Heterocyclic Carbenes:[+] A High-Yielding Synthesis of Novel, Functionalized N-Heterocyclic Carbenes in Liquid Ammonia**

Wolfgang A. Herrmann,* Christian Köcher, Lukas J. Gooßen and Georg R. J. Artus

Abstract: To date the only free carbenes of the imidazoline-2-ylidene type to have been described in the literature are those bearing simple hydrocarbon or haloalkyl and -aryl substituents. We report here a novel, versatile and high-yielding method for the synthesis of N-heterocyclic carbenes in a mixture of liquid ammonia and aprotic organic solvents. Deprotonation of the imidazolium precursor salts proceeds under mild conditions within a few minutes at temperatures below $-30\,^{\circ}C$, and side reactions are thus avoided. The imidazolium salts are much more soluble in organic solvents if liquid ammonia is added. Furthermore, the acidity of the C-2 protons appears to be enhanced by hydrogen bonding. Not only are the known free ylidenes conveniently and quantitatively accessible by this procedure, but also novel functionalized derivatives that are not accessible by known procedures. Imidazoline-2-ylidenes with linear, branched, cyclic, heteroatom-substituted (O, N, P) and chiral hydrocarbon residues are accessible through the novel route. Stable carbene–metal "adducts" are conveniently obtained by treating the free carbenes with chloro- or acetato-bridged dinuclear metal complexes, or by displacement of coordinated ligands such as carbon monoxide, THF or acetonitrile by the free carbenes. The syntheses of novel imidazolium salts, N-heterocyclic carbenes and carbene adducts of Ru^{II}, Rh^{I}, W^{0} and sulfur are reported, and the structures of five products analysed by single-crystal X-ray diffraction. N-Heterocyclic carbenes bearing functionalized side chains are important because a number of these complexes show excellent activity in catalytic reactions. They do not show the typical reactivity of metal–carbon "double bonds" and are remarkably stable both thermally and chemically. For a number of reasons, they are best viewed as donor adducts of the highly Lewis *basic* imidazoline-2-ylidene ligands and the Lewis *acidic* organometallic fragments. The new synthetic procedure reported here makes N-heterocylic carbenes a generally accessible class of useful ligands in coordination chemistry and catalysis.

Keywords
carbenes · heterocycles · ligand design · structure elucidation · transition metal complexes

Introduction

In 1968 Wanzlick and Öfele discovered an interesting class of metal–carbene complexes. They found that heterocyclic carbenes derived from imidazolium and pyrazolium salts form extraordinarily stable complexes with certain transition metals; the syntheses of the complexes pentacarbonyl(1,3-dimethylimidazoline-2-ylidene)chromium(0) and bis(1,3-diphenylimidazoline-2-ylidene)mercury(II) diperchlorate landmarked this discovery.[1, 2] Both Wanzlick and Öfele took advantage of the acidic proton in the imidazolium salts when using them as precursor compounds for metal complexation (e.g., with the nucleophilic carbonylchromate $[Cr(CO)_5H]^-$ or mercury(II) acetate). It was Wanzlick who first used strong bases, such as potassium *tert*-butylate, aiming at metal–carbene complexes,[1] but he did not isolate free carbenes. The latter were discovered as unexpectedly stable compounds by Arduengo et al. in 1991[3] and have been used to prepare metal complexes ever since.[4] In these complexes, the metal–carbon bond is much less reactive than in Fischer- or Schrock-type carbene complexes. The extent of the double-bond contributions is negligible; instead, strong σ-donor bonds are characteristic for this class of metal "carbenes". On account of this stability of the metal–carbon bond, the imidazoline-2-type complexes were outshined by the Fischer- and Schrock-type complexes[5] with their reactive metal–carbon bonds and manifold applications.

We have shown that 1,3-disubstituted imidazoline-2-ylidenes coordinate to transition metals in low and high oxidation states (e.g., Cr^{0}, Mo^{0}, W^{0}, Fe^{0}, Re^{I}, Mn^{I}, V^{II}, Ti^{IV}, Zr^{IV}, Hf^{IV}, Nb^{IV}, Ta^{IV}, Re^{VII},[6a] Mo^{VI} and W^{VI}).[6b] The N-heterocyclic ligand acts as a very strong Lewis base; π-backdonation is not really required, since even Be^{2+} forms an ionic complex with three imidazoline-2-ylidene ligands.[7] Recently we reported several transition Group 8 complexes of Ru^{II}, Os^{II}, Rh^{I}, Ir^{I} and Pd^{II}.[8]

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[**] Heterocyclic Carbenes, Part 6. Part 5: ref. [8].

[+] Carbenes are defined as "divalent" carbon compounds. More precisely, the carbene carbon atom is linked to two adjacent groups by covalent bonds and has two non-bonding electrons with antiparallel spins (singlet state) or parallel spins (triplet state). In other compounds with formally "divalent" carbon (e.g., carbon monoxide, isocyanides), resonance stabilization of the "divalent" carbon by neighbouring groups is rather strong [5j]. The term carbene, conceived by Doering, Winstein and Woodward, seems well suited to describe the class of compounds under discussion, but conflicts with the alkylidene nomenclature of the International Union of Pure and Applied Chemistry (IUPAC). The metal–carbene nomenclature was introduced by E. O. Fischer [5c–i] and has become common in the organometallic literature.

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They are thermally and chemically extremly stable and serve as pre-catalysts for a number of homogeneous reactions, for example, Heck-type olefination (Pd^0),[9] isomerization, hydroformylation, hydrosilylation (Rh^I) and ring-opening metathesis polymeriz[illegible] lidenes resemble trialkylphosphines with respect to their metal bonding, as shown by force constant analysis of the IR data of metal carbonyl derivatives such as $(CO)_4FeL$ (L = carbene).[11]

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Carbene-stabilized organometallic catalysts promise a number of advantages over the conventional systems stabilized by phosphine or phosphite ligands: transition Group 8 metal–carbene complexes are often remarkably stable towards oxygen and moisture. In the course of our investigations, a dissociation of the carbene ligands was never observed; no excess of ligand is thus required, and immobilization of the ligand (in an aqueous phase or on polymers) appears to be realistic. Chiral carbene ligands are likely to bring about asymmetric induction. Functionalization of the sterically not very demanding carbene core with a donor group is very desirable, since the complex of this ligand would contain both a stable carbon–metal bond and a hemilabile metal–donor bond. Species with free coordination sites can thus be stabilized in a catalytic cycle.

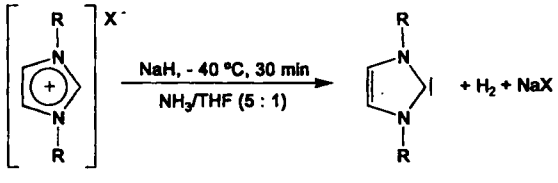
In this paper we report on a straightforward and high-yielding synthetic route to conventional, hydrocarbon-substituted "carbenes" based on imidazoles, as well as to novel functionalized and potentially chelating carbenes. Many of them are not accessible by known methods, such as deprotonation of imidazolium salts in organic polar solvents or desulfurization of thiourea derivatives.[12]

Abstract: *Freie Carbene des Imidazolin-2-yliden-Typs sind bislang lediglich mit einfachen Kohlenwasserstoffresten oder halogenierten Alkyl- oder Arylresten bekannt. Wir beschreiben eine neue, leistungsfähige Methode zur Synthese N-heterocyclischer Carbene in einer Mischung aus flüssigem Ammoniak und einem aprotischen organischen Lösungsmittel. Die Deprotonierung der Imidazoliumsalz-Vorstufen erfolgt schonend ohne Nebenreaktionen innerhalb weniger Minuten bei Temperaturen unterhalb −30 °C. Imidazoliumsalze sind in Gegenwart von flüssigem Ammoniak viel besser in organischen Lösungsmitteln löslich. Darüber hinaus scheint die Acidität der C-2-Protonen durch Wasserstoffbrücken erhöht zu sein. Durch dieses Vorgehen sind bekannte sowie neuartige, funktionalisierte Derivate von freien Carbenen problemlos in quantitativen Ausbeuten zugänglich. Imidazolin-2-ylidene mit unverzweigten, verzweigten, cyclischen, heteroatomsubstituierten (O, N, P) und chiralen Kohlenwasserstoffresten sind über diesen neuen Weg erhältlich. Stabile Carben-Metall-"Addukte" werden auf einfache Weise durch Umsetzung der freien Carbene mit chlor- und acetatverbrückten zweikernigen Metallkomplexen oder durch Verdrängung koordinierter Liganden, wie Kohlenmonoxid, THF oder Acetonitril, durch die freien Carbene erhalten. Wir berichten über die Herstellung neuartiger Imidazoliumsalze, N-heterocylischer Carbene und Carbenaddukte von Ru^{II}, Rh^I, W^0 und Schwefel sowie über fünf Röntgenstrukturanalysen. N-heterocyclische Carbene mit funktionalisierten Resten sind wichtig, da sich eine Reihe von Komplexen durch hervorragende Aktivitäten in katalytischen Reaktionen auszeichnen. Diese Komplexe weisen nicht die typische Reaktivität einer Metall-Kohlenstoff-"Doppelbindung" auf, sind sowohl thermisch als auch chemisch bemerkenswert beständig und sind als Donoraddukte zwischen den Lewis-basischen Imidazolin-2-yliden-Liganden und Lewis-sauren Organometall-Fragmenten zu betrachten. Das beschriebene neue Syntheseverfahren läßt N-heterocyclische Carbene zu einer allgemein zugänglichen Klasse nützlicher Liganden für die Koordinationschemie und für die Katalyse werden.*

Results and Discussion

Why liquid ammonia? Imidazolium salts are heteroaromatic, ionic compounds, which can be deprotonated by strong bases such as potassium *tert*-butylate, NaH or *n*-butyllithium to give N-heterocyclic carbenes. However, no common organic solvent is inert towards free carbenes under conditions that allow a smooth and *rapid* deprotonation. Imidazolium salts are normally suspended in THF, and a soluble base is added in stoichiometric or catalytic amounts together with an insoluble base. The prolonged reaction times required entail thermal decomposition. Although we prepared a broad variety of rhodium and iridium carbene complexes of the imidazole, triazole, benzimidazole and pyrazole type in *ethanol* following a one pot synthesis, the intermediate formation of free carbenes could be ruled out in these particular cases.[13a] 1,3-Dialkylimidazole-2-thiones are also accessible in ethanol from imidazolium salts and sulfur in the presence of a base, but in this case the imidazolium salt should not be in contact with the base in the absence of sulfur.[13b]

Generation of free N-heterocyclic carbenes in mixtures containing liquid ammonia has many advantages. We found that imidazolium salts are much more soluble in mixtures containing liquid ammonia than in organic solvents alone. Liquid ammonia is an excellent solvent for singly-charged ionic or aromatic compounds. It enables hydrogen bonding and has a dielectric constant of 16.9. With an autosolvolysis constant of 10^{-32} it is proton-inactive; numerous (metal) organic reactions are conveniently performed in liquid ammonia. Deprotonation of dissolved imidazolium salts in NH_3/THF or NH_3/acetonitrile (typically 5:1) using stoichiometric amounts of NaH or $K[NH_2]$ yields the free carbenes *within minutes at about −30 °C* (Scheme 1). Methylamine may be employed instead of liquid



Scheme 1. Rapid deprotonation of imidazolium salts in liquid ammonia.

ammonia in syntheses on a larger scale. In contrast to triazole-derived carbenes, which insert into O–H and N–H bonds, imidazoline-2-ylidenes are stable towards NH_3.[13c]

After the ammonia has been removed in vacuo, very pure carbenes are obtained as THF or acetonitrile solutions. In order to remove the alkaline halide, which is the only solid by-product, the imidazoline-2-ylidene solution thus obtained is filled with diethyl ether or *n*-hexane to a calibration mark to give a specific solvent volume. After filtration through a cannula, the carbenes can be used immediately for synthesis of the complexes. Alternatively, the carbenes can be crystallized from *n*-hexane and stored at −30 °C for months. The carbene ligands **1a–8a** and **11a** were used for synthesis of the complexes (Table 1).

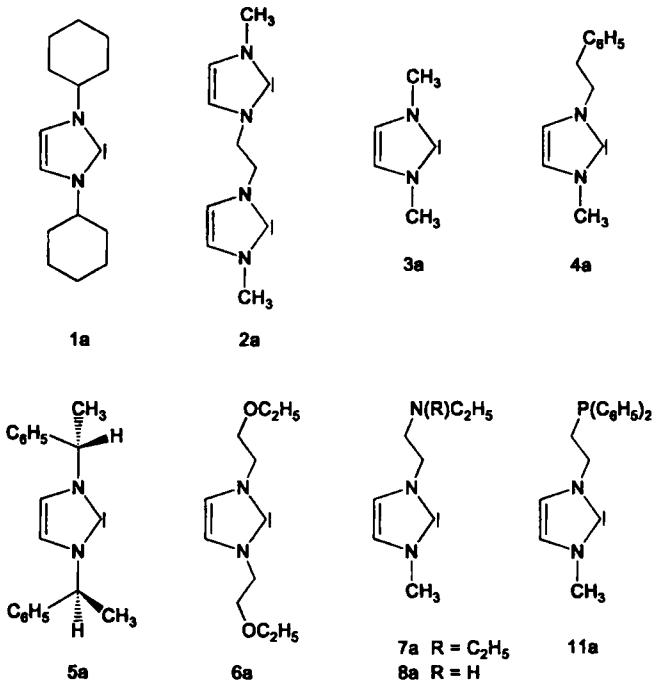
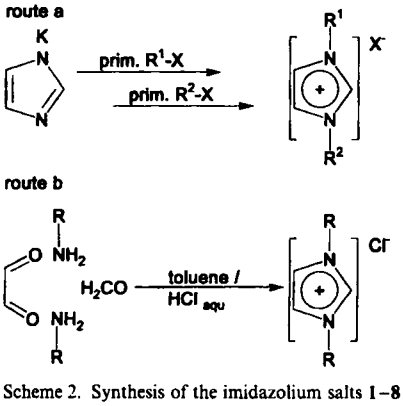


Table 1. ^{13}C NMR data (100 MHz, THF) of N-heterocyclic carbenes synthesized in liquid ammonia.

	Route [a]	$\delta(C_{Carbene})$	δ(NCHCHN)
1a	b	210.1	115.7
2a	a	215.9	119.7, 120.3
3a	a	215.1	120.6
4a	a	214.2	122.3, 122.4
5a	b	211.2	117.8
6a	a	n.o. [b]	119.3
7a	a	210.0	119.1
8a	a	n.o. [b]	120.8, 120.6

[a] See Scheme 2. Route a: quarternization of *N*-alkylated imidazole; Route b: ring-closure synthesis. [b] Not observed, because of low solubility in organic solvents (THF/CD_3NO_2 inlet, $THF/CH_3CN/CD_3NO_2$ inlet, respectively).

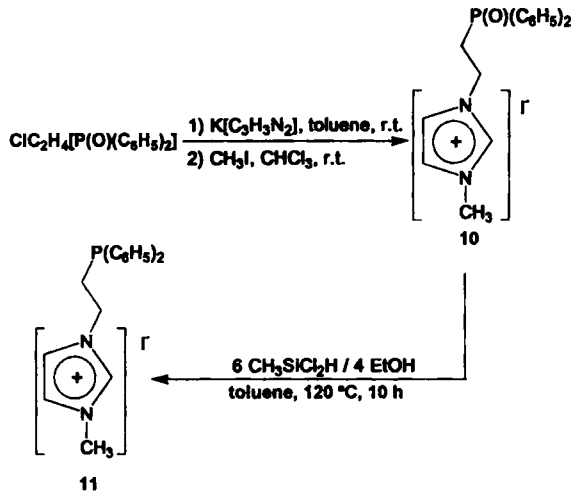
Imidazolium salt syntheses: The imidazolium salts **1**–**8** and **11** employed here were prepared by two different methods, starting from alkyl halides and alkyl amines, respectively (Scheme 2). In route (a) the potassium salt of imidazole was first treated with a primary alkyl halide at elevated temperatures in a nonpolar solvent, such as toluene, to avoid elimination.[14] The resulting N-alkylated imidazoles were then quaternized by a second



Scheme 2. Synthesis of the imidazolium salts **1**–**8** and **11**.

equivalent of alkyl halide in a polar solvent such as chloroform, 2-propanol or dimethylacetamide. In the case of asymmetrically-substituted imidazolium salts (**2**, **4**, **7** and **8**), *N*-methylimidazole was used in a straightforward manner. However, in the preparation of imidazolium salts with *N*-functionalized side chains (**7** and **8**), *N*-methylimidazole was treated with 2-(diethylamino)ethyl chloride hydrochloride and 2-(ethylamino)ethyl chloride hydrochloride, respectively. In order to remove the protecting hydrochloride and to generate the free carbenes in liquid ammonia, two equivalents of base were required.

1,3-Dimethylimidazoline-2-ylidene was found to be stable in THF solution when triphenylphosphine was present. Since no fragmentation of the carbene or generation of phosphorus ylides was observed after several days, we endeavoured to prepare potentially chelating carbene phosphines (Scheme 3): Imidazole was first alkylated at room temperature with phosphine oxides or sulfides, such as 2-(diphenylphosphoryl)ethyl



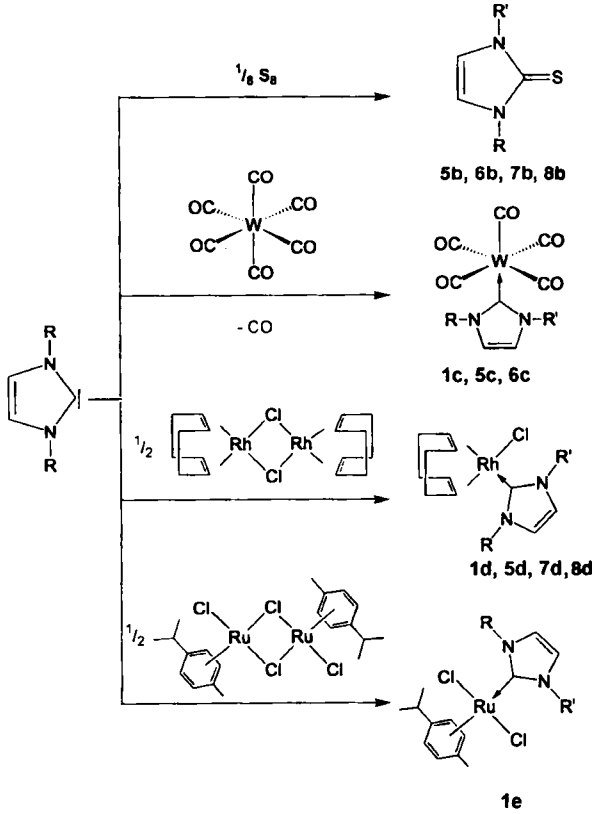
Scheme 3. Synthesis of imidazolium salt **11**.

chloride, to yield **9**. N-quaternization with iodomethane produced **10**. We first tried to reduce the phosphoryl group with methyldichlorosilane or diphenylsilane in toluene. No reaction was observed until we used a sample of **10** that had been recrystallized from ethanol and contained one equivalent of ethanol. Thereafter, smooth reduction of phosphorus in the presence of the imidazolium group was achieved in toluene by using methyldichlorosilane/ethanol (i.e., methylethoxysilanes). Complexes with carbene phosphine **11a** were most conveniently obtained by treating imidazolium phosphine **11** with a dinuclear metal complex, such as bis[μ-chloro-(η^4-1,5-cyclooctadiene)-rhodium(I)], to yield phosphine complexes, such as iodo(η^4-1,5-cyclooctadiene)[1-methyl-3-(diphenylphosphino-1,2-ethyl)-imidazolium chloride)]rhodium(I) (**12**); the imidazolium salt residue was then deprotonated with a noncoordinating base. As COD complexes with **11a** often show fluctional behaviour, it is advantageous to convert them into cationic or carbonyl complexes.[10]

Route (a) (Scheme 2) only worked satisfactorily for primary alkyl halides. For secondary or tertiary alkyl halides elimination was found to be a serious side reaction. In order to introduce two identical residues branched in an α-position into the imidazolium core, route (b) was employed:[15] two equivalents of a primary amine were condensed with aqueous glyoxal (the trimer is not sufficiently reactive) and paraformaldehyde at a pH of

about 3. The two methods complement one another: whereas 1,3-dicyclohexylimidazolium chloride (**1**) and 1,3-di-[(*S*)-1′-phenylethyl]imidazolium chloride (**5**) could not be obtained by route (a) from the corresponding alkyl halides, route (b) worked well. In compound **5** the chirality of the amine is expected to be maintained. X-ray structure analyses of complexes of the carbene **5a** all show the correct absolute configuration.

Synthesis of metal complexes: Halide- or acetate-bridged dinuclear complexes are excellent starting compounds for the synthesis of late transition metal carbene adducts. The extremely Lewis-basic free carbenes open their own coordination site by cleaving the dinuclear complexes. If an excess of carbene or a sterically not very demanding carbene (e.g., **3a**) is employed, the monocarbene adducts can react further. Dicarbene complexes or mixtures of both may then be formed. The transition metal complexes we reported recently mainly derive from **3a** and **2a**.[8] So far we have not been able to isolate the potentially chelating dicarbene ligand 1,1′-(methylene)-3,3′-dimethylimidazoline-2-ylidene in liquid ammonia/THF. In this case the protons of the methylene bridge seem to be too acidic. However, selective deprotonation of imidazolium salts in the presence of benzylic protons is possible in liquid ammonia/THF (e.g., in the generation of the imidazoline-2-ylidenes **4a** and **5a**). With a stoichiometric amount of a sterically more demanding imidazoline-2-ylidene (e.g., 1,3-dicyclohexyl derivative **1a**), immediate and selective adduct formation is achieved. Apart from anion-bridged dinuclear complexes, transition metal carbonyl complexes and solvent adducts (THF, acetonitrile) are useful precursors of carbene complexes. In addition to their Lewis-basic character, N-heterocyclic carbenes show nucleophilic reactivity. For example, the reaction of free carbene with elementary sulfur yields the corresponding thiourea derivative (Scheme 4).



Scheme 4. Reactions of the free carbene. R = R′ = cyclohexyl (**1**), (*S*)-1-phenylethyl (**5**) and 2-ethoxyethyl (**6**); R = methyl, R′ = diethylaminoethyl (**7**); R = methyl, R′ = ethylaminoethyl (**8**).

Reactions of 1,3-dicyclohexylimidazoline-2-ylidene (1a): As we are interested in catalytically active Group 8 complexes, we first endeavoured to vary the carbene substituents in their steric properties. The reaction of **1a** with hexacarbonyltungsten in THF yielded **1c** as a model complex (Scheme 4). The yellow solid is soluble in polar organic solvents such as methylene chloride, chloroform and nitromethane. When a stoichiometric amount of a solution of **1a** in THF or *n*-hexane was added to the chloro-bridged complex bis[μ-chloro-(η^4-1,5-cycloocatadiene)-rhodium(I)] dissolved in THF, **1d** was formed within a few minutes. A side reaction of **1d** with **1a** was not observed. Complex **1d** is a yellow solid, which is stable towards air and moisture and soluble in polar organic solvents. The complex bearing an acetato group instead of the chloro ligand was obtained from the corresponding acetato-bridged dimer. The cycloocatadiene ligand was readily displaced under an atmosphere of carbon monoxide. Reaction of bis{(μ-chloro)chloro[η^6-(isopropyl)-(4-methyl)benzene]ruthenium(II)} with **1a** yielded **1e** as reddish-brown solid.

The crystal and molecular structures of **1c**, **1d** and **1e** (Figs. 1–3) were determined by means of single-crystal X-ray diffraction analysis. Complex **1d** (Fig. 2) exhibits the same geometry as chloro(η^4-1,5-cyclooctadiene)(1,3-dimethylimidazoline-2-ylidene)rhodium(I) (**3d**),[8] and the angle between the coordination sphere and the imidazoline ring is again nearly 90°. In **3d** the methyl groups almost lie in the plane of the carbene ring. On account of the greater steric interaction between the cyclooctadiene ligand and the cyclohexyl groups, the carbon atoms C2 and C10 in **1d** deviate from the best-plane of the ring by 0.19 and 0.16 Å, respectively.

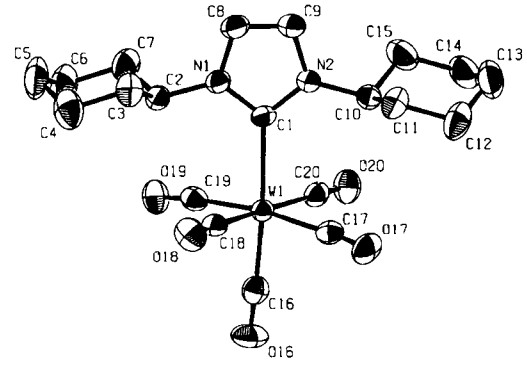


Fig. 1. PLATON plot [33] of the crystal and molecular structure of **1c**. Ellipsoids are drawn at the 50% probability level; hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): W1–C1 = 2.282(3), N1–C1 = 1.370(4), N1–C8 = 1.374(5), N2–C1 = 1.354(4), N2–C9 = 1.394(5), C8–C9 = 1.342(6); C8-N1-C1 = 111.4(3), C9-N2-C1 = 111.2(3), N2-C1-N1 = 103.7(3), C9-C8-N1 = 107.1(3), C8-C9-N2 = 106.6(3).

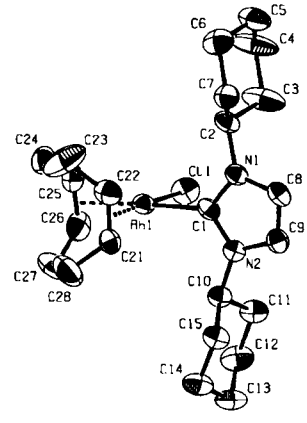


Fig. 2. PLATON plot [33] of the crystal and molecular structure of **1d**. Ellipsoids are drawn at the 50% probability level; hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Rh1–C1 = 2.021(4), N1–C1 = 1.356(5), N1–C8 = 1.392(5), N2–C1 = 1.365(5), N2–C9 = 1.383(5), C8–C9 = 1.328(6); C1-N1-C8 = 110.9(3), C1-N2-C9 = 110.3(3), N1-C1-N2 = 104.4(3), N1-C8-C9 = 106.7(3), N2-C9-C8 = 107.8(4).

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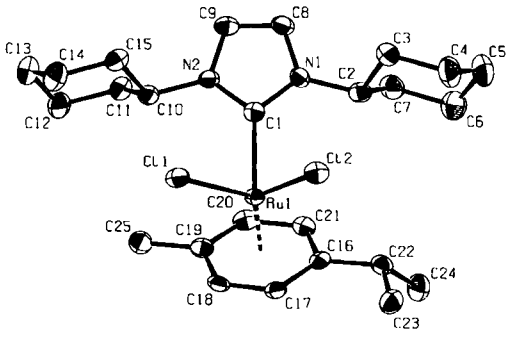


Fig. 3. PLATON plot [33] of the crystal and molecular structure of **1e**. Ellipsoids are drawn at the 50% probability level; hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°) (Cg is the centroid of the *p*-cymene ligand): Ru1–Cl1 = 2.4360(7), Ru1–Cl2 = 2.4181(7), Ru1–C1 = 2.093(3), Ru1–Cg = 1.695(2), N1–C1 = 1.359(4), N1–C8 = 1.374(4), N2–C1 = 1.358(4), N2–C9 = 1.379(4), C8–C9 = 1.327(4); Cl1-Ru1-Cl2 = 84.97(2), Cl1-Ru1-C1 = 90.47(8), Cl2-Ru1-C1 = 89.55(8), Cl1-Ru1-Cg = 126.53(5), Cl2-Ru1-Cg = 126.04(5), C1-Ru1-Cg = 126.63(9), C1-N1-C8 = 110.5(2), C1-N2-C9 = 110.9(2), N1-C1-N2 = 104.1(2), N1-C8-C9 = 107.7(3), N2-C9-C8 = 106.7(3).

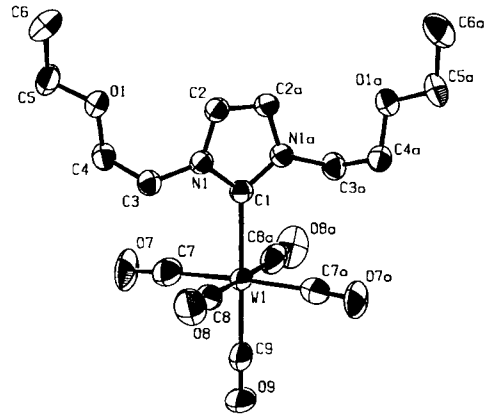


Fig. 4. PLATON plot [33] of the crystal and molecular structure of **6c**. Ellipsoids are drawn at the 50% probability level; hydrogen atoms omitted for clarity. Atoms marked "a" are produced by a twofold axis (1/2 − *x*, *y*, − *z*). Selected bond lengths (Å) and angles (°): W1–C1 = 2.274(5), N1–C1 = 1.361(5), N1–C2 = 1.382(5), C2–C2a = 1.336(8); C2-N1-C1 = 111.4(3), N1-C1-N1a = 103.5(4), C2a-C2-N1 = 106.9(2)

The ruthenium atom in complex **1e** is in a distorted tetrahedral environment (Fig. 3). Bond angles and lengths within the carbene ligand are as expected. Given the different coordination numbers, the distance Ru1–C1 (2.093(3) Å) is comparable to that in *trans*-dichlorotetrakis(1,3-diethylimidazoline-2-ylidene)-ruthenium(II) (2.098(9)–2.111(9) Å);[16] Ru^{II}–methyl bond lengths in tetrahedral complexes are approximately 0.07 Å longer.[17] The Ru–$C_{carbene}$ bond length in **1e** compares well with the Ru^{II}–C_{aryl} bond lengths in tetravalent complexes. Here, the distances vary from 2.077(6) to 2.123(4) Å.[18] The centroid of the *p*-cymene ligand is shifted by 0.05 Å away from the perpendicular projection of the metal onto the ring and away from the carbene ligand. Additionally, the cymene ligand is rotated about the bond between the ruthenium and the *p*-cymene ligand so as to minimize steric interactions between the cyclohexyl substituents of the carbene and the isopropyl group. This results in different intramolecular distances for C25–C10 (3.566(5) Å) and C22–C2 (4.111(5) Å).

Reactions of 1,3-bis(2-ethoxyethyl)imidazoline-2-ylidene (6a): In order to introduce the concept of hemilabile chelating donor ligands to imidazoline-2-ylidenes, we prepared O-, N- and P-functionalized imidazolium salt precursors. For reasons of accessibility and based on geometric considerations, we employed heteroatom substituents spaced by an ethylene group. Deprotonation of **6** to **6a** proceeded smoothly in liquid ammonia/THF. Ethoxyethyl ligand **6a** also serves as a model compound for polyether-substituted "smart" ligands, which allow phase separation in homogenous catalysis by a simple temperature adjustment. Reaction of **6a** with elementary sulfur or hexacarbonyltungsten yielded **6b** and **6c**, respectively (Scheme 4). In **6c** the two ethoxyethyl residues do not coordinate to tungsten. Irradiation of **6c** might possibly lead to displacement of another carbon monoxide ligand.

The crystal and molecular structures of **6c** were determined by means of single-crystal X-ray diffraction (Fig. 4). The two tungsten complexes **6c** and **1c** exhibit the same geometries. The planar carbene ligand adopts a staggered conformation relative to the $W(CO)_4$ plane. Due to the steric demand of the carbene ligand, the four carbonyl groups in the equatorial plane are slightly bent toward the fifth carbonyl ligand; this results in an "umbrella-like" structure for the pentacarbonyltungsten fragment. The imidazoline ring geometries are very similar in all complexes and show no clear differences to the free carbenes[3] and to pentacarbonyl(1,3-dimethylimidazoline-2-ylidene)-tungsten.[19] Compared to $W(CO)_6$, the average W–CO bond lengths are shorter, whilst the CO bond lengths are longer.[20] This effect is most distinct in the carbonyl groups *trans* to the carbene.

The distances W–$C_{carbene}$ are about 0.11 Å longer than the corresponding distances in Fischer-carbene complexes. For example, the average bond length found for complexes of the type pentacarbonyl[alkyl(alkoxy)carbene]tungsten is 2.161 Å.[21] The W–$C_{carbene}$ bond should therefore be considered as a "single bond", although it is otherwise difficult to assign bond orders that correlate with the distances, because of the large differences found for the tungsten–methyl bonds in hexacoordinated complexes—they vary from 2.131(10) to 2.313(17) Å.[22]

Reactions of 1,3-di[(*S*)-1′-phenylethyl]imidazoline-2-ylidene (5a): We wanted to investigate whether racemization takes place under the basic conditions of carbene generation before synthesizing more complex chiral structures. The imidazolium chloride **5** was synthesized as the precursor for the first chiral imidazoline-2-ylidene. After deprotonation, only *one* set of signals was observed in the ^{13}C NMR spectrum indicating that only *one* diastereomer of **5a** had been produced. The solution obtained was treated with sulfur, hexacarbonyltungsten and bis[μ-chloro-(η^4-1,5-cylooctadiene)rhodium(I)] (Scheme 4). The NMR spectra of the carbene adducts **5b–d** all show only single sets of signals for the ligand. In the case of the rhodium complex **5d**, NMR spectroscopy shows all the carbon atoms to be inequivalent and indicates that there is no rotation about the Rh–C axis. This is probably only due to steric hindrance rather than to some double-bond character of the metal–carbene bond. In order to provide stronger evidence that no racemization had taken place, a single-crystal X-ray diffraction study of the thiourea derivative **5b** was performed (Fig. 5). The structure shows only the (*S*,*S*) enantiomer. The catalytic properties of metal complexes with chiral ligands of this type are presently being investigated by our group. Indeed, preliminary results indicate a chiral induction in some catalytic reactions.[23]

The structure of the chiral thiourea **5b** contains no unexpected features. The molecule lies on a crystallographic 2-fold axis

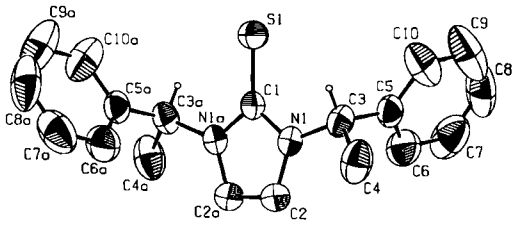


Fig. 5. PLATON plot [33] of the crystal and molecular structure of **5b**. Ellipsoids are drawn at the 50% probability level; uninteresting hydrogen atoms omitted for clarity. Atoms marked "a" are produced by a twofold axis ($y, x, -z$). Selected bond lengths (Å) and angles (°): S1-C1 = 1.671(4), N1-C1 = 1.363(3), N1-C2 = 1.385(4), N1-C3 = 1.465(4), C2-C2a = 1.342(7); C1-N1-C2 = 110.1(3), S1-C1-N1 = 127.4(2), N1-C1-N1a = 105.3(3), N1-C2-C2a = 107.3(2).

through the sulfur–carbon bond. All bond lengths and angles are similar to those found in 1,3-dimethyl-2-thioimidazoline.[24] In addition, the ring systems with the corresponding seleno and telluro compounds[25] reveal no significant differences. The slightly longer C=C bonds in these two compounds might well be a consequence of the additional methyl groups in the position 4 and 5 of the imidazoline ring.

The absolute configuration of the chiral molecule could be determined by refinement of both enantiomers. The refinement of the (*S,S*) enantiomer in the space group $P4_32_12$ converged at $R = 3.55\%$, $R_w = 3.58\%$ and a Flack parameter of 0.01(17). Refinement of the (*R,R*) enantiomer in the space group $P4_12_12$ gives R values of $R = 3.63\%$ and $R_w = 3.65\%$, and the Flack parameter is 1.07(17). The molecule in the crystal is therefore the (*S,S*) enantiomer.

Reactions of 1-(2-diethylaminoethyl)-3-methylimidazoline-2-ylidene (7a): The imidazolium salt **7** was synthesized as a precursor to a donor-functionalized carbene. Deprotonation proceeded smoothly, producing a colourless solution of **7a** in THF. This solution was treated with sulfur and bis[μ-chloro(η^4-1,5-cyclooctadiene)rhodium(I)] (Scheme 4). Reaction with hexacarbonyltungsten gave a mixture of several products, none of which was completely characterized. The most striking feature of the NMR spectra of **7d** is that all the protons of the ethylene bridge between imidazole and amine are clearly separated. This was not observed in the case of other asymmetric carbene ligands. Thus, it appears likely that the diethylamino group coordinates to the rhodium in an axial position. A crystal structure is clearly needed to provide further information about the geometry of this compound.

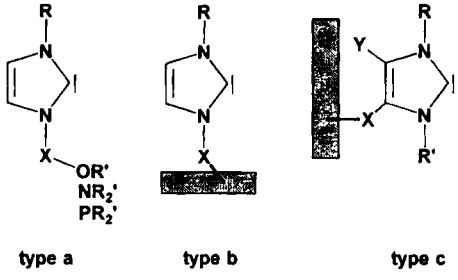
Reactions of 1-(2-ethylaminoethyl)-3-methylimidazoline-2-ylidene (8a): The imidazolium salt **8** is the only precursor with an unprotected functional group. Surprisingly, the deprotonation proceeded without side reactions. In this case acetonitrile was used as a cosolvent because compound **8a** was not soluble enough in THF. It is remarkable that the acetonitrile was not deprotonated by the excess sodium hydride under these conditions. The solution of **8a** was treated with both sulfur and bis[μ-chloro(η^4-1,5-cyclooctadiene)rhodium(I)] leading to almost clean products **8b** and **8d**, respectively. The reaction with hexacarbonyltungsten was not successful, probably due to partial formation of acetonitrile adducts, so that numerous different compounds were produced.

Successful experiments have already been performed to treat the NH functionality of **8b** and **8d** with acid derivatives. Even polymer-fixed acid chlorides reacted successfully with **8b**.[26]

Conclusion

The methodology described in this publication provides a firm base from which a wide range of N-heterocyclic carbenes can be accessed. While derivatives of the imidazole type are now amply documented, other subclasses will follow, such as carbenes of the pyrazole and the triazole series. The major advantages of the new synthesis are the mild reaction conditions and, consequently, the high product yields. Furthermore, the procedure is straightforward to perform owing to the ideal properties of the solvent ammonia.

Considering the recent success in Heck coupling reactions,[9] we expect that N-heterocyclic carbenes will have a broad range of applications in organometallic catalysis. This assessment is based upon both the compatibility of this class of two-electron ligands with practically all metals in various oxidation states[6] and their potential for systematic variation in the N-substitution pattern: functionalized groups can be introduced with the aim of synthesizing chelating O-, N- and P-carbene ligands of type **a** (Scheme 5);[26] in addition, immobilized ligands of general type **b** and **c** might be useful in heterogeneous metal–carbene catalysis,[9] since the bonding of N-heterocyclic carbenes to transition metals, such as palladium and rhodium, is normally very strong.



Scheme 5.

The first chiral imidazoline-2-ylidene has been introduced in the present paper (compound **5a**), and this area warrants further extension in view of the recent success in enantioselective hydrosilylation.[23] We strongly believe that N-heterocyclic carbenes will successfully compete with phosphines, which were hitherto the most established class of ligands in homogeneous catalysis.[9] Further work in this area is in progress.

Experimental Procedure

General techniques: Oxygen-sensitive, moisture-sensitive or hygroscopic materials were handled under purified nitrogen or purified argon by standard Schlenk line techniques. All solvents were degassed and dried by standard procedures unless used for extractions. [D_6]Acetone, [D_3]nitromethane, [D_6]dimethylsulfoxide and $CDCl_3$ were stored over 3 Å molecular sieves.

Instrumentation: ^1H and ^{13}C NMR spectra were recorded on Jeol-JMX-GX-400 or Bruker amx400 instruments with the solvent resonance as internal standard. Infrared spectra were obtained using the Perkin Elmer 1650 Fourier transform IR spectrometer with CaF_2 cells. GC-MS were obtained on a Hewlett Packard 5890 instrument. All other mass spectra were measured in the mass spectrometry laboratory of our institute on a Finnigan MAT90 mass spectrometer using either FAB (xenon/*p*-nitrobenzyl alcohol) or CI (isobutane) technique. All elementary analyses were performed in the microanalytical laboratory of our institute.

1,3-Dicyclohexylimidazolium chloride (1): A 500 mL round-bottomed flask was charged with cyclohexylamine (9.92 g, 100 mmol) in 100 mL of toluene, and paraformaldehyde (3.0 g, 100 mmol) was added under intense stirring. After 30 min at room temperature the flask was cooled to 0 °C and another equivalent of cyclo-

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hexylamine (9.92 g, 100 mmol) was added. After 10 min at 0 °C, 3.3 M aqueous HCl (30 mL, 100 mmol) was added dropwise to the cooled mixture. The solution was allowed to warm to room temperature and 40% aqueous glyoxal (145 mL, 100 mmol) was slowly added. The resulting cloudy mixture was stirred for 12 h at 50 °C. After the mixture had cooled, 100 mL ether and 50 mL saturated Na_2CO_3 solution were added, and the layers separated. The aqueous layer was washed three times with 100 mL portions of ether. The volatiles were removed in vacuo, and the residue extracted with 150 mL CH_2Cl_2, dried over $MgSO_4$ and subsequently filtered. After removal of the solvents, the solid residue was broken down to a white hygroscopic powder by treatment with ether. The overall yield of **1** was 20.9 g (75%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.43 (s, 1H, NCHN), 7.41 (m, 2H, NCH), 4.33 (m, 2H, R_3C–H), 1.0–2.0 (overlapping multiplets, 20H, cyclohexyl CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.9 (N_2C–H), 119.7 (C–H), 59.3 (H–CR_3), 33.1(CH–CH_2), 24.5 (2CH_2), 24.2 (CH_2); MS (FAB): m/z = 501.4 ([$M^+ + M$ – Cl], 6.4), 233 ([M^+ – Cl], 100)

1,1′-(1,2-Ethylene)-3,3′-dimethyldiimidazolium dibromide (2): 1,2-Dibromoethane (5 mL, 58 mmol) and *N*-methylimidazole (9.25 mL, 116 mmol) were placed in a Schlenk tube, and 10 mL of methanol was added. The reaction mixture was heated to 80 °C for 2 h. At ambient temperature all volatile compounds were removed in vacuo yielding 18.5 g of the pure product. Yield: 92%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.85 (s, 6H, NCH_3), 4.77 (s, 4H, NCH_2), 7.42 (s, 2H, NCH), 7.47 (s, 2H, NCH), 9.29 (s, 1H, NCHN); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 36.0 (s, NCH_3), 48.2 (s, NCH_2), 122.8, 123.7 (s, NCH), 137.1 (NCHN).

1,3-Dimethylimidazolium iodide (3): *N*-Methylimidazole (21.3 mL, 267 mmol) was placed in a 500 mL round-bottomed flask and dissolved in 150 mL of 2-propanol. Iodomethane (17.3 mL, 280 mmol) was added at room temperature. The reaction mixture was then heated under reflux for 8 h and left to crystallize at room temperature. Crystalline **3** was filtered off, washed with 50 mL of both diethyl ether and THF and then dried in vacuo. Yield: 57 g (96%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.46 (s, 6H, CH_3), 7.10 (s, 2H, NCH_2CH_2N), 8.97 (s, 1H, NCHN); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 35.29 (s, CH_3), 121.85 (s, NCH_2CH_2N), 134.7 (s, NCHN).

1-Methyl-3-(2-phenylethyl)-imidazolium chloride (4): *N*-Methylimidazole (5.0 mL, 62.7 mmol) and 1-chloro-2-phenylethane (8.23 mL, 62.7 mmol) were placed in a round-bottomed flask and were heated without solvent to 140 °C for 18 h. The reaction mixture was then left at room temperature to crystallize. ^{1}H NMR (400 MHz, D_2O): δ = 2.95 (2H, CH_2Ph), 3.6 (3H, NCH_3), 4.3 (2H, NCH_2), 6.9 (2H, NCH), 7.0–7.2 (5H, Ph), 8.3 (s, 1H, NCHN); ^{13}C NMR (100 MHz, D_2O): δ = 35.75 (CH_2Ph), 35.82 (NCH_3), 50.91 (NCH_2), 122.34, 122.43 (NCH), 123.66, 127.48, 129.0, 129.17 (Ph), 137.04 (NCHN).

1,3-Di-[(*S*)-1′-phenylethyl]imidazolium chloride (5): This compound was prepared following the procedure for **1** from (*S*)-1-phenylethylamine on the same scale. The reaction tempeature was kept below 40 °C to avoid any isomerization of the intermediates. The product (24.5 g, 79%.) was obtained as a white hygroscopic powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.02 (s, 1H, N_2C–H), 7.37 (m, 2H, phenyl-CH), 7.28 (s, 2H, N–CH), 7.21 (m, 3H, phenyl-CH), 5.52 (q, ^3J(H,H) = 7 Hz, 2H, R_3C–H), 1.88 (d, ^3J(H,H) = 7 Hz, 6H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.9 (N_2CH), 135.9 (*p*-phenyl CH), 129.1 (phenyl CH), 129.0 (CR_3), 126.8 (phenyl CH), 120.5 (N–CH), 59.5 (N–CH–Ph), 20.45 (CH_3); MS (FAB): m/z = 589.2 ([$M^+ + M$ – Cl], 4.14), 277 ([M^+ – Cl], 100), 173 (13.6), 105 (43.8)

1,3-Bis(2-ethoxyethyl)imidazolium bromide (6): *N*-(2-Ethoxyethyl)imidazole (4.5 g, 39 mmol) was dissolved in 50 mL of THF, and a slight excess of 2-bromoethyl ethyl ether (7 g, 45 mmol) was added in one portion. The reaction mixture was refluxed for 12 h. During this time the formation of a second liquid phase could be observed. The solution was cooled to 0 °C, the upper layer was decanted and the lower layer was washed with small portions of THF. Removal of the volatiles produced **6** (7.2 g, 75%) as a yellow viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.91 (s, 1H, N_2C–H), 7.53 (d, ^3J(H,H) = 1 Hz, 2H, CH), 4.50 (t, ^3J(H,H) = 5 Hz, 4H, N–CH_2), 3.74 (t, ^3J(H,H) = 5 Hz, 2H, NCH_2CH_2), 3.44 (q, ^3J(H,H) = 7 Hz, 4H, O–CH_2), 1.08 (t, ^3J(H,H) = 7 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.5 (N_2C–H), 122.5 (NC–H), 67.9 (N–CH_2), 66.4 (NCH_2–CH_2), 49.8 (O–CH_2), 14.7 (CH_3); MS (FAB): m/z = 505 ([$M^+ + M$ – Br], 2), 213 ([M^+ – Br], 100).

1-(2-Diethylaminoethyl)-3-methylimidazolium chloride hydrochloride (7): 2-Diethylaminoethylchloride hydrochloride (8.6 g, 50 mmol) was dissolved in 50 mL of dry ethanol, and 1.2 equiv of *N*-methylimidazole (4.9 g, 60 mmol) was added. The solution was stirred for 12 h at 50 °C. The volatiles were removed in vacuo and the residue was washed with THF until it was no longer sticky. Removal of the volatiles produced **7** (108 g, 85%) as a white hygroscopic powder. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 9.56 (s, 1H, C–H), 8.05 (m, 1H, H–C=), 7.79 (m, 1H, =C–H), 4.69 (t, ^3J(H,H) = 6.5 Hz, 2H, N–CH_2), 3.84 (s, 3H, N–CH_3), 3.52 (t, 2H, ^3J(H,H) = 6.5 Hz, 2H, CH_2), 3.08 (q, ^3J(H,H) = 7 Hz, 4H, CH_2), 1.17 (t, ^3J(H,H) = 7 Hz, 6H, CH_3); ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 141.8 (C–H), 127.7 (H–C=), 126.4 (=C–H), 53.9 (imidazole–CH_2), 50.7 (N–CH_2), 47.5 (imidazole–CH_2–CH_2, 39.9 (imidazole–CH_3), 12.8 (CH_3); MS (FAB): m/z = 399 ([$M^+ + M$ – 2 HCl – Cl], 18), 182 ([M^+ – HCl – Cl], 100).

1-(2-Ethylaminoethyl)-3-methylimidazolium chloride hydrochloride (8): 2-Ethylaminoethylchloride hydrochloride (7.7 g, 50 mmol) in 50 mL ethanol was treated with 1.2 equiv of *N*-methylimidazole (4.9 g, 60 mmol). The reaction mixture was stirred for 16 h at 40 °C and then worked up in the same way as compound **7**. The product (9.3 g, 83%) was obtained as a white hygroscopic powder. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 9.31 (s, 1H, N_2C–H), 7.85 (m, 1H, N–CH), 7.71 (m, 1H, N–CH), 4.62 (t, ^3J(H,H) = 6 Hz, 2H, imidazole–CH_2), 3.82 (s, 3H, N–CH_3), 3.38 (t, ^3J(H,H) = 6 Hz, 2H, imidazole–CH_2–CH_2), 2.91 (q, ^3J(H,H) = 7 Hz, 2H, N–CH_2) 1.21 (t, ^3J(H,H) = 7 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, [D$_6$]DMSO): δ = 139.2 (N_2CH), 125.4 (N–CH), 124.1 (N–CH), 47.1 (imidazole-N–CH_2), 46.7 (N–CH_2CH_2), 43.8 (N–CH_2), 37.5 (N–CH_3), 12.4 (CH_3); MS (FAB): m/z = 343 ([$M^+ + M$ – Cl – 2 HCl], 18), 154 ([M^+ – Cl – HCl], 100).

***N*-(2-Diphenylphosphoryl)ethylimidazole (9)**: 1-Chloro-2-(diphenylphosphoryl)-ethane (^{31}P NMR (162 MHz, $CDCl_3$): δ = 29.0) was obtained from 1-chloro-2-(diphenylphosphino)ethane (^{31}P NMR (162 MHz, $CDCl_3$) δ = – 20.0) and hydrogen peroxide (3 wt.%). It (100 mmol, 26.45 g) was suspended in 300 mL of toluene, and the potassium salt of imidazole (100 mmol, 10.62 g) was added at room temperature. The suspension was stirred vigorously for 10 h at room temperature. After removal of the solvent by rotary evaporation, the white solid was extracted with 300 mL of ethanol. The solution was evaporated again and the white residue was washed with water, a minimum amount of cold ethanol, diethyl ether and pentane to give **9** in 96% yield (28.5 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.61 (m, 2H, $CH_2P(O)$), 4.11 (m, 2H, NCH_2), 6.71 (s, 1H, CH), 6.79 (s, 1H, CH), 7.59–7.54, 7.40–7.32 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 32.1 (d, ^1J(C,P) = 68 Hz, $CH_2P(O)$), 40.0 (NCH_2), 118.2 (NCH), 128.6 (d, J(C,P) = 12 Hz), 129.6 (s, NCH), 130.3 (d, J(C,P) = 10 Hz), 131.2 (s), 132.0 (d, J(C,P) = 4 Hz), 136.2 (s, NCHN); ^{31}P NMR (162 MHz, $CDCl_3$): δ = 28.1 (s); $C_{17}H_{17}N_2PO$ (296.3): calcd C 68.91, H 5.78, N 9.45; found C 68.55, H 5.77, N 8.82.

1-Methyl-3-(2-diphenylphosphorylethyl)imidazolium iodide (10): *N*-(Diphenylphosphoryl)ethylimidazole (100 mmol, 29.5 g) was dissolved in 150 mL of absolute chloroform. Iodomethane (110 mmol, 6.8 mL) was then added. The reaction mixture was stirred for 5 h at room temperature, and the solvent removed by evaporation. The resulting sticky solid was washed with 50 mL of pentane. The crude product was dissolved in absolute ethanol/THF/pentane (40:40:40 mL), and the solution cooled to dry-ice temperature for 3 h. The solvent mixture was decanted and the residue recrystallized in the same way once again. Finally, the white solid was washed with THF/pentane (20:20 mL) and evaporated to dryness. The product thus obtained forms adducts with both ethanol or THF. Solvent-free **10** was obtained by washing the crystalline adducts with pentane. Yield: 70% (30.6 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.18 (dt, ^3J(H,H) = 7 Hz, ^2J(H,P) = 10 Hz, 2H, CH_2PO), 3.74 (s, 3H, CH_3), 4.56 (dt, ^3J(H,H) = 7 Hz, ^3J(H,P) = 14 Hz, 2H, NCH_2), 7.17 (s, 1H, NCH), 7.31–7.44 (m, 5H), 7.63 (s, 1H, NCH), 7.67–7.72 (m, 5H), 9.67 (s, 1H, NCHN); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 30.2 (d, ^1J(H,P) = 68 Hz, CH_2PO), 36.5 (s, Me), 43.7 (s, NCH_2), 122.7 (s, NCH), 123.0 (s, NCH), 128.6 (d, J(C,P) = 12 Hz), 130.4 (d, J(C,P) = 10 Hz), 130.6 (s), 132.0 (d, J(C,P) = 3 Hz), 137.0 (s, NCN); ^{31}P NMR (162 MHz, $CDCl_3$): δ = 28.2; $C_{18}H_{20}N_2POI$ (438.24): calcd C 49.3, H 4.6, N 6.4, I 29.0; found C 47.8, H 4.7, N 6.1, I 29.0.

1-Methyl-3-(2-diphenylphosphinoethyl)imidazolium iodide (11): Iodide **10** (20 mmol, 8.8 g) was placed in a 250 mL three-necked round-bottomed flask fitted with a reflux condenser and a pressure valve. Addition of 40 mL of toluene gave a suspension. The mixture was cooled to 0 °C, and 9 mL of ethanol and 25 mL of methyldichlorosilane were added. After the reaction mixture had been vigorously stirred for 30 min at room temperature, the temperature was raised to 130 °C for 24 h by the means of an oil bath. The toluene/siloxane mixture was removed through a cannula at room temperature. The viscous residue was washed with diethyl ether and pentane, then evaporated to dryness. Yield: 89% (7.5 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.75 (s, 1H, NCHN), 7.6–7.0 (m), 4.50 (m, 2H, NCH_2), 3.9 (s, 3H, CH_3), 3.0 (m, 2H, CH_2P); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.6 (d, ^1J(C,P) = 8 Hz, CH_2P), 36.3 (s, CH_3), 46.5 (d, ^2J(C,P) = 20 Hz, NCH_2), 121.9 (s, NCH), 123.0 (s, NCH), 127.5 (s, Ph–C), 128.4 (d, J(C,P) = 8 Hz, Ph–C), 129.5 (s), 132.3 (d, J(C,P) = 18 Hz, Ph–C), 132.7 (s), 136.0 (s, NCHN); ^{31}P NMR (162 MHz, $CDCl_3$): δ = –18.2 (s).

Iodo(η^4-1,5-cyclooctadiene)[1-methyl-3-(diphenylphosphino-1,2-ethyl)imidazolium chloride)]rhodium(I) (12): Bis[μ-chloro-(η^4-1,5-cylooctadiene)rhodium(I)] (300 mg; 0.608 mmol) was slurried in 10 mL of anhydrous ethanol in a Schlenk tube. A solution of **11** (1.22 mmol) in 3 mL anhydrous ethanol was added at room temperature. The slurry was stirred overnight, and the solvent then evaporated in vacuo. The beige residue was washed with *n*-pentane (20 mL) and ethanol (6 mL) and dried. Yield: 725 mg (89%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.9 (br, 1H, NCHN), 7.65–7.17 (m), 5.4–5.3 (2H, COD), 4.13 (2H, NCH_2), 3.8 (3H, NCH_3), 3.5 (2H, CH_2P), 2.98 (2H, COD), 2.2–1.3 (8H, COD); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.3 (NCHN), 133.4 (d, J(C,P) = 11 Hz), 131.6 (d, J(C,P) = 26 Hz), 130.5 (s), 128.5 (d, J(C,P) = 10 Hz), 122.7 (s, NCH), 122.0 (s, NCH), 105.7 (COD, olefin), 72.5 (COD, olefin), 47.5 (d, J(C,P) = 15 Hz), 36.6 (s, NCH_3), 32.6, 31.7–30.8, 28.8, 27.8 (COD, CH_2P); ^{31}P NMR (162 MHz, $CDCl_3$): δ = 25.6 (d,

J(P,Rh) = 149 Hz); IR (KBr): $\tilde{\nu}$ = 3145 (NC–H), 3094 (NC–H), 3050, 2992, 2933, 2916, 2872, 2824, 1627 (NC–C), 1574, 1477, 1431, 1382, 1169 (NC–H, δ), 1159, 1097, 759, 746, 697, 623, 615, 520, 510, 490 cm^{-1}.

1,3-Dicyclohexylimidazoline-2-ylidene (1a): Deprotonation of the imidazolium salts was performed under nitrogen in a specially designed apparatus: A 200 mL Schlenk flask equipped with pressure valve and ammonia inlet, connected by a glass tube with a stopcock to a graduated 200 mL three-necked Schlenk flask equipped with a dry ice cooler with pressure valve, Schlenk pouring tube and magnetic stirrer. In this apparatus the ammonia was conveniently dried by condensing it into the first Schlenk flask onto potassium. It was then directly condensed into the reaction vessel.

Inside the reaction vessel **1** (2.68 g, 10 mmol) was slurried in 20 mL of THF. At −78 °C 100 mL of NH_3 was condensed in, dissolving the salt. The cold bath was removed, and NaH (260 mg, 10.8 mmol) added from the pouring tube. Under vigorous gas evolution an almost colourless solution was formed. The reaction appeared to be complete within minutes. After one hour at reflux temperature, the ammonia was condensed back into the first Schlenk flask leaving a light yellow solution in the reaction vessel. After the ammonia had been completely removed, the reaction vessel was filled to 40 mL with THF, and the solution obtained then filtered through a cannula. In this way a 0.25 M solution of **1a** in THF was produced, which was clean by ^{13}C NMR. The NMR was taken in [D_8]THF with a CD_3NO_2 inlet. ^{13}C NMR (100 MHz, THF, [D_8]THF): δ = 25.9 (CH_2), 34.9 (2CH_2), 59.6 (2CH_2), 66.8 (N–CH), 115.7 (NCHCHN), 210.1 (NCN).

(1,3-Dicyclohexylimidazoline-2-ylidene)pentacarbonyl tungsten(0) (1c): A Schlenk tube was charged with hexacarbonyltungsten (880 mg, 2.5 mmol) in 10 mL of THF. Under an atmosphere of nitrogen, a 0.25 M solution of **1a** in THF (10 mL, 2.5 mmol) was added, and the mixture stirred overnight at room temperature. The solvent was removed in vacuo, and residual hexacarbonyltungsten was sublimed off. The residue was taken up in CH_2Cl_2 and filtered through Celite. After partial evaporation, the product crystallized at −30 °C as yellow plates (854 mg, 61%). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.00 (s, 2H, N–CH=), 4.75 (m, 2H, N–CH), 1.98 (m, 4H, CH_2), 1.87 (m, 4H, CH_2), 1.75 (m, 2H, CH_2), 1.45 (m, 8H, CH_2), 1.24 (m, 2H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.5 ($J(^{183}W-^{13}C)$ = 126 Hz, W–CO), 197.7 ($J(^{183}W-^{13}C)$ = 126 Hz, W–$(CO)_4$), 176.4 ($J(^{183}W-^{13}C)$ = 99 Hz, W–CN_2), 118.34 (C=C), 61.7 (N–CH), 34.4 (CH–CH_2), 25.5 (CH_2), 25.1 ($CH_2(C_2H_4)_2$; MS (CI): m/z = 556 ([M^+], 22), 528 ([M^+ − CO], 6), 233 ([$M^\bullet$ − $W(CO_5)$], 100); $C_{20}H_{24}N_2O_5W$ (556.3): calcd C 43.18, H 4.3, N 5.0; found C 43.17, H 4.46, N 5.04.

Chloro(η^4-1,5-cyclooctadiene)(1,3-dicyclohexylimidazoline-2-ylidene)rhodium(I) (1d): A Schlenk tube was charged with bis[μ-chloro-(η^4-1,5-cyclooctadiene)rhodium(I)] (200 mg; 0.4 mmol) in 5 mL of THF. The resulting yellow solution was treated with a 0.25 M solution of **1a** in THF (3.3 mL, 0.8 mmol) under an atmosphere of nitrogen. The solution immediately turned pale yellow. The reaction mixture was stirred for 1 h at room temperature. The solvent was removed in vacuo, and the residue then taken up in CH_2Cl_2 and filtered through Celite. On addition of pentane the complex precipitated out as a yellow powder (325 mg, 85%). Recrystallization from toluene/pentane gave yellow crystals. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.15–1.87 (overlapping multiplets, 20H, cyclohexyl CH_2), 1.89 (m, 4H, COD CH_2), 2.31 (m, 4H, COD(CH_2)), 3.23 (m, 2H, COD(CH)), 4.93 (m, 2H, N–CH), 5.27 (m, 2H, COD(CH)), 6.78 (s, 2H, NCH); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 180.1 (d, J(Rh–^{13}C) = 51 Hz), Rh–NCN), 117.5 (NCH), 97.5 (d, J(Rh–^{13}C) = 3 Hz), COD), 67.5 (d, J(Rh–^{13}C) = 15 Hz, COD (CH)), 60.5 (N–CH), 34.5 (COD(CH_2)), 34.4 (cyclohexyl CH_2), 33.4 (cyclohexyl CH_2), 29.2 (COD(CH_2)), 26.4 (cyclohexyl CH_2), 26.1 (cyclohexyl CH_2), 25.7 (cyclohexyl CH_2); IR (KBr): $\tilde{\nu}$ = 3115, 2991, 2931, 2852, 1630, 1446, 1446, 1422, 1381, 1241, 1200, 995, 896, 752, 701; $C_{23}H_{36}N_2Cl_1Rh_1$ (478.9): calcd C 57.68, H 7.58, N 5.85, Rh 21.49; found C 57.37, H 7.75, N 6.08, Rh 20.7.

Dichloro(1,3-dicyclohexylimidazoline-2-ylidene)(η^6-1-isopropyl-4-methyl)benzene)-ruthenium(II) (1e): Bis{(μ-chloro)chloro[η^6-(1-isopropyl)(4-methyl)benzene]-ruthenium(II)} (613 mg, 1 mmol) was placed in a Schlenk tube and suspended in 30 mL of THF. A solution of **1a** in hexane (2.2 mmol, 510 mg, 7.5 mL) was added dropwise. The reaction mixture immediatedly turned deep red before compound **1e** started to precipitate. The solvents were removed in vacuo. The brown residue was dissolved in 10 mL of dichloromethane and layered with toluene and pentane (10 mL each). The product was obtained as deep red crystals (720 mg, Yield: 67%). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.13–1.23 (m, cyclohexyl), 1.32 (d, ^3J(H,H) = 7 Hz, $C(CH_3)_2$), 1.41–1.83 (m, cyclohexyl), 2.08 (s, 3H, CH_3), 2.1–2.28 (m, cyclohexyl), 2.79 (sept., ^3J(H,H) = 6.7 Hz, 1H, $CH(CH_3)_2$), 4.78 (m, N–CH, 2H), 5.08 (d, ^3J(H,H) = 6 Hz, C_6H_4, 2H), 5.41 (d, ^3J(H,H) = 6 Hz, C_6H_4, 2H), 7.01 (s, NCHCHN, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.70, 18.73, 22.96, 23.04, 31.11, 33.36 ($CH(CH_3)_2$), 25.26, 25.34, 35.29, 35.71, 59.17, 59.28 ($N(C_6H_{11})$), 83.36, 83.47, 85.32, 85.43, 97.28, 105.15 (C_6H_4), 119.24 (NCHCHN), 171.30 (NCN); IR (KBr): $\tilde{\nu}$ = 3092, 3071, 3034, 2921, 2850, 1467, 1451, 1421, 1408, 1382, 1287, 1274, 1231, 1195, 895, 741, 695; $C_{25}H_{38}N_2Cl_2Ru \cdot 0.8\ CH_2Cl_2$ (606.5): calcd C 51.09, H 6.58, N 4.62; found C 51.04, H 6.67, N 4.52.

1,1′-(1,2-Ethylene)-3,3′-dimethyl-imidazoline-2,2′-diylidene (2a): As previously described for compound **1a**, **2** (3.5 g, 10 mmol) was deprotonated with NaH (530 mg, 22 mmol) in a mixture of 20 mL THF and 100 mL NH_3. The reaction was complete after 30 min and a clear light yellow solution was formed. ^{13}C NMR (100 MHz, THF, [D_8]THF): δ = 37.7 (NCH_3), 52.7 (NCH_2), 119.7, 120.3 (NCHCHN), 215.9 (NCN).

1,3-Dimethylimidazoline-2-ylidene (3a): As previously described for compound **1a**, **3** (20 mmol) was deprotonated in a mixture of 20 mL THF and 100 mL NH_3 with NaH (530 mg, 22 mmol). The reaction was complete after 30 min and a clear colourless solution was formed. After the ammonia had been completely removed, the reaction vessel was filled up to 40 mL with THF or diethyl ether, and the solution obtained then transferred through a cannula to a filter. ^{13}C NMR (100 MHz, THF, [D_8]THF): δ = 36.2 (s, CH_3), 120.6 (NCHCHN), 215.1 (NCN).

1-Methyl-3-(2-phenylethyl)imidazole-2-ylidene (4a): As previously described for compound **1a**, **4** (4.5 g, 20 mmol) was deprotonated in a mixture of 20 mL THF and 100 mL NH_3 with NaH (530 mg, 22 mmol). The reaction was complete after 30 min, and a clear, colourless solution was formed. ^{13}C NMR (100 MHz, THF, [D_8]THF): δ = 37.8 (s, CH_2Ph), 39.2 (s, NCH_3), 53.0 (s, NCH_2), 122.3, 122.4 (NCH) 126.4, 129.5, 130.0, 140.3 (Ph), 214.2 (NCN).

1,3-Di-(*S*)-1′-phenylethylimidazoline-2-ylidene (5a): As previously described for compound **1a**, **5** (3.12 g, 10 mmol) was deprotonated in a mixture of 20 mL THF and 100 mL NH_3 with NaH (260 mg, 10.8 mmol). The substance is less soluble so that the reaction is somewhat slower. However, a clear yellowish solution was formed after 1 h. The ammonia was removed, and the resulting solution filled up to 40 mL. A sample of this solution was examined by ^{13}C NMR. The rest was decanted from the precipitate and used without further workup. ^{13}C NMR (100 MHz, THF, [D_3]nitromethane): δ = 22.3 (CH_3), 59.5 (N–CH), 117.8 (NCHCHN), 126.6 (phenyl CH), 127.1 (*p*-phenyl CH), 128.3, (phenyl CH), 144.3 (phenyl CR), 211.2 (NCN).

1,3-Di-(*S*)-1′-phenylethylimidazoline-2-thione (5b): A Schlenk tube was charged with sulfur (80 mg, 2.5 mmol) suspended in 10 mL of THF. Under intense stirring, a 0.25 M solution of **5a** in THF (10 mL, 2.5 mmol) was added. The reaction mixture immediately turned green, then dark red. After 1 h at room temperature the solvent was removed in vacuo, and the residue taken up in CH_2Cl_2. After filtration, the product was crystallized by slow evaporation of the solvent. The product was obtained as large colourless crystals (690 mg, 89%). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.3–7.1 (overlapping multiplets, 10H, Ph–CH), 6.53 (s, 2H, =C–H), 6.30 (q, ^3J(H,H) = 7 Hz, 2H, CH), 1.66 (d, ^3J(H,H) = 7 Hz, 6H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.6 (C=S), 140.0 (Ph–CR), 128.41 (Ph–CH), 27.35 (*p*-Ph–CH), 126.6 (Ph–CH), 114.3 (=CH), 54.7 (CH), 19.1 (CH_3); $C_{19}H_{20}N_2S$ (308.5): calcd C 73.99, H 6.54, N 9.08; found C 74.06, H 6.51, N 9.14.

(1,3-Di-(*S*)-1′-phenylethylimidazoline-2-ylidene)pentacarbonyltungsten(0) (5c): Compound **5c** was prepared in the same was as described above for **1c**, from tungstenhexacarbonyl (880 mg, 2.5 mmol) and a 0.25 M solution of **5a** in THF. Crystallization from toluene/pentane furnished yellow crystals of **5c** (945 mg, 63%). ^1H NMR (400 MHz, [D_6]benzene): δ = 7.14–7.29 (overlapping multiplets, 10H, Ph–CH), 6.48 (q, ^3J(H,H) = 3 Hz, 2H, N–CH–Ph), 6.28 (s, 2H, CH=), 1.55 (d, ^3J(H,H) = 6.5 Hz, 6H, CH_3); ^{13}C NMR (100 MHz, [D_6]benzene): δ = 200.9 (*trans*-CO), 198.5 (*cis*-CO), 180.3 (CN_2), 141.2 (*p*-Ph–CH), 129.4(Ph–CH), 128.6 (Ph–CR), 127.1 (Ph–CH), 120.4 (=CH), 60.9 (CH), 21.7 (CH_3).

Chloro(η^4-1,5-cyclooctadiene)(1,3-di-(*S*)-1′-phenylethylimidazoline-2-ylidene)rhodium(I) (5d): Compound **5d** was prepared in the same way as compound **1d**, from bis[μ-chloro-(η^4-1,5-cyclooctadiene)rhodium(I)] (200 mg; 0.4 mmol) and a 0.25 M solution of **5a** in THF. Crystallization from toluene/pentane gave yellow crystals of **5d** (327 mg, 79%). ^1H NMR (400MHz, $CDCl_3$): δ = 7.66–7.25 (overlapping multiplets, 10H, Ph–CH), 6.91 (q, ^3J(H,H) = 7 Hz, 1H, N–CH–Ph), 6.89 (q, ^3J(H,H) = 7 Hz, 1H, N–CH–Ph), 6.82 (d, ^3J(H,H) = 2 Hz, N–CH=), 6.65 (d, ^3J(H,H) = 2 Hz, N–CH=), 5.06 (m, 2H, COD CH), 3.45 (m, 1H, COD (CH)), 3.21 (m, 1H, COD CH), 2.5–2.3 (m, 4H, COD CH_2), 2.2–1.8 (overlapping multiplets, 4H, COD CH_2), 1.91 (d, ^3J(H,H) = 7 Hz, 3H, CH_3), 1.83 (d, ^3J(H,H) = 7 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 182.0 (d, J(Rh–^{13}C) = 51 Hz, Rh–CN_2), 142.2 (Ph–CR), 140.2 (Ph–CR), 128.8 (Ph–CH), 128.6 (Ph–CH), 127.9 (*p*-Ph–CH), 127.6 (Ph–CH), 126.2 (Ph–CH), 125.8 (*p*-Ph–CH), 118 (N–CH=), 118.2 (N–CH=), 98.5 (d, J(Rh–^{13}C) = 7 Hz, COD (CH)), 98.3 (d, J(Rh–^{13}C) = 7 Hz, COD (CH)), 68.7 (d, J(Rh–^{13}C) = 14 Hz, COD (CH)), 67.5 (d, J(Rh–^{13}C) = 14 Hz, COD (CH)), 59.7 (N–CH), 58.2 (N–CH), 33.0 (COD (CH_2)), 32.7 (COD CH_2), 28.7 (COD (CH_2)), 22.8 (CH_3), 20.8 (CH_3); MS (CI): m/z = 522 ([M^+], 38), 487 ([M^+ − Cl], 100), 414 ([M^+ − COD], 22), 378 ([M^+ − COD − Cl]), 277 (8), 137 (10)

1,3-Bis(2-ethoxyethyl)imidazoline-2-ylidene (6a): As previously described for compound **1a**, **6** (2.93 g, 10 mmol) was deprotonated in a mixture of 20 mL THF and 100 mL of NH_3 with NaH (260 mg, 10.8 mmol). The reaction was complete after 30 min, and a clear light yellow solution was formed. ^{13}C NMR (100 MHz, THF/[D_3]nitromethane inlet): δ = 119.3 (NCHCHN), 70.4 (NCH_2), 66.3, 50.4 (CH_2 each), 15.0 (CH_3).

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1,3-Bis(2-ethoxyethyl)imidazoline-2-thione (6b): Compound **6b** was prepared in the same way as **5b**, from sulfur (80 mg, 2.5 mmol) in 10 mL THF and a 0.25 M solution of **6a** in THF (10 mL, 2.5 mmol). Pale yellow crystals were obtained by slow evaporation of CH_2Cl_2 (446 mg, 84%). ^1H NMR (400MHz, $CDCl_3$): $\delta = 6.75$ (s, 2H, N–CH=), 4.16 (t, $^3J(H,H) = 5.5$ Hz, 4H, N–CH_2), 3.63 (t, $^3J(H,H) = 5.5$ Hz, 4H, N–CH_2CH_2), 3.39 (q, $^3J(H,H) = 7$ Hz, 4H, O–CH_2), 1.08 (t, $^3J(H,H) = 7$ Hz, 6H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 161.2$ (C=S), 117.7 (N–CH=), 69.2 (N–CH_2), 66.3 (NCH_2CH_2), 47.7 (OCH_2), 14.9 (CH_3).

[1,3-(2-Ethoxyethyl)imidazoline-2-ylidene)]pentacarbonyltungsten(0) (6c): Compound **6c** was prepared in the same was as **1c**, from hexacarbonyltungsten (880 mg, 2.5 mmol) in 10 mL THF and a 0.25 M solution of **6a** in THF (10 mL, 2.5 mmol). Crystallization from CH_2Cl_2 produced yellow crystals (1005 mg, 75%). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.23$ (NCH=), 4.38 (t, J = 5 Hz, 4H, N–CH_2), 3.69 (t, J = 5 Hz, 4H, N–CH_2-CH_2), 3.49 (q, $^3J(H,H) = 7$ Hz, 4H, OCH_2), 1.17 (t, $^3J(H,H) = 7$ Hz, 6H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 200.7$ ($J(^{183}W-^{13}C) = 125$ Hz, W–CO), 197.9 ($J(^{183}W-^{13}C) = 125$ Hz, $W(CO)_4$), 178.6 (W–CN_2), 122.2 (N–CH), 70.0 (N–CH_2), 66.8 (NCH_2–CH_2), 52.7 (OCH_2), 15.0 (CH_3); MS (CI): $m/z = 536$ ([M^+], 6), 508 ([$M^+ - CO$], 12), 480 ([$M^+ - 2CO$], 6), 213 ([$M^+ - W(CO)_5$], 100); $C_{16}H_{20}N_2O_7W$ (536.2): calcd C: 35.84, H 3.79, N 5.22, W 34.28 found C 35.86, H 3.86, N 5.29, W 34.04.

1-(2-Diethylaminoethyl)-3-methylimidazoline-2-ylidene (7a): Hydrochloride **7** (2.54 g, 10 mmol) was slurried in 20 mL of THF. At −78 °C, 100 mL of NH_3 was condensed in, dissolving the salt. At the same temperature 2.2 equiv of NaH (520 mg, 21.6 mmol) was added from the pouring tube. The first equivalent of NaH reacted with the hydrochloride with vigorous evolution of gas. After 5 min the cold bath was removed and the temperature allowed to rise to −35 °C. Once again, evolution of gas could be observed, indicating that a deprotonation reaction was taking place. A colourless solution was formed which was stirred 1 h at reflux temperature. After complete removal of the ammonia, the solution was filled up to 40 mL. A sample of this solution was examined by ^{13}C NMR spectroscopy. The rest was decanted from the precipitate and used without further workup. ^{13}C NMR (100 MHz, THF/[D_3]nitromethane): $\delta = 210.0$ (NCN), 119.1 (NCHCHN), 118.5 (NCHCHN), 53.9 (CH_2), 49.2 (CH_2), 46.8 (N–CH_3), 37.5 (CH_2), 11.9 (CH_3).

1-(2-Diethylaminoethyl)-3-methylimidazoline-2-thione (7b): Compound **7b** was prepared from sulfur (80 mg, 2.5 mmol) and a 0.25 M solution of **7a** in THF as previously described for **5b**. It was obtained as a yellow oil (478 mg, 89%). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 6.63$ (d, $^3J(H,H) = 2.5$ Hz, 1H, H–C=), 6.49 (d, $^3J(H,H) = 2.5$ Hz, 1H, H–C=) 3.86 (t, $^3J(H,H) = 6$ Hz, 2H, imidazole-N–CH_2), 3.37 (s, 3H, N–CH_3), 2.53 (t, $^3J(H,H) = 6$ Hz, 2H, imidazole-N–CH_2–CH_2), 2.33 (q, $^3J(H,H) = 7$ Hz, 4H, N–CH_2), 0.76 (t, $^3J(H,H) = 7$ Hz, 6H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 161.4$ (C=S), 117.3 (H–C=), 116.7 (H–C=), 51.0 (imidazole-N–CH_2), 46.9 (N–CH_3), 45.9 (imidazole-N–CH_2CH_2), 34.5 (N–CH_2), 11.6 (CH_3); MS (GC-MS): $m/z = 213$ ([M^+], 13), 141 ([$M^+ - NEt_2$], 13), 113 ([$M^+ - C_2H_4NEt_2$], 8), 99 ([$M^+ - NC_2H_4NEt_2$], 100), 86 (99), 71 (59), 56 (41), 42 (31).

Chloro(η^4-1,5-cyclooctadiene)[1-(2-diethylaminoethyl)-3-methylimidazoline-2-ylidene]rhodium(I) (7d): Compound **7d** was prepared from bis[μ-chloro-(η^4-1,5-cyclooctadiene)rhodium(I)] (200 mg, 0.4 mmol) and a 0.25 M solution of **7a** in THF (3.3 mL 0.8 mmol) as described above for **1d**. The product was obtained as a yellow oil (281 mg, 81%). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 6.93$ (d, $^3J(H,H) = 1.6$ Hz, 1H, H–C=), 6.72 (d, $^3J(H,H) = 1.6$ Hz, 1H, =C–H), 4.95 (m, 2H, COD CH), 4.69 (m, 1H, imidazole-CH_2), 4.29 (m, 1H, imidazole-CH_2), 4.00 (s, 3H, N–CH_3), 3.29 (m, 1H, COD CH), 3.18 (m, 1H, COD CH), 2.97 (m, 1H, imidazole–CH_2–CH_2), 2.75 (m, 1H, imidazole–CH_2–CH_2), 2.60 (m, 4H, N–CH_2), 2.35 (m, 4H, COD CH_2), 1.95 (m, 2H, COD CH_2), 1.8 (m, 2H, COD CH_2), 1,06 ("t", $^3J(H,H) = 7$ Hz, 6H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 182.2$ (d, J(Rh–^{13}C) = 49.5 Hz, C–Rh), 121.5 (H–C=), 121,2 (=C–H), 98.37 (COD CH), 98.1 (COD CH), 68.1 (COD CH), 67.3 (COD CH), 53.8 (imidazole–CH_2), 49.0 (imidazole–CH_2–CH_2), 47.5 (N–CH_2), 37.5 (imidazole–CH_3), 33.3 (COD CH_2), 32.4 (COD CH_2), 29.1 (COD CH_2), 28.3 (COD CH_2), 12.0 (CH_3).

1-(2-Ethylaminoethyl)-3-methylimidazoline-2-ylidene (8a): As previously described for compound **1a**, **8** (2.26 g, 10 mmol) was deprotonated. A colourless solution was formed. Upon complete removal of the ammonia, part of the product precipitated. THF (60 mL) was added redissolving only part of the product. The resulting slurry was used without workup. ^{13}C NMR (100 MHz, THF/CH_3CN/[D_3]nitromethane): $\delta = 120.8$, 120.6 (NCHCHN), 51.4, 51.3, 44.4 (CH_2 each), 37.9 (NCH_3), 15.6 (CH_3).

1-(2-Ethylaminoethyl)-3-methylimidazoline-2-thione (8b): Compound **8b** was prepared from sulfur (80 mg, 2.5 mmol) and a 0.25 M solution of **8a** in THF as previously described for **5b**. **8b** was obtained as a yellow oil (393 mg, 85%). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 6.73$ (d, $^3J(H,H) = 2.5$ Hz, 1H, H–C=), 6.62 (d, $^3J(H,H) = 2.5$ Hz, 1H, H–C=) 4.07 (t, $^3J(H,H) = 6$ Hz, 2H, imidazole N–CH_2), 3.53 (s, 3H, N–CH_3), 2.92 (t, $^3J(H,H) = 6$ Hz, 2H, imidazole N–CH_2–CH_2), 2.60 (q, $^3J(H,H) = 7$ Hz, 2H, N–CH_2), 1.01 (t, $^3J(H,H) = 7$ Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 162.1$ (C=S), 117.4 (H–C=), 117.3 (H–C=), 47.9 (imidazole N–CH_2), 47.8 (N–CH_3), 43.7 (imidazole N–CH_2CH_2), 34.9 (N–CH_2), 15.2 (CH_3).

Chloro(η^4-1,5-cyclooctadiene)[1-(2-diethylaminoethyl)-3-methylimidazoline-2-ylidene]rhodium(I) (8d): Compound **8d** was prepared from bis[μ-chloro-(η^4-1,5-cyclooctadiene)rhodium(I)] (200 mg, 0.4 mmol) and a 0.25 M solution of **8a** in THF (3.3 mL, 0.8 mmol) in the same way as **7d**. The product was obtained as a yellow powder (225 mg, 70%). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 6.93$ (d, $^3J(H,H) = 1.6$ Hz, 1H, H–C=), 6.72 (d, $^3J(H,H) = 1.6$ Hz, 1H, =C–H), 4.95 (m, 2H, COD CH), 4.69 (m, 1H, imidazole–CH_2), 4.29 (m, 1H, imidazole–CH_2), 4.00 (s, 3H, N–CH_3), 3.29 (m, 1H, COD CH), 3.18 (m, 1H, COD CH), 2.97 (m, 1H, imidazole–CH_2–CH_2), 2.75 (m, 1H, imidazole–CH_2–CH_2), 2.60 (m, 2H, N–CH_2), 2.35 (m, 4H, COD CH_2), 1.95 (m, 2H, COD CH_2), 1.8 (m, 2H, COD CH_2), 1,06 ("t", $^3J(H,H) = 7$ Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 182.2$ (d, J(Rh–^{13}C) = 49.5 Hz, C–Rh), 121.5 (H–C=), 121,2 (=C–H), 98.37 (COD CH), 98.1 (COD CH), 68.1 (COD CH), 67.3 (COD CH), 53.8 (imidazole–CH_2), 49.0 (imidazole–CH_2–CH_2), 47.5 (N–CH_2), 37.5 (imidazole–CH_3), 33.3 (COD CH_2), 32.4 (COD CH_2), 29.1 (COD CH_2), 28.3 (COD CH_2), 12.0 (CH_3). MS (CI): $m/z = 399$ ([M^+], 40), 364 ([$M^+ - Cl$], 100), 291 (6), 254 (10).

X-ray Structure Determinations: Table 2 summarizes the important parameters. All data were collected with $Mo_{K\alpha}$ radiation and were corrected for Lorentz and polarization terms. In the case of **1d** 2.5% decay was corrected, all other structures showed no decrease in intensity. Extinction effects were observed in the case of **1c** and **1e**; Larson's extinction parameters were 323 and 299, respectively [27]. The data for **5b** were measured in two sets from $(0 < \phi < 60°$ and $50 < \phi < 133°)$. Part two was scaled to fit part one and both sets were merged together. Structures **6c**, **1c**, **1d** and **1e** were solved by using the Patterson method [28,29] and structure **5b** using direct methods [30]. All structures were refined by standard difference Fourier techniques [29]. All non-hydrogen atoms were refined anisotropically.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1220-37. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: Int. code +(1223)336-033; e-mail: teched@chemcrys.cam.ac.uk).

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Table 2. Crystallographic data for **5b**, **6c**, **1c**, **1d** and **1e**.

	5b	**6c**	**1c**	**1d**	**1e**
formula	$C_{19}H_{20}N_2S$	$C_{16}H_{20}N_2O_7W$	$C_{20}H_{24}N_2O_5W$	$C_{23}H_{36}ClN_2Rh$	$C_{25}H_{38}Cl_2N_2Ru$
crystal	colourless fragment	yellow fragment	yellow fragment	yellow brick	red fragment
size (mm^3)	not measured	$0.1\times0.18\times0.18$	$0.08\times0.23\times0.33$	$0.15\times0.15\times0.35$	$0.13\times0.15\times0.38$
M_r	308.45	536.19	556.27	478.91	538.57
system	tetragonal	monoclinic	monoclinic	tetragonal	monoclinic
space group (no.)	$P4_32_12$ (96)	$I2/a$ (15)	$P2_1/n$ (14)	$P\bar{4}2_1c$ (114)	$P2_1/c$ (14)
a (Å)	10.6577(8)	7.606(1)	10.964(1)	20.013(1)	12.846(4)
b (Å)		18.888(2)	16.638(2)		15.780(5)
c (Å)	14.946(1)	13.825(1)	12.545(1)	11.6305(9)	13.175(4)
β (°)		93.318(9)	112.471(6)		113.45(2)
V ($Å^3$)	1697.6	1982.9	2114.9	4658.2	2450.2
ρ_{calcd} ($g\,cm^{-3}$)	1.21	1.80	1.75	1.37	1.46
Z	4	4	4	8	4
$F(000)$	656	1040	1088	2000	1120
μ (cm^{-1})	1.8	58.6	54.9	8.5	8.6
diffractometer	IPDS	IPDS	IPDS	CAD4	IPDS
2θ range (°)	$2.86<2\theta<48.4$	$3.07<2\theta<50.3$	$3.07<2\theta<50.3$	$2.0<2\theta<50.0$	$3.07<2\theta<50.3$
T (°C)	$26(\pm3)$	$-50(\pm0.3)$	$-60(\pm0.3)$	$-80(\pm4)$	$-80(\pm0.3)$
abs. corr.	none	[a]	[a]	none	[a]
data measured	7605	12551	27107	8704	31590
$I<0$, syst. abs.	581	243 [b]	599	1343	733
unique data	1333	1688	3666	3912	4065
refl. used	1103	1688	3301	3502	3552
$I/\sigma(I)$	1.0	0.0	1.0	1.0	1.0
hydrogens	calculated refined (U_{iso})	found refined (U_{iso})	calculated not refined	calculated not refined	found refined (U_{iso})
parameters	141	160	254	244	424
refl./param.	7.8	10.6	13	14.4	8.4
weighting w	1	[d]	[d]	[d]	[d]
resd. dens. ($e\,Å^{-3}$)	+0.19, −0.25	+0.55, −1.1	+1.7, −1.5	+0.88, −0.67	+0.55, −0.66
R [c]	0.036	0.027	0.032	0.036	0.037
R_w [c]	0.036	0.027	0.036	0.034	0.027

[a] Systematic oscillation of the mean image intensity caused by absorption was corrected [31]. [b] Without centering. [c] $R=\sum(||F_o|-|F_c||)/\sum|F_o|$, $Rw=[\sum w(|F_o|-|F_c|)^2/\sum wF_o^2]^{0.5}$. [d] Chebyshev-polynomial weighting [32].

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