazoline-2-ylidene)[η^6-(1-isopropyl)(4-methyl)benzene]ruthenium(II) (17): Ligand **2a** (96 mg, 1 mmol) was added in portions to a well stirred solution of **16** (306 mg, 0.5 mmol) in anhydrous THF (15 mL). The colour changed immediately from clear red to deep red. After removal of the solvent in vacuo, the remaining residue was washed successively with ether (2 × 20 mL) and *n*-pentane (2 × 20 mL). The product was recrystallized from methylene chloride (10 mL) and *n*-pentane (30 mL). The solvent was decanted, and the resulting red crystals were dried in vacuo. The compound was very soluble in chloroform and methylene chloride, relatively soluble in toluene and THF, and less soluble in ether and *n*-pentane. Yield: 360 mg (90%); ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$, 20 °C): $\delta = 6.97$ (s, 2H; NCH), 3.96 (s, 6H; $\mathrm{NCH_3}$), 5.36 (d, $^3J = 5.9$ Hz, 2H), 5.10 (d, $^3J = 5{,}9$ Hz, 2H), 2,04 (s, 3H; $\mathrm{CH_3}$), 1.21 (d, $^3J = 6.9$ Hz, 6H; $\mathrm{CH_3}$), 2.88 (septet, $^3J = 6.9$ Hz, 1H) (Ar); ^{13}C{^{1}H} NMR ($\mathrm{CDCl_3}$, 100.1 MHz, 20 °C): $\delta = 173.17$ (carbene C), 123.71 (NCH), 39.56 ($\mathrm{NCH_3}$), 105.2, 97.3, 84.71, 82.80, 30.78, 22.46, 18.62 (aromat); MS (chemical ionization): m/z 400 (M^+, correct isotope pattern), 266 ($M - \mathrm{C_{10}H_{14}}$), 231 (266 – Cl), 196 (231 – Cl), 134 ($\mathrm{C_{10}H_{14}}$), 119 (134 – $\mathrm{CH_3}$), 43 (propyl).

11. Tricarbonyldichloro(1,3-dimethylimidazoline-2-ylidene)osmium(II) (19): Ligand **2a** (42 mg, 0.43 mmol) in anhydrous THF (5 mL) was added in portions to a well stirred solution of bis[(μ-chloro)chlorotricarbonylosmium(II)] **(18)** (150 mg, 0.22 mmol) in anhydrous THF (15 mL). After removal of the solvent in vacuo, the remaining residue was washed successively with ether (2 × 20 mL) and *n*-pentane (2 × 20 mL). The product was recrystallized from nitromethane. The solvent was decanted, and the resulting colourless crystals were dried in vacuo. The compound was very soluble only in nitromethane. Yield: 85 mg (89%); ^{1}H NMR (400 MHz, $\mathrm{CD_3NO_2}$, 20 °C): $\delta = 7.23$ (s, 2H; NCH), 4.14 (s, 6H; $\mathrm{NCH_3}$); ^{13}C{^{1}H} NMR (100.1 MHz, $\mathrm{CD_3NO_2}$, 20 °C): $\delta = 171.54$ (carbene C), 168.94, 168.49 (CO), 125.70 (NCH), 40.30 ($\mathrm{NCH_3}$); IR (KBr, cm^{-1}): $\tilde{\nu} = 2115.9$ (s, CO), 2014.3 (vs, CO), 1932.9 (s, CO); MS (CI) m/z: 442 (M^+, correct isotope pattern), 407 (M – Cl, correct isotope pattern), 379 (407 – CO, correct isotope pattern); $\mathrm{C_8H_8Cl_2N_2O_3Os}$ (441.27): calcd C 21.78, H 1.83, N 6.35; found C 22.55, H 2.24, N 6.05.

12. X-ray crystal structure determinations:

a) Compound **10a**: Formula: $\mathrm{C_{13}H_{20}ClN_2Rh}$, f_w: 342.67 g mol^{-1}, $F_{000} = 696$, space group $P2_1/n$ (I. T. no. 14). Lattice constants by least-squares refinement of 25 well-centred reflections in the range $40.0 < 2\theta < 47.7°$ ($\lambda = 0.70930$ Å, Mo(K$_{\alpha1}$)): $a = 10.162(2)$, $b = 11.137(1)$, $c = 13.223(2)$ Å, $\beta = 112.40(1)°$, $V = 1383.6(3)$ Å^3, $Z = 4$, $\rho_{\text{calcd}} = 1.65$ g cm^{-3}. CAD4 (Enraf Nonius), graphite monochromator ($\lambda = 0.71073$ Å, Mo(K_α^-)). Temperature: -50 ± 3 °C; scan range: $1.0 < \theta < 25.0°$, scan mode: ω scan, max. 60 s; scan width: $(0.80 + 0.20 \tan\theta)°$, 4131 measured data, 171 systematically absent, 249 with negative intensity ($I/\sigma(I) < 0.01$) rejected, all remaining 2583 ($I > 0.0\,\sigma(I)$) unique reflections used for refinement. Empirical absorption correction based on ψ scan data was applied to the data set, $\mu = 13.9$ cm^{-1}. Data were corrected for extinction effects, Larson's extinction parameter [23]: 138.17. The structure was solved using the Patterson method (SHELXS-86 [24]) and refined using standard difference Fourier techniques (CRYSTALS [25]). All hydrogen atoms could be found and were refined isotropically. 235 parameters refined, $w = 1/\sigma^2$, 11 data per parameter, shift/error: < 0.0001 in the last cycle, $R = \sum(||F_o| - |F_c||)/\sum|F_o| = 0.021$, $Rw = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2} = 0.017$; residual electron density: max. $+0.38$ e Å^{-3} at 0.12 Å from Rh, min. -0.27 e Å^{-3}.

b) Compound **13**: Formula: $2([\mathrm{C_{18}H_{28}N_4Rh}][\mathrm{Cl}]\cdot 1\,\mathrm{H_2O}\cdot 0.5\,\mathrm{CH_2Cl_2})$ in the asymmetric unit, f_w: 438.80 g mol^{-1} ($[\mathrm{C_{18}H_{28}N_4Rh}][\mathrm{Cl}]$), $F_{000} = 2056$, space group $P2_1/c$ (I. T. no. 14). Lattice constants by least-squares refinement of 25 well-centred reflections in the range $30.4 < 2\theta < 35.5°$ ($\lambda = 0.70930$ Å, Mo(K$_{\alpha1}$)): $a = 17.493(8)$, $b = 13.858(2)$, $c = 18.729(8)$ Å, $\beta = 104.66(2)°$, $V = 4392$ Å^3, $Z = 4$, $\rho_{\text{calcd}} = 1.51$ g cm^{-3}. CAD4 (Enraf Nonius), graphite-monochromator ($\lambda = 0.71073$ Å; Mo(K_α^-)). Temperature: -50 ± 3 °C, scan range: $1.0 < \theta < 25.0°$, scan mode: ω scan, max. 60 s, scan width: $(1.50 + 0.30 \tan\theta)°$, 8385 measured data, 373 systematically absent, 1385 with negative intensity ($I/\sigma(I) < 0.01$) rejected, 4998 data out of 6388 unique reflections ($I > 2.0\,\sigma(I)$) used for refinement. The structure was solved using the Patterson method (SHELXS-86 [24]) and refined using standard difference Fourier techniques (CRYSTALS [25]). All hydrogen atoms were calculated in ideal positions and were not refined. 478 parameters refined, $w = 1$, 10.5 data per parameter, shift/error: < 0.0001 in the last cycle, $\mathrm{R} = \sum(||F_o| - |F_c||)/\sum|F_o| = 0.050$, $Rw = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2} = 0.055$; residual electron density: max. $+0.89$ e Å^{-3} at 0.98 Å from Rh1, min. -0.55 e Å^{-3}.

c) Compound **15**: Formula: $\mathrm{C_{26}H_{38}Cl_2N_4Rh_2\cdot CH_2Cl_2}$, f_w: 683.33 g mol^{-1} ($\mathrm{C_{26}H_{38}Cl_2N_4Rh_2}$), $F_{000} = 3104$, space group $Pbcn$ (I. T. no. 60). Lattice constants by least-squares refinement of 25 well-centred reflections in the range $30.4 < 2\theta < 40.7°$ ($\lambda = 0.70930$ Å, Mo(K$_{\alpha1}$)): $a = 20.489(2)$, $b = 11.617(1)$, $c = 25.293(3)$ Å, $V = 6020$ Å^3, $Z = 8$, $\rho_{\text{calcd}} = 1.70$ g cm^{-3}. CAD4 (Enraf Nonius), graphite-monochromator ($\lambda = 0.71073$ Å, Mo(K_α^-)). Temperature: -50 ± 3 °C, scan range: $1.0 < \theta < 25.0°$, scan mode: ω scan, max. 60 s, scan width: $(0.90 + 0.10 \tan\theta)°$, 5875 measured data, 596 systematically absent, 667 with negative intensity ($I/\sigma(I) < 0.01$) rejected, 4270 data out of 4612 unique reflections ($I > 1.0\cdot\sigma(I)$) used for refinement. Data were corrected for extinction effects, Larson's extinction parameter [23]: 45.27. The structure was solved using the Patterson method (SHELXS-86 [24]) and refined using standard difference Fourier techniques (CRYSTALS [25]). All hydrogen atoms could be found and were refined isotropically. 495 parameters refined, weighting scheme of Tukey und Prince [26] with 3 refined parameters: $p1 = 0.923$; $p2 = 0.549$; $p3 = 0.636$, 8.6 data per parameter, shift/error: < 0.001 in the last cycle, $R = \sum(||F_o| - |F_c||)/\sum|F_o| = 0.033$, $Rw = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2} = 0.037$, residual electron density: max. $+0.48$ e Å^{-3} at 0.79 Å from C13, min. -0.54 e Å^{-3}.

d) Compound **19**: Formula: $\mathrm{C_8H_8Cl_2N_2O_3Os_1}$, f_w: 441.27 g mol^{-1}, $F_{000} = 1632$, space group $Pbca$ (I. T. no. 61). Lattice constants by least-squares refinement of 25 well-centred reflections in the range $31.3 < 2\theta < 42.1°$ ($\lambda = 0.70930$ Å, Mo(K$_{\alpha1}$)): $a = 9.910(1)$, $b = 11.949(1)$, $c = 20.163(2)$ Å, $V = 2387.6$ Å^3, $Z = 8$, $\rho_{\text{calcd}} = 2.46$ g cm^{-3}, CAD4 (Enraf-Nonius), graphite monochromator ($\lambda = 0.71073$ Å, Mo(K_α^-)). Temperature: -50 ± 3 °C, scan range: $1.0 < \theta < 25.0°$, scan mode: ω scan, max. 60 s, scan width: $(1.0 + 0.2 \tan\theta)°$, 2410 measured data, 522 data systematically absent or measured with negative intensity ($I/\sigma(I) < 0.01$), 2 reflections merged, out of 1887 unique data 1763 reflections ($I > 1.0\,\sigma(I)$) used for refinement. Empirical absorption correction based on ψ scan data was applied to the data set, $\mu = 111.2$ cm^{-1}. Data were corrected for extinction effects, Larson's extinction parameter: 45.34. The structure was solved using the Patterson method (SHELXS-86 [24]) and refined using standard difference Fourier techniques (CRYSTALS [25]). All hydrogen atoms could be found and were refined isotropically. 178 parameters refined, 9.9 data per parameter, weighting scheme of Tukey and Prince [26] with three refined parameters: $p1 = 1.01$; $p2 = 0.265$; $p3 = 0.759$, shift/error < 0.001 in the last cycle, $\mathrm{R} = \sum(||F_o| - |F_c||)/\sum|F_o| = 0.030$, $Rw = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2} = 0.033$, residual electron density: max. $+1.6$ e Å^{-3} at 0.99 Å from Os1, min. -1.5 e Å^{-3}.

Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein Leopoldshafen (Germany), on quoting the depository numbers CSD-380098–380101 (**10**, **13**, **15** and **19**, respectively) and CSD-59066 (**5**).

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