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Functionalized imidazoline-2-ylidene complexes of rhodium and palladium [1]

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Abstract

N-Heterocyclic 'carbene' ligands derived from imidazole are alternatives for the well-established phosphine ligands in organometallic catalysis. In contrast to phosphines, the carbene ligands do not undergo ready dissociation from palladium and rhodium so that immobilization techniques appear reasonable. The synthesis of novel, functionalized imidazoline-2-ylidene complexes suitable for reactions with functionalized polymers is reported, as well as the synthesis of a water-soluble metal complex. Furthermore, model compounds for polyether-substituted imidazoline-2-ylidene complexes are presented. © 1997 Elsevier Science S.A.

Keywords: Functionalized *N*-heterocyclic carbenes; Imidazoline-2-ylidenes; X-ray structure; Transition-metal complexes

1. Introduction

Metal complexes of *N*-heterocyclic carbenes were shown to be alternatives for the widely used phosphine complexes in homogeneous catalysis [1–8]. Palladium and rhodium 'carbene' complexes show an excellent catalyst performance in *Heck* olefinations, hydroformylation, hydrogenation, and isomerization [3–8]. The metal–carbon bond of the *N*-heterocyclic carbene ligands is very robust so that dissociation from these metal centres (Pd, Rh) is not observed, even at elevated temperatures [9]. Thus, it appears reasonable to immobilize these catalytically active complexes by linking the imidazoline-2-ylidene ligand with a polymer. To this end, imidazoline-2-ylidene metal complexes containing reactive functional groups are required. Other methods of catalyst recycling are based on two-phase systems where the catalyst is dissolved in just one phase and thus, can easily be separated. An example is the Rhône-Poulenc process for the hydroformylation of propene with water-soluble rhodium complexes as catalysts [10]. Imidazoline-2-ylidene complexes are in principle also suitable for biphasic homogeneous catalysis because of their resistance against moisture and oxygen. Another development in this field is the application of polyethers instead of water as the second phase [11]. At higher temperatures, polyethers are completely miscible with organic solvents, whereas at lower temperatures the layers separate. In this context, polyether-substituted phosphines are used as ligands for the catalytically active metals. It appears likely that corresponding imidazoline-2-ylidene complexes could be suitable as well.

The present paper reports on the synthesis of compounds which meet the requirements of these three aspects of organometallic catalysis.

2. Results and discussion

2.1. Synthetic strategy

For the synthesis of imidazoline-2-ylidene complexes different routes and starting materials have been used [12–19]. The most common route is the reaction of the free carbene with a metal precursor following Scheme 1. This path is useful for unfunctionalized derivatives or compounds with protected functional groups, especially if the carbenes are generated from readily available imidazolium salts by deprotonation under the mild conditions of the ammonia route [20].

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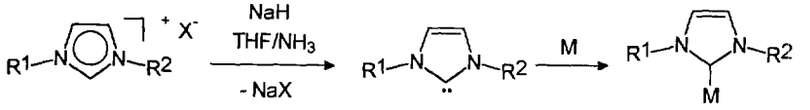


Scheme 1.

However, the generation of free carbenes with hydroxy-, ester-, oxo-, or acid groups has not been successful as a result of their high proton acidity. Hence, the imidazoline-2-ylidene complexes are only accessible directly from the imidazolium salts in the presence of a comparably weak base. Reaction of imidazolium salts with metal complexes containing basic ligands to the imidazoline-2-ylidene complexes and the corresponding acid as shown in Scheme 2 appeared to be promising. This synthetic principle was first utilized by Wanzlick and Schönherr [21] and Öfele [22] and was recently extended to catalytically active metals, e.g., rhodium [23].

2.2. New metal complexes

The functionalized imidazolium salts **1** were synthesized by consecutive alkylation of imidazole with functionalized alkyl halides (Scheme 3).

For our model compounds, preferably symmetric compounds with $R^1 = R^2$ were chosen because they crystallize readily. In principle, many combinations of different R^1 and R^2 are possible. Following this synthetic route, imidazolium salts **1a–c** with ether-, ester-, or ketone side chains were obtained in good yields (Fig. 1).

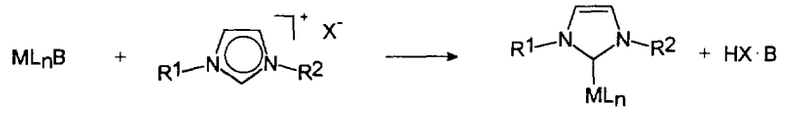
N-Hydroxyalkyl substituted imidazolium salts e.g. **1d** were synthesized in a slightly different way. In a first step, imidazole was converted to 1-(2′-hydroxyethyl)imidazole by reaction with ethylene oxide [24]. If an excess of ethylene oxide is employed, imidazoles with a polyether side chain are produced [25]. The average length of the polyether chain depends on the amount of ethylene oxide. In a second step, the monosubstituted imidazoles were quaternized with 2-bromoethanol to their corresponding imidazolium salts (Scheme 4). The yields are generally high, and only inexpensive starting materials are needed.

The deprotonation to the free carbene was possible only in the case of the diether-functionalized imidazolium salt **1a** [20]. In case of the ketone **1b**, the ester **1c**, and the alcohol **1d**, the proton acidity in the side chain was too high so that the attempted deprotonation even under mild conditions just led to product mixtures and decomposition. In case of **1c** an additional problem was the instability of the ester against ammonolysis so that the reaction could not be performed in liquid ammonia.

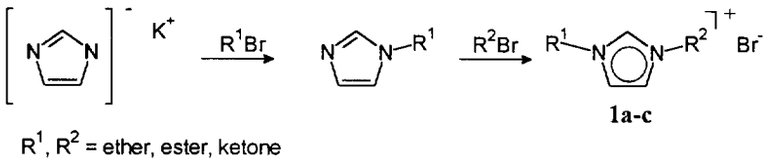
The direct conversion of the imidazolium salts to the corresponding rhodium complexes (Scheme 3) proceeded smoothly. Only in case of the *N*-methyl imidazolium salt **1b**, bis(carbene) rhodium complexes were obtained as a by product, probably due to the small steric hindrance of the ligands. In this case, the yield was improved by using lithium *tert*-butylate as a sterically more demanding base (yield 90%). Side reactions other than the formation of the bis(carbene) complexes were not observed; it thus appears unlikely that free carbenes were formed as intermediates [23]. However, the generation of low equilibrium concentrations of carbenes can not be excluded [26] (Scheme 5).

The mixed carbene–phosphine complex **3c** was synthesized as an example for a functionalized palladium compound (Scheme 6). Palladium(II) acetate was first converted into the iodo-bridged dimeric monocarbene complex by reaction with the imidazolium salt **1c** in the presence of sodium iodide and sodium ethoxide [27]. This dinuclear complex was directly converted into the mixed phosphine–carbene complex by addition of triphenylphosphine.

The X-ray single-crystal diffraction study of **3c** (Fig. 2) revealed a square-planar arrangement of the ligands, as it is published for similar unfunctionalized palladium carbene complexes [27,29]. The carbene and one phosphine ligand are in a *cis* conformation. The angle between the plane of the carbene heterocycle and the coordination plane amounts to 80.38(3)°. The distances between the palladium and the carbene carbon (d(Pd–C1) = 1.997(4) Å) and between the palladium and the phosphorus atom (d(Pd–P) = 2.2812(10) Å) are in the



Scheme 2.



Scheme 3.

expected range. The distance between the palladium and the iodine *trans* to the carbene (d(Pd–I2) = 2.6519(5) Å) is significantly longer than the distance between the palladium and the iodine *trans* to the phosphine (d(Pd–I2) = 2.6370(5) Å). This confirms that the carbene is indeed a stronger donor than the phosphine.

2.3. Reactivity

All complexes were obtained as air-stable yellow (**2a–d**) or orange (**3c**) crystals. Both the diether **2a** and the dihydroxy complex **2d** are stable against water. The ketone **2b** turned out to be a rather unreactive compound. Attempted reductive amination of the oxo group did not proceed satisfactorily. The ester groups of **2c** and **3c** were expected to be highly reactive since the corresponding acids are rather strong. We were predominately interested in the aminolysis, transesterification and cleavage of **2c** (Scheme 7). The palladium complex **3c** shows a similar reactivity.

(a) Ester cleavage of **2c** under basic conditions proceeds smoothly within minutes at room temperature. Only a stoichiometric amount of base (KOH) is needed. The resulting dianion **2f** is very soluble in water and methanol and almost insoluble in less polar organic solvents.

(b) If the ester **2c** is treated with an excess of an alcohol under basic conditions, a clean transesterification is observed. From the methyl ester **2e** crystals suitable for an X-ray diffraction study were obtained. The X-ray single-crystal diffraction study of **2e** (Fig. 3) revealed the same square-planar arrangement of the ligands, as it is published for analogous rhodium carbene complexes [9]. The angle of 88.4 (3)°, between the carbene heterocycle and the coordination plane, and the distance between the rhodium and the carbene carbon (d(Rh–C11) = 2.021(3) Å) are also typical for this type of compounds. The angles between the planes of the carboxylic groups and the plane of the imidazole heterocycle amount to 64.7 (2)° and 81.5 (2)°, respectively. The restricted rotation of the substituent at the imidazoline-2-ylidene ligand is confirmed by ^{1}H NMR spectroscopy where the geminal methylene protons are detected at significantly different chemical shifts (4.87 and 5.93 ppm).

(c) The aminolysis of the ester **2c** to the amide **2g** also proceeds under mild conditions. Both ester groups were converted into the corresponding isopropylamides within a few hours at room temperature by treatment of **2c** with dimethylaluminium isopropylamide [30]. Both transesterification and aminolysis reactions can be looked at as model reactions for the polymer-grafting of imidazoline-2-ylidene metal complexes. An intermediate cleavage and reformation of the metal–carbon bond is extremely unlikely since free imidazoline-2-ylidenes would not be stable under the reaction conditions especially of the aminolysis or the ester cleavage. All observations thus lead to the conclusion that the metal–carbon bond remains intact during reactions at the side chains.

In an ongoing effort, the reaction of such complexes with funtionalized polymers is being investigated in our group. Preliminary results indicate that the resulting polymers are indeed catalytically active.

3. Conclusion

Novel functionalized imidazoline-2-ylidene rhodium complexes are accessible for the first time from appropriately *N*-substituted imidazolium salts. Ester derivatives such as **1c** show excellent reactivity for alcohols and amines, thus, being potential precursors for polymer-supported complexes and catalysts. All observations lead to the conclusion that the metal–carbon bond remains intact during reactions at the side chains.

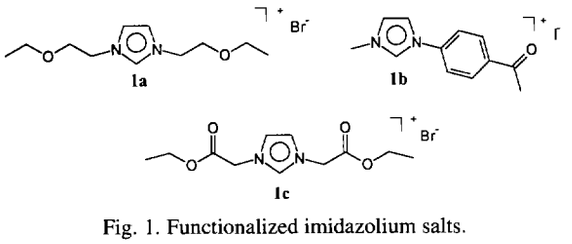
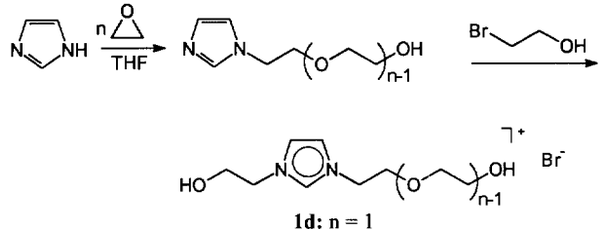
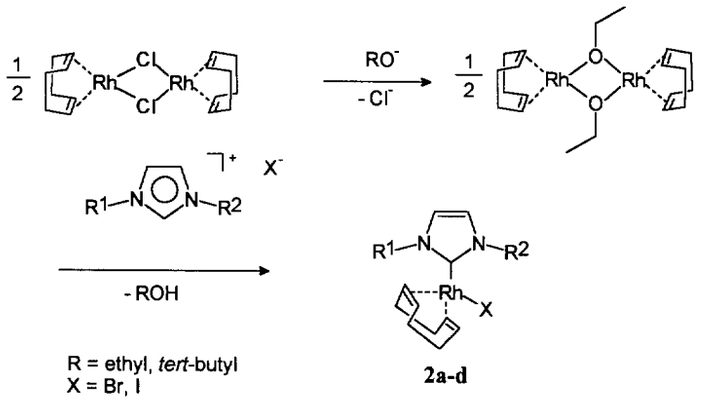


Fig. 1. Functionalized imidazolium salts.



Scheme 4.



Scheme 5.

The polyether model compounds **2a,d** and the water soluble complex **2f** obtained by base-induced cleavage of **2c** are thermally and chemically stable. They exhibit a number of prerequisites for future applications in biphasic homogeneous catalysis.

4. Experimental

4.1. General procedures

Oxygen-, moisture-sensitive or hygroscopic materials were handled under purified nitrogen or purified argon using standard Schlenk line techniques. All solvents were degassed and dried using standard procedures unless used for extractions. Acetone-d_6, nitromethane-d_3, DMSO-d_6, and $CDCl_3$ were stored over 3 Å molecular sieves. The 1-alkylimidazoles, if not commercially available, were synthesized following literature procedures.

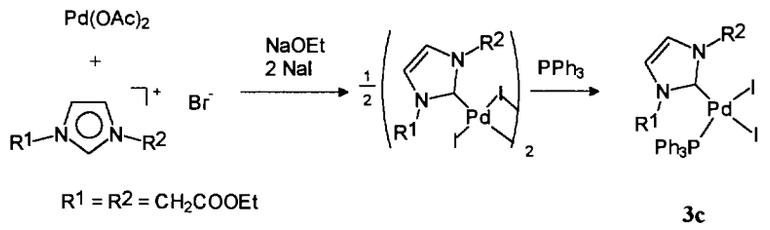
4.2. Instrumentation

^1H and ^{13}C NMR spectra were recorded on Jeol-JMX-GX-400 or Bruker amx 400 instruments using the solvent resonance as internal standard. Infrared spectra were obtained using the Perkin Elmer 1650 Fourier transform IR spectrometer with CaF_2 cells. GC-mass spectra were obtained on a Hewlett Packard 5890 instrument. All other mass spectra were measured at the TU München Mass Spectrometry Laboratory on a Finnigan MAT 90 mass spectrometer using either FAB (xenon/*p*-nitrobenzylalcohol) or CI (isobutane) technique. All elemental analyses were performed by the Technische Universität München Microanalytical Laboratory (M. Barth).

4.2.1. 1,3-Di-(2'-ethoxyethyl)imidazolium bromide (1a)

1-(2-Ethoxyethyl)imidazol (4.50 g, 39 mmol) was dissolved in 50 ml of THF and a slight excess of 2-bromoethyl-ethylether (7.00 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 was 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 **1a** (7.21 g, 75%) as a yellow, viscous oil. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 9.91$ (s, 1H, N_2C–H), 7.53 (d, $^4J(H,H) = 1$ 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) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta = 136.5$ (N_2C–H), 122.5 (NC–H),



Scheme 6.

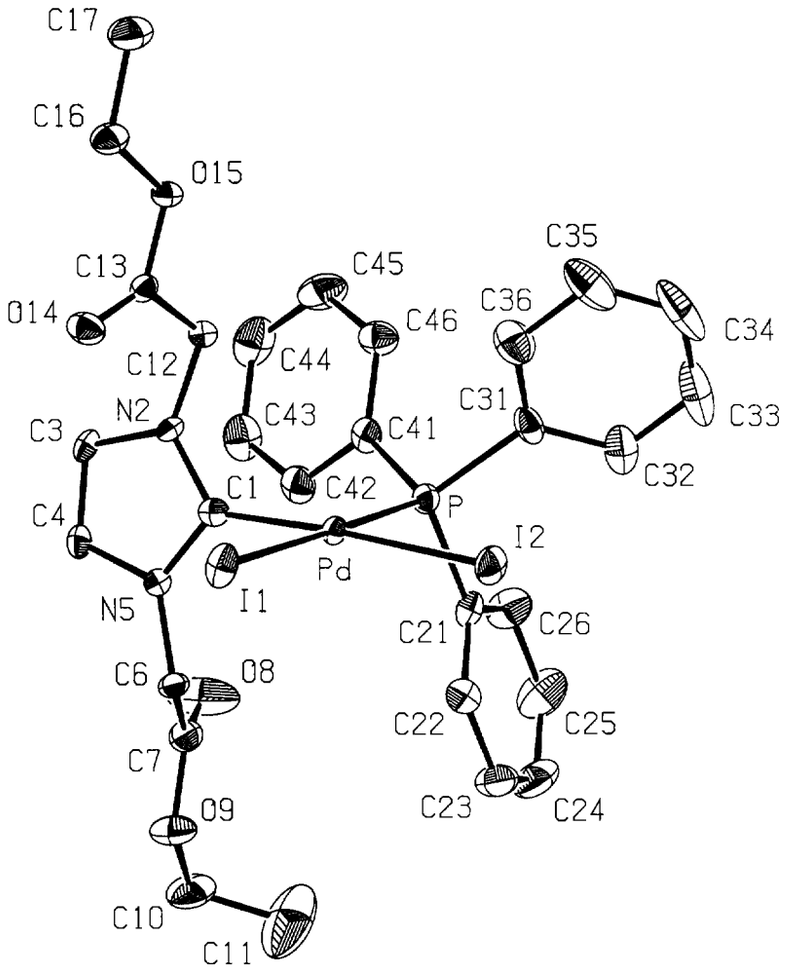


Fig. 2. PLATON-drawing [28] of the molecular and crystal structure of **3c**. Ellipsoids are drawn at the 50% probability level, hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Pd–I1 = 2.6370(5), Pd–I2 = 2.6519(5), Pd–P = 2.2812(10), Pd–C1 = 1.997(4), C1–N2 = 1.345(5), N2–C3 = 1.396(6), C1–N5 = 1.350(5), N5–C4 = 1.380(6), C3–C4 = 1.340(6), I1–Pd–I2 = 93.27(1), I1–Pd–P = 177.59(3), I1–Pd–C1 = 84.89(9), P–Pd–C1 = 92.71(10), N2–C1–N5 = 105.2(3), N2–C3–C4 = 106.0(4).

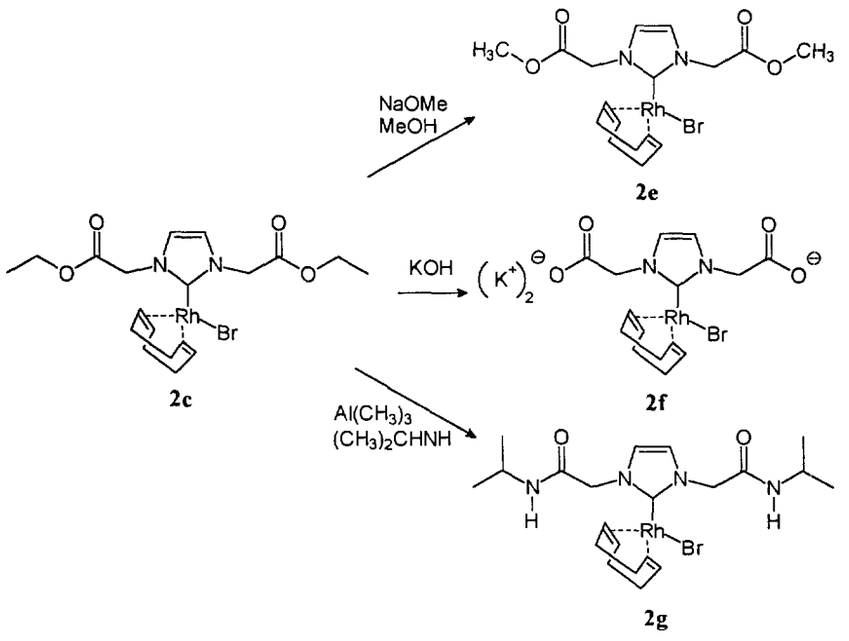
67.9 (N–CH_2), 66.4 (NCH_2–CH_2), 49.8 (O–CH_2), 14.7 (CH_3) ppm; MS (FAB): $m/z = 505$ ([M^+ + M–Br], 2), 213 ([M^+–Br], 100).

4.2.2. *3-Methyl-1-[4'-(1''-oxoethyl)phenyl]imidazolium iodide (**1b**)*

p-Imidazoyl-1-acetophenone (2.00 g, 10.74 mmol) was treated with excess iodomethane (2.00 g, 14.09 mmol) in THF. The reaction mixture was stirred overnight at room temperature. Upon treatment with ether, the product precipitated as a brown powder which was filtered off and was washed with small portions of THF and ether. After removal of the volatiles in vacuo the product was used without further workup. ^{1}H NMR (400 MHz, DMSO-d_6): $\delta = 9.89$ (s, 1H, N_2CH), 8.40 (s, 1H, NCH), 8.21 (*d*, ^3J(H,H) = 9 Hz, 2H, phenyl–CH), 7.98 (s, 1H, NCH), 7.93 (*d*, ^3J(H,H) = 9 Hz, 2H, phenyl–CH), 3.95 (s, 3H, NCH_3), 2.65 (s, 3H, $COCH_3$) ppm; ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): $\delta = 197.0$ (CO), 137.2, 136.3, 137.9, 130.1, 124.6, 121.6, 120.7 (phenyl–C, NCH, N_2CH), 36.3 (CH_3), 27.0 ($COCH_3$) ppm; MS (FAB): $m/z = 529$ ([M^+ + M–Br], 5), 201 ([M^+–Br], 100).

4.2.3. *1,3-Di-(2'-ethoxycarbonylmethyl)-imidazolium bromide (**1c**)*

Potassium imidazolide (52 mmol, 5.50 g) was alkylated with 8.35 g (50 mmol) bromoacetic acid ethyl ester in 50 ml THF. The potassium bromide was filtered off and the solvent was removed in vacuo yielding 2-(1-imidazoyl)-acetic acid ethyl ester as a colourless liquid (6.20 g, 81%). The purity of the product was confirmed by GC-MS. All of this was dissolved in 50 ml THF and bromoacetic acid ethyl ester (6.68 g, 40 mmol) was added. The mixture was refluxed for 12 h. During this time the product separated as a second oily



Scheme 7.

layer. The solvent was decanted and the residue was washed twice with THF. Removal of the solvent produced **1c** (10.21 g, 79%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 10.19$ (s, 1H, N_2CH), 7.64 (d, $^4J(H,H) = 1.4$ Hz, 2H, N–CH), 5.38 (s, 4H, N–CH_2), 4.23 (q, $^3J(H,H) = 7$ Hz, 4H, O–CH_2), 1.28 (t, $^3J(H,H) = 7$ Hz, 6H, CH_3) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta = 165.8$ (C=O), 139.0 (N_2CH), 123.3 (N–CH), 63.1 (N–CH_2), 50.4 (O–CH_2), 14.0 (CH_3) ppm; MS (FAB) $m/z = 561$ ([M^+ + M–Br], 3), 241 ([M^+–

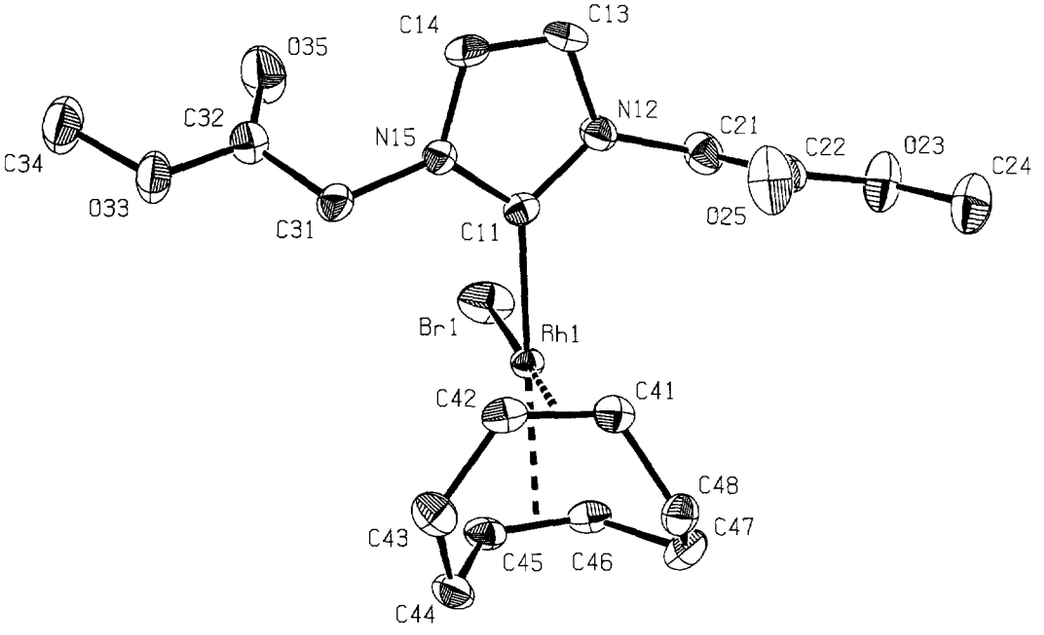


Fig. 3. PLATON-drawing [28] of the molecular and crystal structure of **2e**. Ellipsoids are drawn at the 50% probability level, hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Rh1–Br1 = 2.4941(6), Rh1–C11 = 2.021(3), Rh1–C41 = 2.120(3), Rh1–C45 = 2.226(4), N12–C11 = 1.355(4), N12–C13 = 1.384(5), N15–C11 = 1.361(4), N15–C14 = 1.393(5), C13–C14 = 1.325(5), Br1–Rh1–C11 = 89.82(10), C11–Rh1–C41 = 92.94(15), C11–N12–C13 = 111.6(3), C11–N12–C21 = 123.8(3), C11–N15–C14 = 110.7(3), N12–C11–N15 = 103.7(3), N12–C13–C14 = 106.8(3).

Br], 100); $C_{11}H_{17}N_2O_4Br$ (321.2): calcd.: C, 41.15; H, 5.29; N, 8.72; found: C, 40.79; H, 5.21; N, 8.89.

*4.2.4. 1,3-Di-(2'-hydroxyethyl)imidazolium bromide (**1d**)*

A high pressure glass vessel was charged with a solution of imidazole (0.13 mol, 9.00 g) in 15 ml THF and ethylene (0.12 mol, 6.00 ml) oxide was condensed in. The solution was heated to 100°C for 30 min. During this time the product separated from the reaction mixture as a second oily layer. The product layer was washed twice with THF, the solvent was removed in vacuo, and the residue was purified by Kugelrohr distillation yielding 9.72 g (72%) of 1-(2'-hydroxyethyl)imidazole. 4.1 g (37 mmol) of this was dissolved in ethanol and was alkylated with 4.6 g (37 mmol) 2-bromoethanol yielding **1d** (5.01 g, 86%) as a colourless oil. ^{1}H NMR (400 MHz, DMSO-d_6): $\delta = 9.14$ (s, 1H, N_2CH) 7.75 (d, $^4J(H,H) = 3$ Hz, 2H, NCH), 5.16 (s, 2H, OH), 4.23 (t, $^3J(H,H) = 5$ Hz, 4H, NCH_2), 3.72 (t, $^3J(H,H) = 5$ Hz, 4H, OCH_2) ppm; $^{13}C\{^1H\}$ NMR (100 MHz,): $\delta = 136.5$ (N_2C), 122.5 (NCH), 59.3 (NCH_2), 51.5 (CH_2O) ppm MS; (FAB): $m/z = 157$ ([M^+–Br], 100), 113 (17).

*4.2.5. Bromo(η^4-1,5-cyclooctadiene)[1,3-di-(2'-ethoxyethyl)imidazoline-2-ylidene]rhodium (**2a**)*

[Rh(COD)Cl]$_2$ (200 mg, 0.41 mmol) was dissolved in 10 ml THF and a slight excess of LiO*t*Bu (80.06 mg 1.00 mmol) was added under vigorous stirring. After 30 min at room temperature 1,2-di-(2'ethoxyethyl)-imidazolium bromide **1a** (263 mg, 0.9 mmol) was added and the mixture was placed in an ultrasonic bath. Within minutes a clear, yellow solution formed which was stirred for 3 h at room temperature. The progress of the reaction was monitored by TLC. After the starting material had disappeared the solvent was removed in vacuo and the residue was purified by column chromatography (CH_2Cl_2/MeOH 1–3%). Crystallization from CH_2Cl_2 afforded **2a** as yellow crystals (366 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 6.99$ (s, 2H, NCH), 5.02 (m, 2H, COD–CH), 4.8 (m, 2H, NCH_2), 4.46 (m, 2H, NCH_2), 3.82 (t, $^3J(H,H) = 5$ Hz, 4H, NCH_2CH_2), 3.48 (m, 4H, OCH_2), 3.29 (m, 2H, COD–CH), 2.31 (m, 4H, COD-CH_2), 1.86 (m, 4H, COD-CH_2), 1.15 (t, $^3J(H,H) = 7$ Hz, 6H, CH_3) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta = 181.5$ (d, $^1J(^{103}Rh,^{13}C) = 49$ Hz, CN_2), 121.5 (NCH), 97.7 (d, $^1J(^{103}Rh,^{13}C) = 7$ Hz, COD–CH), 69.87 (NCH_2), 69.1 (d, $^1J(^{103}Rh,^{13}C) = 15$ Hz, COD–CH), 66.55 (NCH_2CH_2), 50.5 (OCH_2), 32.6 (COD–CH_2), 29.0 (COD–CH_2), 15.1 (CH_3); MS (CI): $m/z = 502$ ([M^+], 78), 423 ([M^+–Br], 57), 350 (58), 314 (100); $C_{19}H_{32}N_2O_2RhBr$ (503.28): calcd.: C, 45.34; H, 6.41; N, 5.57; found: C, 45.59; H, 6.41; N, 5.62%.

*4.2.6. Iodo(η^4-1,5-cyclooctadiene){1-methyl-3-[4'-(1''-oxoethyl)phenyl]imidazoline-2-ylidene}rhodium (**2b**)*

Iodo(η^4-1,5-cyclooctadiene){1-methyl-3-[4'-(1''-oxoethyl)phenyl]imidazoline-2-ylidene}rhodium (**2b**) was prepared in the same way as **2a** from 3-methyl-1-[4'-(1''-oxoethyl)phenyl]imidazolium iodide (295 mg, 0.90 mmol) and [Rh(COD)Cl]$_2$ (200 mg, 0.4 mmol). Crystallization from CH_2Cl_2/Pentane afforded **2b** as yellow crystals (344 mg, 79%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.40$ (d, $^3J(H,H) = 8.52$ Hz, 2H, CH), 8.08 (d, $^3J(H,H) = 9$ Hz, 2H, CH), 7.20 (d, $^3J(H,H) = 2$ Hz, 1H, NCH), 7.02 (d, $^3J(H,H) = 2$ Hz, 1H, NCH), 5.23 (m, 1H, COD–CH), 5.16 (m, 1H, COD–CH), 4.10 (s, 3H, NCH_3), 3.37 (m, 1H, COD–CH), 2.64 (s, 3H, $COCH_3$), 2.63 (m, 1H, COD–CH), 2.23 (m, 2H, COD–CH_2), 2.04 (m, 1H, COD–CH_2), 1.80 (m, 2H, COD–CH_2), 1.72 (m, 1H, COD–CH_2), 1.42 (m, 2H, COD–CH_2) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta =$ 197.0 (CO), 184.0 (d, $^1J(^{103}Rh,^{13}C) = 51$ Hz, CN_2), 143.6 (CN), 136.0 (*C*–CO), 128.8 (CH), 123.9 (CH), 123.4 (NCH), 121.1 (NCH), 96.42 (d, $^1J(^{103}Rh,^{13}C) = 7$ Hz, COD–CH), 96.0 (d, $^1J(^{103}Rh,^{13}C) = 7$ Hz, COD–CH), 71.6 (d, $^1J(^{103}Rh,^{13}C) = 14$ Hz, COD–CH), 71.5 (d, $^1J(^{103}Rh,^{13}C) = 14$ Hz, COD–CH), 39.35 (CH_3), 32.8, 30.9, 29.8, 28.9 (COD–CH_2), 26.7 ($COCH_3$) ppm; MS (CI) $m/z = 538$ ([M^+], 57), 411 ([M^+–I], 100); $C_{20}H_{24}N_2ORhI$ (538.23): calcd.: C, 44.63; H, 4.49; N, 5.20; found: C, 44.87; H, 4.60; N, 5.18%.

*4.2.7. Bromo(η^4-1,5-cyclooctadien)[1,3-di-(ethoxycarbonylmethyl)-imidazoline-2-ylidene]rhodium(I) (**2c**)*

To a cooled solution of [Rh(COD)Cl]$_2$ (200 mg, 0.41 mmol) in 15 ml ethanol–THF (2:3) 0.70 ml of a 1.6 M *n*-butyllithium solution was added via syringe. The solution was allowed to warm up to room temperature and 1,3-di-(ethoxycarbonylmethyl)-imidazolium bromide **1c** (350 mg, 1.10 mmol) was added. The solution was stirred for 3 h. After the reaction was complete, the solvent was removed in vacuo and the residue was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH 1–3%). Crystallization from CH_2Cl_2/diethylether afforded **2c** as yellow crystals (347 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 6.97$ (s, 2H, NCH), 5.95 (d, $^3J(H,H) = 18$ Hz, 2H, NCH_2), 5.10 (m, 2H, COD–CH), 4.81 (d, $^3J(H,H) = 18$ Hz, 2H, NCH_2), 4.27 (m, 4H, OCH_2), 3.27 (m, 2H, COD–CH), 2.28 (m, 4H, COD–CH_2), 1.91 (m, 2H, COD–CH_2), 1.83 (m, 2H, COD–CH_2), 1.31 (t, $^3J(H,H) = 8$ Hz, 6H, CH_3) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta =$ 185.6 (d, $^1J(^{103}Rh,^{13}C) = 51$ Hz, CN_2), 168.3 (C=O), 122.3 (CH), 99.2 (d,$^1J(^{103}Rh,^{13}C) = 10$ Hz, COD–CH), 69.6 (d, $^1J(^{103}Rh,^{13}C) = 14$ Hz, COD–CH), 61.9 (OCH_2), 51.7 (NCH_2), 32.5 (COD–CH_2), 28.9 (COD–CH_2), 14.1 (CH_3) ppm; MS (CI): $m/z = 530$ ([M^+], 62), 451([M^+–Br], 71), 422 ([M^+–COD], 80), 149

(100); IR (THF): ν(COOEt) = 1755 cm^{-1}; $C_{19}H_{28}N_2O_4RhBr$ (531.25): calcd.: C, 42.95; H, 5.31; N, 5.27; found: C, 42.99; H, 5.25; N, 5.21%.

4.2.8. *Bromo(η^4-1,5-cyclooctadiene)[1,3-di-(2'-hydroxyethyl)imidazoline-2-ylidene]rhodium (2d)*

Bromo(η^4-1,5-cyclooctadiene)[1,3-di-(2'-hydroxyethyl)imidazoline-2-ylidene]rhodium (**2d**) was prepared in the same way as **2c** from 1,3-di(2'hydroxyethyl)imidazolium bromide (213 mg, 0.90 mmol) and $[Rh(COD)Cl]_2$ (200 mg, 0.41 mmol). Crystallization from CH_2Cl_2/Pentane afforded **2d** as yellow crystals (221 mg, 62%). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.17 (s, 2H, NCH), 4.92 (m, 2H, COD-CH), 4.84 (m, 4H, NCH_2), 4.60 (br s, 2H, OH), 4.02 (m, 4H, OCH_2), 3.45 (m, 2H, COD–CH), 2.34 (m, 4H, COD–CH_2), 1.92 (m, 4H, COD–CH_2); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 181.8 (d, $^1J(^{103}Rh,^{13}C)$ = 50 Hz, CN_2), 123.1 (NCH), 98.7 (d, $^1J(^{103}Rh,^{13}C)$ = 7 Hz, COD–CH), 70.9 (d, $^1J(^{103}Rh,^{13}C)$ = 15 Hz, COD–CH), 62.4 (NCH_2), 49.9 (OCH_2), 33.6 (COD–CH_2), 29.9 (COD–CH_2) ppm; $C_{15}H_{26}N_2O_2RhBr$ (447.18): calcd.: C, 40.29; H, 5.41; N, 6.26; found: C, 40.26; H, 5.53; N, 6.24%.

4.2.9. *Diiodo[1-3-di-(ethoxycarbonylmethyl)imidazoline-2-ylidene](triphenylphosphine)palladium(II) (3c)*

A Schlenk tube was charged with $Pd(OAc)_2$ (200 mg, 0.89 mmol), NaOEt (68 mg, 1 mmol), NaI (450 mg, 3 mmol) and 1,3-di-(2'ethoxycarbonylmethyl)-imidazolium bromide **1c** (321 mg, 1 mmol). A mixture of THF and ethanol was added via syringe and the solution was placed in an ultrasonic bath. Within minutes a dark red solution formed. After 30 min, a slight excess of triphenylphosphine was added and the solution was stirred overnight at room temperature. The solvent was then removed in vacuo and the residue was purified by column chromatography (CH_2Cl_2/MeOH 1–3%). Crystallization from CH_2Cl_2 afforded **3c** as orange crystals (408 mg, 53%). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.57–7.31 (m, 15H, phenyl-CHs), 6.94 (s, 2H, NCH), 4.74 (s, 4H, NCH_2), 4.01 (m, 4H, OCH_2), 1.24 (t, ^3J(H,H) = 8 Hz, 6H, CH_3) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 166.3 (C=O), 156.3 (CN_2), 135.3, 134.4, 130.8, 128.4 (phenyl-C), 123.4 (NCH), 62.2 (OCH_2), 51.5 (NCH_2), 13.9 (CH_3) ppm; MS (FAB): m/z = 735 ([M^+–I], 16), 307 (22), 154 (100), IR (THF): ν(COOEt) = 1751 cm^{-1}; $C_{29}H_{31}N_2O_4P_1Pd_1I_2 \cdot CH_2Cl_2$ (862.78): calcd.: C, 38.02; H, 3.51, N, 2.96; found: C, 38.22; H, 3.54; N, 2.97%.

4.2.10. *Bromo(η^4-1,5-cyclooctadiene)[1,3-di-(methoxycarbonylmethyl)imidazoline-2-ylidene]rhodium (2e)*

A solution of the diester **2c** (100 mg, 0.19 mmol) in MeOH was treated with a stoichiometric amount of NaOMe (10.6 mg, 0.19 mmol) in methanol. After 1 h at room temperature the solvent was removed in vacuo and the residue was purified by column chromatography (SiO_2, CH_2Cl_2/MeOH 1–3%). Crystallization from CH_2Cl_2 afforded **2e** as yellow crystals (86.8 mg, 92%). ^1H NMR (400 MHz, $CDCl_3$): δ = 6.94 (s, 2H, NCH), 5.93 (d, ^3J(H,H) = 17 Hz, 2H, NCH_2), 5.10 (m, 2H, COD–CH), 4.87 (d, ^3J(H,H) = 17 Hz, 2H, NCH_2), 3.82 (s, 3H, CH_3), 3.25 (m, 2H, COD–CH), 2.28 (m, 4H, COD–CH_2), 1.89 (m, 4H, COD–CH_2); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 168.7 (C=O), 186.1 (d, $^1J(^{103}Rh,^{13}C)$ = 50 Hz, CN_2), 122.4 (NCH), 99.4 (d, $^1J(^{103}Rh,^{13}C)$ = 6 Hz, COD–CH), 69.6 (d, $^1J(^{103}Rh,^{13}C)$ = 15 Hz, COD–CH), 52.6 (CH_2), 51.7 (CH_3), 32.6 (COD–CH_2), 28.9 (COD–CH_2); MS (CI): m/z = 502 ([M^+], 63), 423 ([M^+–Br], 100); IR (THF): $\tilde{\nu}$(COOEt) = 1754 cm^{-1}; $C_{17}H_{24}N_2O_4RhBr$ (503.20): calcd.: C, 40.58; H, 4.81; N, 5.57; found: C, 40.75; H, 4.80; N, 5.68%.

4.2.11. *Bromo(η^4-1,5-cyclooctadiene)[1,3-di-(potassiumcarboxylatomethyl)imidazoline-2-ylidene]rhodium (2f)*

A solution of the diester **2c** (100 mg, 0.19 mmol) in MeOH was treated with a stoichiometric amount of KOH (10.5 mg, 0.19 mmol) as a solution in methanol. The resulting solution was stirred for 1 h at room temperature while the progress of the reaction was monitored by IR spectroscopy. After the reaction appeared to be complete, the solvent was removed in vacuo and the residue was washed with THF leaving **2f** as a yellow powder (93 mg, 90%). ^1H NMR (400 MHz, CD_3OD): δ = 7.10 (s, 2H, NCH), 5.13 (s, 4H, NCH_2), 4.89 (m, 2H, COD–CH), 3.37 (m, 2H, COD–CH), 2.28 (m, 4H, COD–CH_2), 1.90 (m, 4H, COD–CH_2); $^{13}C\{^1H\}$ NMR (100 MHz, CD_3OD): δ = 181.6 (d, $^1J(^{103}Rh,^{13}C)$ = 50 Hz, CN_2), 175.2 (C=O), 123.8 (NCH), 98.7 (d, $^1J(^{103}Rh,^{13}C)$ = 6 Hz, COD–CH), 75.8 (d, $^1J(^{103}Rh,^{13}C)$ = 15 Hz, COD–CH), 54.9 (CH_2), 33.6 (COD–CH_2), 29.8 (COD–CH_2) ppm; IR (MeOH) $\tilde{\nu}$ = 1617.4 (COO^-) cm^{-1}.

4.2.12. *Bromo(η^4-1,5-cyclooctadiene)[1,3-di-(isopropylaminocarbonylmethyl)imidazoline-2-ylidene]rhodium (2g)*

A solution of the diester **2c** (100 mg, 0.19 mmol) in CH_2Cl_2 was treated with an excess of isopropylamine (30 mg, 0.51 mmol). At 0°C a slight excess of a 2 M solution of trimethylaluminium in toluene (0.2 ml, 0.4 mmol) was added. The resulting solution was stirred for 4 h at room temperature while the progress of the reaction was monitored by IR spectroscopy. After the reaction appeared to be complete, the solvent was removed in vacuo and the residue was crystallized from CH_2Cl_2 as yellow crystals (91 mg, 90%). ^1H NMR (400 MHz, $CDCl_3$): δ = 6.99 (s, 2H, NCH), 6.81 (d, ^3J(H,H) = 6 Hz, 2H, NH), 5.81 (d, ^3J(H,H) = 15 Hz,

Table 1
Crystal data

	2e	3c
Formula	$C_{17}H_{24}N_2O_4BrRh$	$C_{30}H_{33}Cl_2I_2N_2O_4P\,Pd$
fw	503.20	947.70
Color, habit	yellow, prism	orange, prism
Space group	monoclinic, $P2_1/c$	triclinic, $P-1$
a, pm	1047.8 (1)	961.86 (5)
b, pm	861.1 (1)	1102.71 (7)
c, pm	2127.3 (2)	1636.29 (10)
α, deg	90 (0)	85.410 (6)
β, deg	99.45 (1)	81.387 (6)
γ, deg	90 (0)	85.037 (6)
V, 10^6 pm	1893.3 (3)	1705.56 (18)
Z	4	2
D_{calc}, g cm^{-3}	1.765	1.845
λ, pm	MoK_α/71.073	MoK_α/71.073
F (000)	1008	920
2Θ range, deg	2–52	3.1–50.2
h,k,l range	−12/12, 0/10, −26/25	−10/10, −12/12, −19/19
μ, cm^{-1}	30.4	25.9
Crystal size, mm	0.2, 0.2, 0.1	0.32, 0.16, 0.12
Temp., K	193	193
No. of measured reflections	4919	20070
No. of unique reflections	3352	5385
No. of observed reflections ($>4\sigma(F_o)$)	2875	4188
R_1^a (all reflections/$>4\sigma(F_o)$)	0.036/0.026	0.025/0.041
wR_2^b	0.060	0.056
GOF[c]	1.018	0.913
No. of reference parameters	322	379
$(\Delta\rho)_{max}$, eÅ^{-3}	0.48	0.92
$(\Delta\rho)_{min}$, eÅ^{-3}	−0.78	−0.72

[a] $R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$; [b] $wR_2 = [\Sigma w (F_o^2 - F_c^2)^2/\Sigma w (F_o^2)^2]^{1/2}$; [c] $GOF = [\Sigma w (F_o^2 - F_c^2)^2/(NO - NV)]^{1/2}$.

2H, NCH_2), 5.13 (m, 2H, COD–CH), 4.59 (d, ^3J(H,H) = 15 Hz, 2H, NCH_2), 4.03 (m, 2H, $NCHR_2$), 3.32 (m, 2H, COD–CH), 2.37 (m, 4H, COD–CH_2), 1.95 (m, 4H, COD–CH_2), 1.17 (d, ^3J(H,H) = 6 Hz, 6H, CH_3), 1.03 (d, ^3J(H,H) = 6 Hz, 6H, CH_3); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 184.3 (d, $^1J(^{103}Rh,^{13}C)$ = 51 Hz, CN_2), 166.0 (C=O), 121.9 (NCH), 99.8 (d, $^1J(^{103}Rh,^{13}C)$ = 7 Hz, COD–CH), 70.5 (d, $^1J(^{103}Rh,^{13}C)$ = 14 Hz, COD–CH), 54.6 (CH_2), 42.1 ($NCHR_2$), 32.6 (COD–CH_2), 29.0 (COD–CH_2), 22.2 (CH_3), 22.1 (CH_3) ppm; IR (MeOH) $\tilde{\nu}$ = 1665.9 (amide I), 1548.1 (amide II) cm^{-1} $C_{21}H_{32}N_4O_2RhBr$ (555.31): calcd: C, 45.26; H, 6.18; N, 10.05; found: C, 45.06; H, 5.78; N, 9.79%.

4.2.13. Single-crystal X-ray diffraction studies of 2e and 3c

The X-ray diffraction data for **2e** were measured on a Nonius CAD4 four-circle diffractometer and those for **3c** were measured on a STOE IPDS. In both cases no decay was detected and no correction was thus applied. For **2e** an empirial absorption correction was carried out on the basis of psi scan data (T_{min} = 82.27/T_{max} = 99.66). The structures of **2e** and **3c** were solved by direct methods (Program: Sir 92) [31] and refined by a full-matrix least-square procedure using SHELXL 93 [32]. All atoms were refined anisotropically, except for hydrogens. In the structure of **2c** the hydrogen atoms were found in a difference fourier map and were refined with individual isotropic temperature parameters. In the case of structure **3c** the hydrogen atoms were placed in ideal geometric positions. One additional molecule of methylenechloride was found in the asymmetric unit of **3c**. Further details of single-crystal data measurement and refinement are given in Table 1.

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References

[1] M. Regitz, Angew. Chem. 122 (1996) 791–794.
[2] M. Regitz, Angew. Chem. Int. Edn. Engl. 35 (1996) 725–728.
[3] W.A. Herrmann, M. Elison, J. Fischer, C. Köcher, G.R.J. Artus, Angew. Chem. 121 (1995) 2602–2605.

[4] W.A. Herrmann, M. Elison, J. Fischer, C. Köcher, G.R. Artus, Angew. Chem. Int. Edn. Engl. 34 (1995) 2371–2374.
[5] M.F. Lappert, in: Transition Metal Chemistry, A. Müller, E. Diemann (Eds.), 1981, Verlag Chemie, Heidelberg.
[6] W.A. Herrmann, M. Elison, J. Fischer, C. Köcher, DE4447068 (Hoechst), 1994; EP0719758, 1996; DE4447067 (Hoechst), 1994; EP0719753, 1996; DE4447066 (Hoechst), 1994; EP0721953, 1996.
[7] W.A. Herrmann, L.J. Gooßen, C. Köcher, G.R.J. Artus, Angew. Chem. 108 (1996) 2980–2982.
[8] W.A. Herrmann, L.J. Gooßen, C. Köcher, G.R.J. Artus, Angew. Chem. Int. Edn. Engl. 35 (1996) 2805–2807.
[9] W.A. Herrmann, M. Elison, J. Fischer, C. Köcher, G.R.J. Artus, Chem. Eur. J. 2 (1996) 772.
[10] I.T. Horvath, F. Joó, Aqueous Organomet. Chem. Catal., 1996, ASI-Series 3/5, Kluver Academic Publishers, Dordrecht, Boston, London.
[11] D.E. Bergbreiter, L. Zang, V.M. Mariaganam, J. Am. Chem. Soc. 115 (1993) 9295–9296.
[12] N. Kuhn, T. Kratz, Synthesis, 1993, pp. 561–562.
[13] N. Kuhn, T. Kratz, D. Bläser, R. Boese, Inorg. Chim. Acta 238 (1995) 179–181.
[14] W.P. Fehlhammer, T. Bliss, U. Kernbach, I. Brüdgam, J. Organomet. Chem. 490 (1995) 149–153.
[15] U. Kernbach, M. Ramm, P. Luger, W.P. Fehlhammer, Angew. Chem. 108 (1996) 333–335.
[16] U. Kernbach, M. Ramm, P. Luger, W.P. Fehlhammer, Angew. Chem. Int. Edn. Engl. 35 (1996) 310–312.
[17] A.J. Arduengo III, R.L. Harlow, M. Kline, J. Am. Chem. Soc. 113 (1991) 361–363.
[18] A.J. Arduengo III, H.V. Rasika Dias, R.L. Harlow, M. Kline, J. Am. Chem. Soc. 114 (1992) 5530–5534.
[19] A.J. Arduengo III, S.F. Gamper, M.J. Thamm, C. Calabrese, F. Davidson, H.A. Craig, J. Am. Chem. Soc. 117 (1995) 572–573, and references.
[20] W.A. Herrmann, C. Köcher, L.J. Gooßen, G.R.J. Artus, Chem. Eur. J. 2 (1996) 1627–1636.
[21] H.-W. Wanzlick, H.-J. Schönherr, Angew. Chem. 80 (1968) 154.
[22] K. Öfele, J. Organomet. Chem. 12 (1968) C42.
[23] C. Köcher, W.A. Herrmann, J. Organomet. Chem., in press (1997).
[24] BASF, D.B.P. 854955, 1955.
[25] J. Falbe, M. Regitz (Eds.), Römpp Lexikon Chemie, 10th edn., Thieme Verlag, Stuttgart, 1996.
[26] A.J. Arduengo III, R.L. Harlow, W.J. Marshall, T.K. Prakasha, Heteroat. Chem. 6 (1996) 421–425.
[27] D. Enders, H. Gielen, G. Raabe, J. Runsink, T.H. Teles, Chem. Ber. 129 (1996) 1483–1488.
[28] A.L. Spek, PLATON, Acta Crystallogr. A46 (1990) C34.
[29] W.A. Herrmann, J. Fischer, J. Organomet. Chem., in press (1997).
[30] A. Basha, M. Lipton, S.M. Weinreb, Tetrahedron Lett. 48 (1977) 4171–4174.
[31] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M.C. Burla, G. Polidori, M. Camalli, SIR-92, 1992, Univ. of Bari, Italy.
[32] G.M. Sheldrick, SHELXS-86, Acta Crystallogr. A46 (1990) 467–473.