Articles

Multicomponent Synthesis of N-Heterocyclic Carbene Complexes

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N-Heterocyclic carbenes (NHCs) are valuable ligands in transition metal catalysis, due to their unique electronic properties. However, only a few routes toward unsymmetrically substituted, saturated NHCs are known. We have successfully applied the multicomponent synthesis of 2*H*-2-imidazolines for the preparation of a range of diversely substituted imidazolidin-2-ylidene complexes under mild conditions. In the desired NHC precursors the substituents at N-1, N-3, C-4, and C-5 were varied easily and independently by choosing the appropriate amine, aldehyde, isocyanide, or halide as starting material. Subsequent formation of the imidazolium salts followed by deprotonation with KO^{t}Bu and direct complexation of the *in situ*-generated NHCs at room temperature affords Rh− and Ir−NHC complexes. Properties of the resulting complexes were studied with ^{13}C NMR spectroscopy and X-ray crystallography.

Introduction

N-Heterocyclic carbenes (NHCs) attract considerable attention as valuable ligands in coordination chemistry and homogeneous catalysis.[1] This can be attributed to some rather unique properties of NHC ligands, such as their stronger σ-donor ability compared to, for example, tertiary phosphine ligands. Further, their strong nucleophilic character and weak π back-donating ability make NHC ligands comparable to P- or N-donating ligands rather than to classical Fischer- or Schrock-type carbenes.[2] Important advantages of NHC metal complexes are their low sensitivity to air (oxidation), heat, and moisture compared to the corresponding phosphine complexes.[3] As a result, NHC ligands serve as good alternatives to electron-rich phosphine ligands, which makes them increasingly popular in transition metal (TM) catalysis.[1] In addition to beneficial electronic properties robust synthetic procedures give access to NHCs bearing additional functional groups, leading to easily recoverable catalysts,[4] water-[5] or methanol[6]-soluble catalysts, and catalysts containing "flexible steric bulk"[7] as well as chiral ligands[8a] and bidentate and pincer ligands,[1f,9] although it should be noted that the potential of monodentate NHC complexes for asymmetric catalysis is believed to be only modest.[8b−8d]

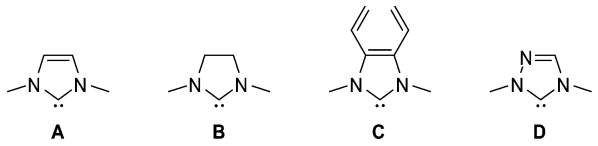

Figure 1. Commonly used N-heterocyclic carbenes.

NHCs derived from three-, four-, six-, and seven-membered

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[§] Institut für Anorganische und Analytische Chemie, Westfälische Wilhelms-Universität Münster, Corrensstr. 36, D-48149 Münster, Germany.

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(8) (a) Seiders, T. J.; Ward, D. W.; Grubbs, R. H. *Org. Lett.* **2001**, *3*, 3225−3228. (b) Rivas, F. M.; Riaz, U.; Giessert, A.; Smulik, J. A.; Diver, S. T. *Org. Lett.* **2001**, *3*, 2673−2676. (c) Baskakov, D.; Herrmann, W. A.; Herdtweck, E.; Hoffmann, S. D. *Organometallics* **2007**, *26*, 626−632.
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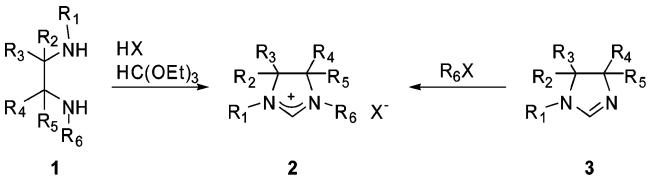
Scheme 1. Syntheses of Imidazolinium Salts



heterocycles have been reported.[10−13] However, the most frequently used NHC ligands are the five-membered imidazolin-2-ylidenes **A**, imidazolidin-2-ylidenes **B**, benzimidazolin-2-ylidenes **C**, and triazolin-2-ylidenes **D** (Figure 1). A straightforward procedure to synthesize the "saturated" carbenes **B** is by deprotonation of the corresponding imidazolinium salts $\mathbf{BH^+X^-}$ with bases such as NaH, KH, LDA, KHMDS, or KO^t-Bu. The imidazolinium salts $\mathbf{BH^+X^-}$ can be obtained by condensation of 1,2-diamines with triethyl orthoformate. A quick way to generate symmetrically substituted 1,2-diamines is via reduction of 1,2-diimines or via amination of 1,2-dibromides.[14] Variation of the C-4 and C-5 side groups of carbenes of type **B** can in principle be achieved by using available 1,2-diamines **1** or by alkylation of imidazolines **3** containing various R^1-R^5 groups (Scheme 1). However, methods for the synthesis of NHCs containing distinct side groups in the carbon backbone (R^2-R^5) are limited. In fact, the only general procedure involves a one-pot synthesis of imidazolidin-2-thiones followed by reduction of its thiourea moiety,[15] although the harsh reaction conditions are only compatible with nonfunctionalized alkyl substituents.

Recently, we reported a versatile multicomponent synthesis of 2*H*-2-imidazolines **7**.[16] The mild reaction conditions render this multicomponent reaction (MCR) compatible with a broad spectrum of aliphatic, aromatic, heteroaromatic, and olefinic substituents and even with more delicate functional groups such as amines, alcohols, esters, and primary chlorides. Because the substituents on C-4 and C-5 of the resulting 2*H*-2-imidazolines can be varied independently, we envisioned this MCR as a valuable tool for the synthesis of unprecedented types of NHC−transition metal complexes. In this contribution, we report a very short and flexible synthetic protocol for the synthesis of a structurally diverse set of Rh− and Ir−NHC metal complexes of type **9** (Scheme 2). All substituents R^1-R^5 at N-1, N-3, C-4, and C-5 in **9** were varied easily and independently by choosing an appropriate amine, aldehyde, isocyanide, or halide as starting materials.

Scheme 2. Multicomponent Approach toward NHC Complexes

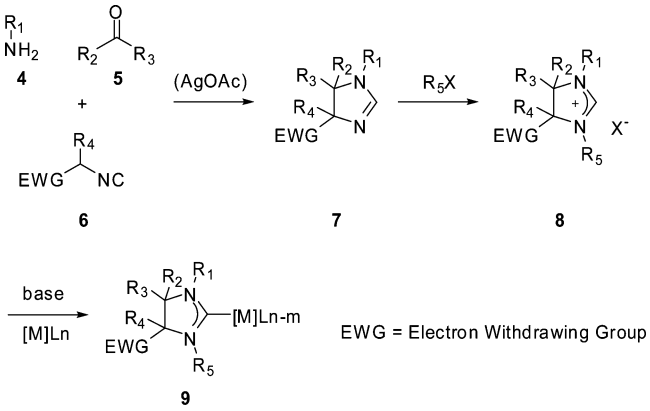
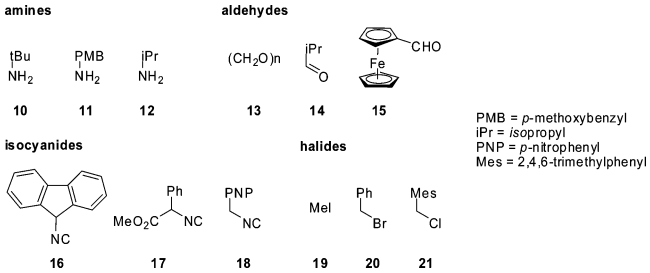


Chart 1. Building Blocks for NHC Precursors



Results and Discussion

For the synthesis of a diverse set of NHC precursors **8**, three amines, three aldehydes, three isocyanides, and three halides were chosen (Chart 1). Thus, after the synthesis of 2-imidazolines **22, 25**, **27**, **29**, and **31**, which proceeds smoothly via our three-component approach, alkylation gives the corresponding imidazolinium halides **23**, **24**, **26**, **28**, **30**, and **32** in high yields (Table 1; entries 1−6). Although conversions are generally quantitative, small amounts of the product are sometimes lost during washing of the salts with ether or pentane. Quarternization with **19** or **20** can be performed in CH_2Cl_2, but for the less reactive chloride **21**, more polar solvents such as DMF are preferred (entry 2).

Imidazolinium salts **23** and **24** seemed useful to investigate since it is known that free NHCs are stabilized toward dimerization by one or two bulky N-substituents. Application of ferrocene carboxaldehyde **15** as the aldehyde component in our MCR gives easy access to 4-ferrocenyl-substituted 2-imidazoline **27**, and subsequent alkylation with MeI affords the corresponding imidazolinium salt **28** (entry 4) as an interesting NHC precursor. Such NHC ligands with ferrocenyl substituents in the carbon backbone are not yet studied, although NHCs and NHC complexes containing (remote) ferrocenyl substituents at

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(14) (a) Arduengo, A. J., III; Krafczyk, R.; Schmutzler, R.; Craig, H. A.; Goerlich, J. R.; Marshall, W. J.; Unverzagt, M. *Tetrahedron* **1999**, *55*, 14523−14534. (b) Delaude, L.; Szypa, M.; Demonceau, A.; Noels, A. F. *Adv. Synth. Catal.* **2002**, *344*, 749−756.

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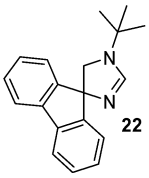
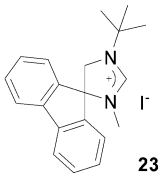
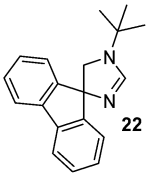
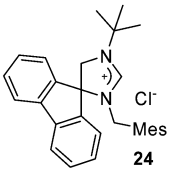
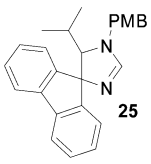
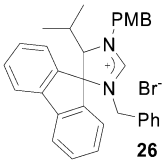
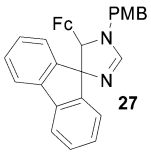
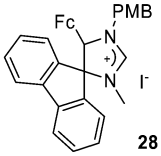
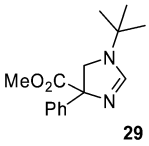
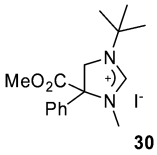
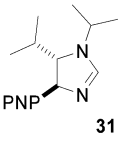
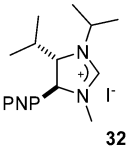
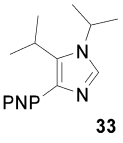
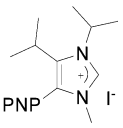
Table 1. Synthesis of Imidazol(in)ium Salts

entry	amine	aldehyde	isocyanide	imidazol(in)e	yield[a]	halide	salt	yield[a]
1	**10**	**13**	**16**	 **22**	89%[b]	**19**	 **23**	98%[c]
2	**10**	**13**	**16**	 **22**	89%[b]	**21**	 **24**	84%[d]
3	**11**	**14**	**16**	 **25**	91%[b]	**20**	 **26**	93%[d]
4	**11**	**15**	**16**	 **27**	69%[e]	**19**	 **28**	99%[c]
5	**10**	**13**	**17**	 **29**	86%[b]	**19**	 **30**	93%[c]
6	**12**	**14**	**18**	 **31**	39%[b]	**19**	 **32**	86%[c]
7	**12**	**14**	**18**	 **33**	27%[b]	**19**	 **34**	70%[f]

[a] Isolated yields are reported. [b]Conditions: Na_2SO_4, CH_2Cl_2, rt, 18 h, see also ref 16. [c]Conditions: R−X, CH_2Cl_2, rt, 18 h. [d]Conditions: R−X, DMF, rt, 18 h. [e]Conditions: MeOH, rt, 18 h. [f]Conditions: 8 equiv of MeI, CH_2Cl_2, 100 °C (microwave), 20 min. Mes = 2,4,6-trimethylphenyl; PMB = *p*-methoxybenzyl; Fc = ferrocenyl; PNP = *p*-nitrophenyl.

the nitrogens have been reported.[17] Recently, even the generation of a metallocene-fused imidazol-2-ylidene and its mercury complex was reported.[18] An elegant application of NHCs with redox-active ferrocenyl groups in an easily recyclable olefin metathesis catalyst has been described by Plenio.[6] In addition, also the imidazole **33**[16] was used as NHC precursor in order to compare unsymmetrically substituted imidazolidin-2-ylidenes with their unsaturated analogues. Methylation of imidazole **33** was successful using microwave heating and an excess of MeI and gave the corresponding salt **34** in good yield (entry 7). The imidazol(in)ium salts were all isolated as stable but somewhat hygroscopic solids.

Deprotonation of **23** with NaH followed by refluxing with $[Rh(cod)Cl]_2$ in THF provided the stable, crystalline NHC complex **35** in 52% yield (Table 2, entry 1). Replacement of the chloride on rhodium by the iodide that was present in **23** was confirmed by mass spectroscopy and X-ray crystallography (Figure 2). To ensure complete substitution of chloride by iodide, excess KI was added to the reaction mixture. Although deprotonation of imidazolinium salts is usually faster with KO*t*-Bu than with NaH, *tert*-butanol reacts with the resulting carbenes to form their corresponding alcohol adducts, which can be liberated again at elevated temperatures. Instead, a one-pot

(17) (a) Bildstein, B.; Malaun, M.; Kopacka, H.; Ongania, K.-H.; Wurst, K. *J. Organomet. Chem.* **1998**, *552*, 45−61. (b) Bildstein, B.; Malaun, M.; Hopacka, H.; Wurst, K.; Mitterböck, M.; Ongania, K.-H.; Opromolla, G.; Zanello, P. *Organometallics* **1999**, *18*, 4325−4336. (c) Bolm, C.; Kesselgruber, M.; Raabe, G. *Organometallics* **2002**, *21*, 707−710. (d) Seo, H.; Park, H.; Kim, B. Y.; Lee, J. H.; Son, S. U.; Chung, Y. K. *Organometallics* **2003**, *22*, 618−620.

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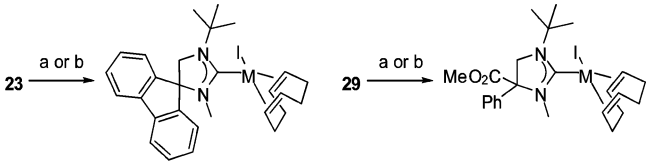
Table 2. Synthesis of Rh− and Ir−NHC Complexes[a]



entry	compound	method	yield	ratio[b]
1	**35**	a	52%	
2	**35**	b	82%	
3	**36**	a	55%	
4	**36**	b	63%	
5	**37**	a	51%	89:11
6	**37**	b	63%	78:22
7	**38**	a	51%	52:48
8	**38**	b	49%[c]	57:43

[a] Reagents and conditions: (a) (1) NaH, THF, rt, 18 h; (2) $[Rh(cod)Cl]_2$, KI (xs), reflux, 20 h; (b) KO^{t}Bu, $[Rh(cod)Cl]_2$, KI, rt, 18 h. [b]Isolated yields and ratios are reported. Ratios refer to relative amounts of rotamers. [c]This yield could be improved by performing the reaction in refluxing THF: 57% (67:33).

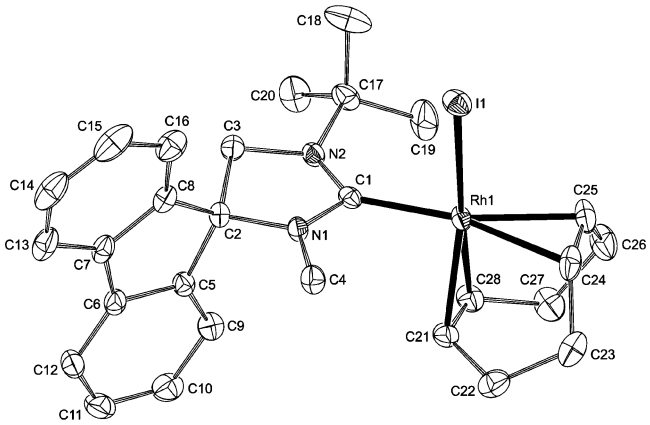


Figure 2. Displacement ellipsoid plot of **35** drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å], angles [deg], and torsion angles [deg]: I1−Rh1 2.70624(17), Rh1−C1 2.0197(14), N1−C1 1.3481(18), N2−C1 1.3576(19); I1−Rh1−C1 86.10(4), Rh1−C1−N1 120.53(10), Rh1−C1−N2 131.58(10), N1−C1−N2 107.88(12); I1−Rh1−C1−N1−85.36(11).

reaction between **23**, KO^{t}Bu, KI, and $[Rh(cod)Cl]_2$ at room temperature results in deprotonation of **23** followed by trapping of the *in situ*-generated NHC, giving rhodium complex **35** in 82% yield (entry 2). Apparently, halogen exchange already takes place at room temperature.

Both the two-step and the one-step method were used for the synthesis of several rhodium and iridium complexes. The NHC complexes **35**−**38** were isolated as stable, crystalline solids. In general, the one-step deprotonation and complexation (method b) gives higher yields (entries 1−6). The yield of Ir−NHC complex **38** could be enhanced by performing the reaction in refluxing THF (entry 8). Also at iridium, halogen exchange already takes place at room temperature.

The NMR spectra of **37** and **38** show double sets of signals, which are caused by the formation of rotamers. Rotation of the carbene ligand around the TM−NHC axis is hindered for steric reasons. High-temperature NMR experiments have shown that this rotation does not occur once the complex has formed. In the case of iridium complex **38**, the rotational isomers could be separated using flash column chromatography.[20] Ultimate proof for the existence of the two rotational isomers was provided by X-ray crystal structure analysis of the two products. In the major, least polar fraction of **38**, the carboxylic ester and the iodide are on opposite sides of the NHC plane (Figure 3), while in the minor, most polar fraction, they are on the same side (Figure 4).

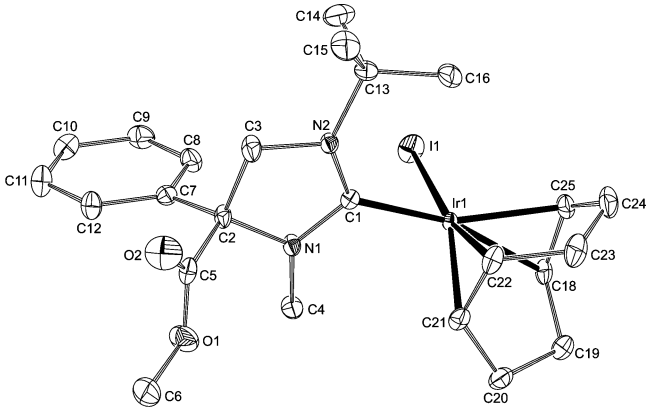


Figure 3. Displacement ellipsoid plot of **38a**, the major, least polar isomer of **38**, drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å], angles [deg], and torsion angles [deg]: Ir1−I1 2.67288(19), Ir1−C1 2.023(2), N1−C1 1.354(3), N2−C1 1.343(3); I1−Ir1−C1 90.11(6), Ir1−C1−N1 121.82(15), Ir1−C1−N2 129.67(16), N1−C1−N2 108.48-(19); I1−Ir1−C1−N1 89.20(17).

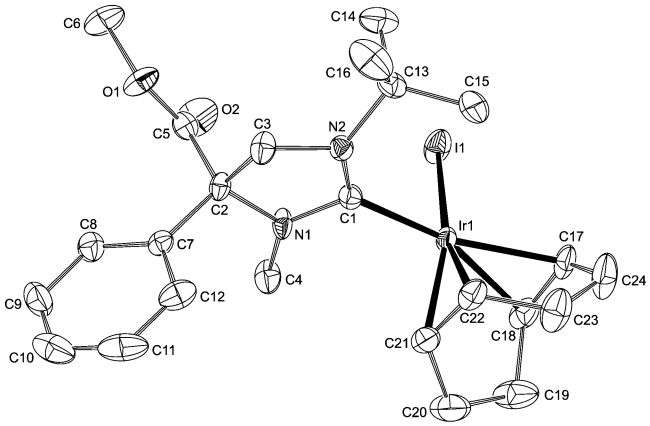


Figure 4. Displacement ellipsoid plot of **38b**, the minor, most polar isomer of **38**, drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å], angles [deg], and torsion angles [deg]: Ir1−I1 2.6716(2), Ir1−C1 2.030(3), N1−C1 1.344(3), N2−C1 1.351(3); I1−Ir1−C1 92.09(7), Ir1−C1−N1 121.34(18), Ir1−C1−N2 129.94(19), N1−C1−N2 108.2(2); I1−Ir1−C1−N1 86.9(2).

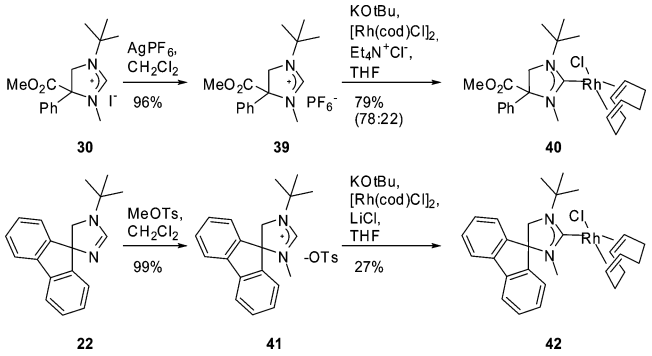
Several methods exist to circumvent halogen exchange during the formation of TM−NHC complexes. For example, an azolium salt containing a noncoordinating anion can be used as precursor.[21] Imidazolinium hexafluorophosphate **39** can be obtained in nearly quantitative yield from reaction of imidazolinium iodide **30** with $AgPF_6$ (Scheme 3). This reaction is driven by the precipitation of AgI from the DCM solution. Deprotonation of **39** and *in situ* complexation of the resulting carbene

(19) Small differences in ratios depicted in Table 2 may be attributed to small losses during chromatographic purification.

(20) Heating a solution of a single rotamer of **38** in toluene-d_8 at 150 °C (microwave) for 30 min does not provide a mixture of rotamers. At 200 °C, the product decomposes completely.

(21) Baker, M. V.; Brayshaw, S. K.; Skelton, B. W.; White, A. H. *Inorg. Chim. Acta* **2004**, *357*, 2841−2849.

Scheme 3. Multicomponent Approach toward NHC Complexes

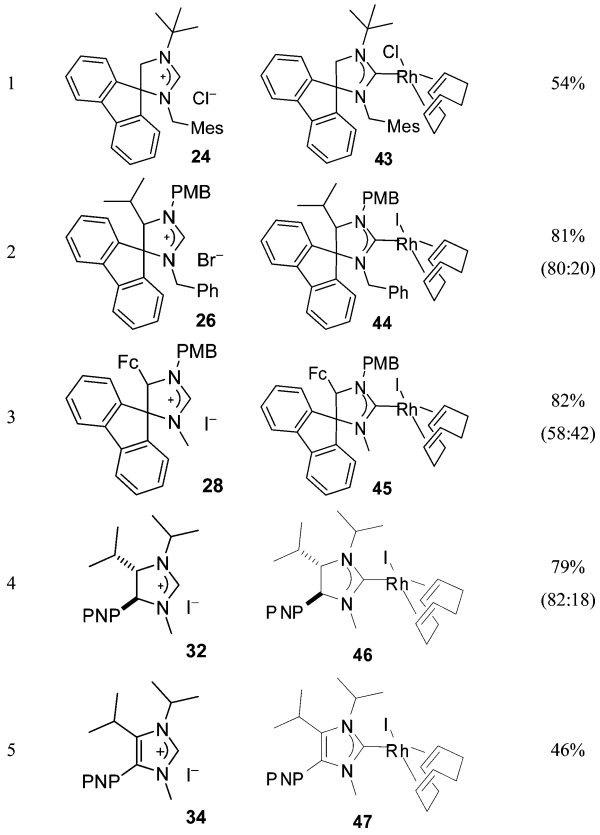


gave chloro complex **40** in high yield as a mixture of rotamers. When the same reaction sequence was applied to imidazolinium iodide **23**, an inseparable mixture of chloro complex **42** and bis(carbene) complex Rh(cod)$(NHC)_2$·PF_6 was isolated. Consequently, complex **42** was synthesized from imidazolinium tosylate **41**, which was obtained in quantitative yield by alkylation of imidazoline **22** with methyl tosylate. In this case, the contaminating bis(carbene) complex, as its tosylate salt, can be easily removed by washing with water.

Rhodium (and iridium)−NHC complexes are being increasingly applied as catalysts for, among others, (asymmetric) hydrosilylations[22] and cycloaddition reactions.[23] Furthermore, an established method for determining the ligand properties of NHCs involves studying Rh−NHC complexes.[24] In order to compare our NHCs, we decided to synthesize a broader range of unsymmetrically substituted NHC complexes of rhodium (Table 3). Our one-step deprotonation/complexation procedure proved compatible with all imidazol(in)ium salts from Table 1 and provided complexes **43**−**47** in reasonable to high yields. Again, chiral NHCs gave rise to mixtures of rotamers (entries 2−4). The major isomers of **44** and **46** could be obtained as pure compounds easily by slow crystallization. Complexes **44**, **46**, and **47** were studied using X-ray crystal structure analysis.

Interestingly, crystals of the major isomer of complex **44** undergo a solid−solid phase transition upon cooling. The high-temperature phase **44-I** crystallizes in the centrosymmetric space group $P2_1/n$ with one independent molecule in the asymmetric unit (Figure 5). Close to the isopropyl group there is a small void. The low-temperature phase **44-II** crystallizes in the noncentrosymmetric space group $P2_1$, which is a subgroup of $P2_1/n$ (Figure 6). In the $P2_1$ phase there are two independent molecules in the asymmetric unit, which differ mainly in the conformation of the isopropyl group. Additionally, due to the phase transition, there are significant changes of intermolecular distances, which make the packing motif of **44-II** incompatible with $P2_1/n$. Over a wide temperature range (110−250 K) both phases are present. The different molecular structures show only slight variations in the bond lengths and angles around the carbene center.

Table 3. Synthesis of Rh−NHC Complexes



[a] Isolated yields and ratios are reported. Ratios refer to relative amounts of rotamers. Fc = ferrocenyl.

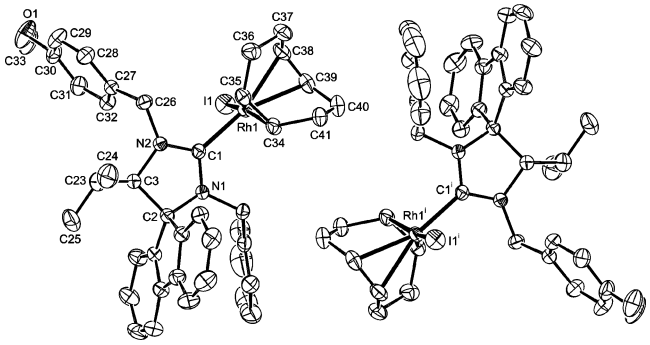


Figure 5. Displacement ellipsoid plot of two symmetry-related molecules in the high-temperature phase **44-I** of the major isomer of **44** (200 K), drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å], angles [deg], and torsion angles [deg]: I1−Rh1 2.6748(3), Rh1−C1 2.023(3), N1−C1 1.351(3), N2−C1 1.342(3); I1−Rh1−C1 88.72(7), Rh1−C1−N1 125.12(18), Rh1−C1−N2 126.67(19), N1−C1−N2 108.2-(2); I1−Rh1−C1−N1 85.5(2), N2−C3−C23−C24−56.2(4), N2−C3−C23−C25 176.3(3), N2−C26−C27−C28 157.8(3), C29−C30−O1−C33 163.9(3). Symmetry operation i: $1-x$, $1-y$, $1-z$.

The $^{13}C_{carbene}$ NMR chemical shifts (208−218 ppm) and Rh−$C_{carbene}$ coupling constants (43−47 Hz) of our saturated NHC transition metal complexes are in good agreement with values reported for complexes of other saturated NHCs (Table 4, entries 1−11).[15a,29] Furthermore, complex **47** shows a typical chemical

(22) (a) Chianese, A. R.; Crabtree, R. H. *Organometallics* **2005**, *24*, 4432−4436. (b) Viviano, M.; Mas-Marzá, E.; Sanaú, M.; Peris, E. *Organometallics* **2006**, *25*, 3063−3069. (c) Herrmann, W. A.; Baskakov, D.; Herdtweck, E.; Hoffmann, S. D.; Bunlaksananusorn, T.; Rampf, F.; Rodefeld, L.; *Organometallics* **2006**, *25*, 2449−2456.

(23) (a) Evans, P. A.; Baum, E. W.; Fazal, A. N.; Pink, M. *Chem. Commun.* **2005**, 63−65. (b) Lee, S. I.; Park, S. Y.; Park, J. H.; Jung, I. G.; Choi, S. Y.; Chung, Y. K. *J. Org. Chem.* **2006**, *71*, 91−96.

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(28) (a) Karkhanis, D. W.; Field, L. *Phosphorus Sulfur* **1985**, *22*, 49−57. (b) Marshall, C.; Ward, M. F.; Harrison, W. T. A. *J. Organomet. Chem.* **2005**, *690*, 3970−3975.

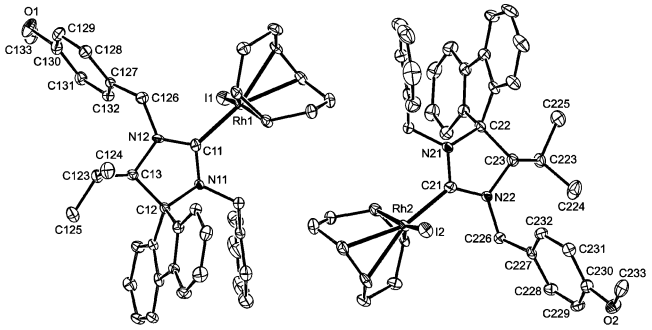

Figure 6. Displacement ellipsoid plot of the two independent molecules in the low-temperature phase **44-II** of the major isomer of **44** (110 K) drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å], angles [deg], and torsion angles [deg]. Values for the second molecule are given in square brackets: I1−Rh1 2.6821(3) [2.6592(3)], Rh1−C11 2.020(3) [2.022(3)], N11−C11 1.346(4) [1.347(4)], N12−C11 1.337(4) [1.341(4)]; I1−Rh1−C11 89.01(9) [89.01(9)], Rh1−C11−N11 125.5(2) [124.1(2)], Rh1−C11−N12 126.8(2) [126.7(2)], N11−C11−N12 107.6(3) [109.0(3)]; I1−Rh1−C11−N11 84.4(3) [−88.2(3)], N12−C13−C123−C124−53.8(4) [−71.7(4)], N12−C13−C123−C125 179.3(3) [168.5(3)], N12−C126−C127−C128 159.2(3) [−165.9(3)], C129−C130−O1−C133 168.5(3) [−176.3-(3)].

shift (180.0 ppm) for Rh complexes of imidazolin-2-ylidenes **A** (entry 12).[24,30] However, recent studies have shown that chemical shifts of carbene carbons and the coupling constants J(Rh−C) in ^{13}C NMR, although usually specific for the type of carbon, do not show systematic order for an estimation of the σ donor strength.[24]

The X-ray crystal structures of the NHC complexes all show (slightly disturbed) square-planar coordination geometries, as expected for 16e Rh and Ir complexes. The different Rh complexes show only small differences in Rh−$C_{carbene}$ distances (Table 5, entries 1−5). However, the saturated NHC complexes show characteristic N1−C1−N2 angles around 108° (entries 1−4), which are 3−4° larger than that in complex **47** (entry 5), bearing an unsaturated NHC. To accommodate the steric requirements of *tert*-butyl substituents in complexes **35**, **38a**, and **38b**, their M−C1−N2 angles are about 10° larger than their M−C1−N1 angles (entries 1, 6, 7). When the two nitrogen substituents are sterically more alike, these angles are almost equal (entries 2−5). Furthermore, the plane of the five-membered carbene ring is almost perpendicular to the coordination plane of the complex (>85°).

Conclusion

We have successfully applied the multicomponent synthesis of 2*H*-2-imidazolines in the preparation of a range of unsymmetrically substituted imidazolidin-2-ylidene complexes under mild conditions. Substituents at N-1, N-3, C-4, and C-5 can be varied easily and independently by choosing the appropriate amine, aldehyde, isocyanide, or halide in the two-step synthesis of the NHC precursors. Deprotonation of the imidazolium salts with KO^{t}Bu and direct complexation of the *in situ*-generated NHCs at room temperature affords Rh− and Ir−NHC complexes. The existence and stability of two hindered rotamers of M(cod)X(NHC) complexes have been unambiguously proven by the separation and X-ray crystal structure determination of two rotamers of Ir complex **38.** Also 4-(*p*-nitrophenyl)imidazoles, which are side products of reactions between amines, aldehydes, and *p*-nitrobenzyl isocyanide **18**, can be used in the synthesis of NHC complexes. Data obtained from NMR spectroscopic and X-ray crystallographic studies of the complexes correspond well with earlier reported properties of NHCs.

Experimental Section

General Information. All reactions were carried out under an inert atmosphere of argon or dry nitrogen (glovebox). Standard syringe techniques were applied for transfer of air-sensitive reagents and dry solvents. Melting points were measured using a Stuart Scientific SMP3 melting point apparatus and are uncorrected. Infrared (IR) spectra were obtained from $CHCl_3$ films on NaCl tablets (unless noted otherwise), using a Matteson Instruments 6030 Galaxy Series FT-IR spectrophotometer, and wavelengths (ν) are reported in cm^{-1}. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 400 (400.13 and 100.61 MHz, respectively), a Bruker Avance 250 (250.13 and 62.90 MHz, respectively), or a Bruker Avance 200 (200.13 and 50.32 MHz, respectively) with chemical shifts (δ) reported in ppm downfield from tetramethylsilane. Peak assignment was also done with the aid of gs-COSY, gs-HMQC, and gs-HMBC measurements. EIMS and HRMS spectral data were recorded on a Finnigan Mat 900 spectrometer. ESIMS and HRMS spectra were recorded on a LTQ XL Orbitrap spectrometer. Chromatographic purification refers to flash chromatography using the indicated solvent (mixture) and Baker 7024-02 silica gel (40 μm, 60 Å). Thin-layer chromatography was performed using silica plates from Merck (Kieselgel 60 F_{254}) on aluminum with fluorescence indicator. Compounds on TLC were visualized by UV detection. THF and Et_2O were dried and distilled from sodium benzophenone ketyl prior to use. DCM was dried and distilled from CaH_2 prior to use. Petroleum ether (PE) with a boiling range of 40−65 °C was distilled prior to use as eluent for chromatography. Isocyanides **16**, **17**, and **18**,[13] $[Rh(cod)Cl]_2$,[31] and $[Ir(cod)Cl]_2$[32] as well as imidazolines **25**,[16a] **29**,[16b] **31**,[16b] and **33**[16b] were prepared according to literature procedures. Other commercially available reagents were used as purchased.

Microwave Experiments. Microwave-assisted reactions were performed in a Discover (CEM Corporation) single-mode microwave instrument producing controlled irradiation at 2450 MHz, using standard sealed microwave glass vials. Reaction temperatures were monitored with an IR sensor on the outside wall of the reaction vials. Reaction times refer to hold times at the indicated temperatures, not to total irradiation times.

General Procedure I for the Synthesis of 2-Imidazolines. Reactions were carried out at a concentration of 1 M amine, 1 M aldehyde, and 0.5 M isocyanide in dry DCM, unless noted otherwise. Na_2SO_4 and the aldehyde were added, at rt, to a stirred solution of the amine. After the mixture was stirred for 2 h, the isocyanide was added and the reaction mixture was stirred at rt for an additional 18 h. The reaction mixture was filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography (PE/EtOAc/Et_3N = 2:1:0.01, gradient, unless stated otherwise).

2-Imidazoline 22. According to General Procedure I, reaction between *tert*-butylamine **10** (1.46 g, 20 mmol), *p*-formaldehyde **13** (600 mg, 20.0 mmol), and isocyanide **16** (2.0 g, 10.5 mmol), followed by flash column chromatography, afforded **22** (2.58 g, 89%) as a light yellow solid. Crystallization from pentane/Et_2O affords white crystals. Mp: 95−96 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) 7.68 (d, J = 6.9 Hz, 2H), 7.50−7.32 (m, 7H), 3.73 (s, 2H), 1.42 (s, 9H). ^{13}C NMR (63 MHz, $CDCl_3$): δ (ppm) 155.6 (CH), 150.6 (2×C), 140.3 (2×C), 128.7 (2×CH), 128.4 (2×CH), 124.2 (2×CH), 120.1 (2×CH), 79.1 (C), 55.6 (CH_2), 53.1

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Table 4. ^{13}C NMR Chemical Shifts δ of M(cod)X(NHC) Complexes and Rh−$C_{carbene}$ Coupling Constants J of Rh(cod)X(NHC) Complexes[a]

entry	complex	M	X	δ $C_{carbene}$ (ppm)	J(Rh−$C_{carbene}$) (Hz)
1	**35**	Rh	I	213.3	43.5
2	**36**	Ir	I	209.0	
3	**37**[b]	Rh	I	213.3	43.8
4	**38a**	Ir	I	208.8	
5	**38b**	Ir	I	209.2	
6	**40**[b]	Rh	Cl	213.8	45.9
7	**42**	Rh	Cl	214.0	45.6
8	**43**	Rh	Cl	217.8	46.2
9	**44**[b]	Rh	I	217.8	45.6
10	**45**[b]	Rh	I	216.4	44.7
11	**46**[b]	Rh	I	213.7	44.5
12	**47**	Rh	I	180.0	48.8

[a] Spectra were recorded in $CDCl_3$. [b]Chemical shifts and coupling constants of main isomer are reported.

Table 5. Selected Bond Distances (Å), Bond Angles (deg), and Torsion Angles (deg) for M(cod)I(NHC) Complexes

entry	complex	M	M−C1	N1−C1−N2	M−C1−N1	M−C1−N2	I−M−C1−N1
1	**35**	Rh	2.0197(14)	107.88(12)	120.53(10)	131.58(10)	−85.36(11)
2	**44I**	Rh	2.023(3)	108.2(2)	125.12(18)	126.67(19)	85.5(2)
3	**44-II**[a]	Rh	2.020(3)	107.6(3)	125.5(2)	126.8(2)	84.4(3)
			2.022(3)	109.0(3)	124.1(2)	126.7(2)	−88.2(3)
4	**46**	Rh	2.0183(15)	108.57(13)	125.59(11)	125.78(10)	88.22(13)
5	**47**	Rh	2.028(2)	104.84(17)	128.43(15)	126.72(14)	90.56(18)
6	**38a**	Ir	2.023(2)	108.48(19)	121.82(15)	129.69(16)	89.20(17)
7	**38b**	Ir	2.030(3)	108.2(2)	121.34(18)	129.94(19)	86.9(2)

[a] Values of both molecules in the asymmetric unit are reported.

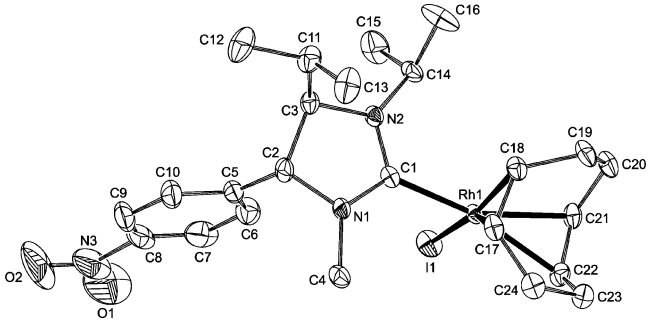

Figure 7. Displacement ellipsoid plot of the major isomer of **46** drawn at the 50% probability level. Hydrogen atoms and disordered solvent molecules are omitted for clarity. Selected bond lengths [Å], angles [deg], and torsion angles [deg]: I1−Rh1 2.68360(17), Rh1−C1 2.0183(15), N1−C1 1.3473(18), N2−C1 1.339(2); I1−Rh1−C1 88.86(4), Rh1−C1−N1 125.59(11), Rh1−C1−N2 125.78-(10), N1−C1−N2 108.57(13); I1−Rh1−C1−N1 88.22(13).

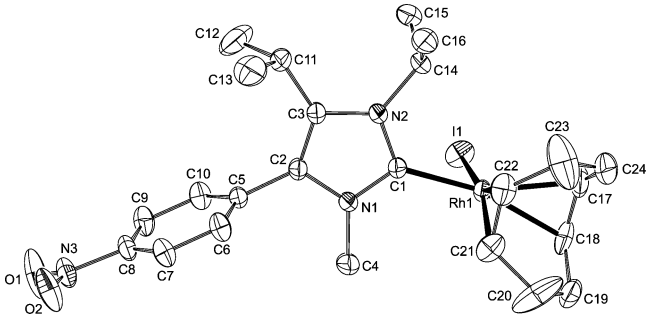

Figure 8. Displacement ellipsoid plot of **47** drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å], angles [deg], and torsion angles [deg]: I1−Rh1 2.6652(2), Rh1−C1 2.028(2), N1−C1 1.348(3), N2−C1 1.360(3); I1−Rh1−C1 87.58(6), Rh1−C1−N1 128.43(15), Rh1−C1−N2 126.72(14), N1−C1−N2 104.84(17); I1−Rh1−C1−N1 90.56(18).

(C), 28.9 (3×CH_3). IR (neat): 2973 (s), 1674 (m), 1585 (s), 1450 (s), 1236 (s). HRMS (EI, 70 eV): calcd for $C_{19}H_{20}N_2$ (M^+) 276.1626, found 276.1617. Anal. Calcd for $C_{19}H_{20}N_2$ (%): C 82.57, H 7.29, N 10.14. Found: C 82.42, H 7.44, N 10.06.

General Procedure II for the Synthesis of 2-Imidazolinium Salts. Reactions were carried out at a concentration of 0.15−0.25 M of imidazoline in dry DCM, unless noted otherwise. The halide was added to a stirred solution of the imidazoline, and the reaction mixture was stirred at rt for 18 h. Then, the reaction mixture was concentrated *in vacuo*. The crude product was washed with pentane or Et_2O.

2-Imidazolinium Iodide 23. According to General Procedure II, alkylation of imidazoline **22** (1.99 g, 7.2 mmol) with methyl iodide **19** (1.08 g, 7.6 mmol) followed by washing with Et_2O afforded salt **23** as a white solid (2.95 g, 98%). ^1H NMR (250 MHz, $CDCl_3$): δ (ppm) 7.75−7.70 (m, 4H), 7.57−7.43 (m, 4H), 4.26 (s, 2H), 2.91 (s, 3H), 1.69 (s, 9H). ^{13}C NMR (50 MHz, $CDCl_3$): δ (ppm) 157.2 (CH), 141.7 (2×C), 140.2 (2×C), 131.1 (2×CH), 129.4 (2×CH), 124.3 (2×CH), 120.7 (2×CH), 74.8 (C), 57.9 (C), 56.6 (CH_2), 30.7 (CH_3), 28.2 (3×CH_3). IR (neat): 1633 (s), 1450 (m), 1307 (m), 1269 (m). HRMS (ESI): calcd for $C_{20}H_{23}N_2^+$ (cation) 291.1856, found 276.1856.

2-Imidazolinium Iodide 24. According to General Procedure II, alkylation of imidazoline **22** (770 mg, 2.8 mmol) with 2,4,6-trimethylbenzyl chloride **21** (475 mg, 2.8 mmol) in DMF (15 mL), followed by washing with pentane, afforded **24** (1.04 g, 84%) as a white solid. ^1H NMR (250 MHz, $CDCl_3$): δ (ppm) 10.44 (s, 1H), 7.60 (d, J = 7.5 Hz, 2H), 7.52 (d, J = 7.6 Hz, 2H), 7.45−7.38 (m, 2H), 7.28−7.23 (m, 2H), 6.45 (s, 2H), 4.78 (s, 2H), 4.23 (s, 2H), 2.09 (s, 3H), 1.92 (s, 6H), 1.67 (s, 9H); ^{13}C NMR (63 MHz, $CDCl_3$): δ (ppm) 158.6 (CH), 142.2 (2×C), 139.9 (2×C), 137.9 (C), 137.6 (2×C), 130.5 (2×CH), 129.1 (2×CH), 128.9 (2×CH), 126.3 (C), 124.0 (2×CH), 120.4 (2×CH), 74.5 (C), 58.0 (CH_2), 57.8 (C), 44.6 (CH_2), 28.3 (3×CH_3), 20.7 (CH_3), 19.7 (2×CH_3). IR (neat): 1626 (s), 1450 (m), 1217 (m). HRMS (ESI): calcd for $C_{29}H_{33}N_2^+$ (cation) 409.2638, found 409.2631.

2-Imidazolinium Bromide 26. According to General Procedure II, alkylation of imidazoline **25** (1.4 g, 3.7 mmol) with benzyl bromide **20** (751 mg, 4.4 mmol), followed by washing with cold Et_2O, afforded **26** (1.9 g, 93%) as a white solid. ^1H NMR (250 MHz, $CDCl_3$): δ (ppm) 10.50 (s, 1H), 7.71 (d, J = 7.5 Hz, 1H), 7.62 (d, J = 7.6 Hz, 1H), 7.56−7.35 (m, 5H), 7.29−7.20 (m, 1H),

7.18−6.97 (m, 7H), 6.90−6.87 (m, 2H), 5.37 (d, J = 14.4 Hz, 1H), 4.72 (d, J = 14.4 Hz, 1H), 4.32 (d, J = 5.3 Hz, 1H), 4.30 (d, J = 14.4 Hz, 1H) , 4.06 (d, J = 14.4 Hz, 1H), 3.86 (s, 3H), 2.19−2.13 (m, 1H), 0.77 (d, J = 6.9 Hz, 3H), 0.60 (d, J = 7.0 Hz, 3H). ^{13}C NMR (63 MHz, $CDCl_3$): δ (ppm) 160.9 (CH), 160.1 (C), 143.1 (C), 141.5 (C), 140.1 (C), 137.9 (C), 133.2 (C), 131.0 (CH), 130.6 (CH), 130.4 (2×CH), 129.1 (2×CH), 129.0 (CH), 128.5 (2×CH), 128.4 (CH), 127.9 (CH), 127.4 (CH), 125.3 (CH), 124.6 (C), 120.7 (CH), 120.2 (CH), 114.7 (2×CH), 79.2 (C), 74.2 (CH), 55.4 (CH_3), 51.8 (CH_2), 49.3 (CH_2), 28.0 (CH), 19.3 (CH_3), 18.6 (CH_3). IR (neat): 1626 (s), 1514 (m), 1452 (m), 1252 (m). HRMS (ESI): calcd for $C_{33}H_{33}N_2O^+$ (cation) 473.2587, found 473.2581.

2-Imidazoline 27. According to General Procedure I, reaction between *p*-methoxybenzylamine **11** (685 mg, 5.0 mmol), ferrocenecarboxaldehyde **15** (1.07 g, 5.0 mmol), and isocyanide **16** (500 mg, 2.6 mmol) in MeOH (15 mL), followed by flash column chromatography, afforded **27** (936 mg 69%) as an orange solid. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) 7.67−7.63 (m, 1H), 7.54−7.31 (m, 7H), 7.23−7.17 (m, 1H), 7.11−6.96 (m, 4H), 4.98 (d, J = 14.5 Hz, 1H), 4.95 (s, 1H), 4.50 (d, J = 14.5 Hz, 1H), 4.14 (br s, 1H), 3.95 (br s, 1H), 3.92 (s, 3H), 3.90 (s, 5H), 3.77 (br s, 1H), 3.13 (d, J = 1.1 Hz, 1H). ^{13}C NMR (63 MHz, $CDCl_3$): δ (ppm) 159.3 (C), 159.1 (CH), 149.6 (C), 145.7 (C), 141.4 (C), 139.9 (C), 129.2 (2×CH), 129.1 (C), 128.5 (CH), 128.0 (CH), 127.7 (CH), 126.7 (CH), 126.0 (CH), 124.4 (CH), 119.5 (CH), 119.1 (CH), 114.5 (2×CH), 85.0 (C), 84.1 (C), 69.4 (CH), 66.5 (5×CH), 67.8 (CH), 66.9 (CH), 66.3 (CH), 65.1 (CH), 55.4 (CH_3), 50.2 (CH_2). IR (neat): 1599 (s), 1512 (s), 1448 (m), 1248 (s). HRMS (EI, 70 eV): calcd for $C_{33}H_{28}FeN_2O$ (M^+) 524.1551, found 524.1533.

2-Imidazolinium Iodide 28. According to General Procedure II, alkylation of imidazoline **27** (380 mg, 0.73 mmol) with methyl iodide **19** (109 mg, 0.77 mmol) followed by washing with pentane afforded salt **28** (481 mg, 99%) as a light brown solid. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) 9.10 (s, 1H), 8.23−8.20 (m, 1H), 7.69 (d, J = 8.6 Hz, 2H), 7.68−7.37 (m, 6H), 7.20−7.09 (m, 1H), 7.06 (d, J = 8.6 Hz, 2H), 5.65 (s, 1H), 5.21 (d, J = 13.6 Hz, 1H), 5.17 (d, J = 13.8 Hz, 1H), 4.26−4.25 (m, 1H), 4.17−4.16 (m, 1H), 3.96−3.94 (m, 1H), 3.92 (s, 5H), 3.89 (s, 3H), 3.21−3.20 (m, 1H), 2.70 (s, 3H). ^{13}C NMR (63 MHz, $CDCl_3$): δ (ppm) 160.2 (C), 159.3 (CH), 141.4 (C), 141.2 (C), 140.9 (C), 138.3 (C), 131.2 (CH), 131.0 (2×CH), 130.8 (CH), 129.5 (CH), 127.7 (CH), 126.5 (CH), 126.0 (CH), 125.4 (C), 120.4 (CH), 120.3 (CH), 114.9 (2×CH), 80.0 (C), 78.3 (C), 72.3 (CH), 69.2 (5×CH), 68.5 (CH), 68.2 (CH), 68.1 (CH), 66.0 (CH), 55.4 (CH_3) 50.3 (CH_2), 31.3 (CH_3). IR (neat): 1639 (s), 1514 (m), 1250 (s). HRMS (ESI): calcd for $C_{34}H_{31}FeN_2O^+$ (cation) 539.1780, found 539.1772.

2-Imidazolinium Iodide 30. According to General Procedure II, alkylation of imidazoline **29** (1.28 g, 4.9 mmol) with methyl iodide **19** (734 mg, 5.17 mmol) followed by washing with pentane afforded salt **30** (1.8 g, 93%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 9.73 (s, 1H), 7.51−7.46 (m, 3H,), 7.37−7.36 (m, 2H), 4.80 (d, J = 12.2 Hz, 1H), 4.01 (s, 3H), 3.94 (d, J = 12.2 Hz, 1H), 3.43 (s, 3H), 1.58 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 168.9 (C), 156.6 (CH), 134.0 (C), 130.1 (CH), 129.8 (2×CH), 126.4 (2×CH), 75.9 (C), 58.1 (C), 57.7 (CH_2), 54.1 (CH_3), 33.8 (CH_3), 28.1 (3×CH_3). IR (neat): 2974 (s), 1743 (s), 1633 (s), 1265 (s), 1230 (s), 1196 (s). HRMS (ESI): calcd for $C_{16}H_{23}N_2O_2^+$ (cation) 275.1754, found 275.1754.

2-Imidazolinium Iodide 32. According to General Procedure II, alkylation of imidazoline **31** (500 mg, 1.8 mmol) with methyl iodide **19** (284 mg, 2.0 mmol) followed by washing with Et_2O afforded salt **32** (656 mg, 86%) as a white solid. ^{1}H NMR (250 MHz, DMSO-d_6): δ (ppm) 8.77 (s, 1H), 8.34 (d, J = 8.2 Hz, 2H), 7.73 (d, J = 8.3 Hz, 2H), 5.34 (d, J = 4.6 Hz, 1H), 4.26−4.11 (m, 1H), 3.64−3.53 (m, 1H), 2.94 (s, 3H), 2.60−2.39 (m, 1H), 1.43 (d, J = 4.8 Hz, 3H), 1.27 (d, J = 4.7 Hz, 3H), 0.92 (d, J = 4.4 Hz, 6H). ^{13}C NMR (63 MHz, DMSO-d_6): δ (ppm) 156.3 (CH), 147.9 (C), 144.5 (C), 128.7 (2×CH), 124.4 (2×CH), 72.4 (CH), 63.4 (CH), 47.7 (CH), 32.6 (CH_3), 27.4 (CH), 21.2 (CH_3), 20.7 (CH_3),-16.7 (CH_3),13.8 (CH_3). IR (KBr): 1743 (s), 1633 (s), 1265 (m), 1230 (m), 1196 (m). HRMS (ESI): calcd for $C_{16}H_{24}N_3O_2^+$ (cation) 290.1863, found 290.1863.

2-Imidazolium Iodide 34. Methyl iodide **19** (988 mg, 7.0 mmol) was added to a solution of imidazole **33** (238 mg, 2.8 mmol) in DCM (4 mL) in a microwave vessel. The reaction mixture was heated in the microwave at 100 °C for 20 min. After cooling, the reaction mixture was concentrated *in vacuo*. After washing with Et_2O, salt **34** (253 mg, 70%) was isolated as a white solid. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) 10.38 (s, 1H), 8.41 (d, J = 8.6 Hz, 2H), 7.80 (d, J = 8.6 Hz, 2H), 4.68−4.62 (m, 1H), 3.82 (s, 3H), 3.15−3.11 (m, 1H), 1.82 (d, J = 6.7 Hz, 6H), 1.22 (d, J = 7.1 Hz, 6H). ^{13}C NMR (63 MHz, $CDCl_3$): δ (ppm) 149.2 (C), 136.5 (C), 135.7 (CH), 132.9 (2×CH), 132.4 (C), 128.3 (C), 124.2 (2×CH), 51.1 (CH), 35.2 (CH_3), 24.7 (CH), 24.0 (2×CH_3), 22.1 (2×CH_3). IR (neat): 1522 (s), 1348 (s). HRMS (ESI): calcd for $C_{16}H_{22}N_3O_2^+$ (cation) 288.1707, found 288.1707.

General Procedure III for the Synthesis of M(cod)X(NHC) Complexes. In a glovebox, NaH (12 mg, 0.5 mmol) was added to a solution of imidazolinium halide (0.5 mmol) in THF (5−8 mL). After stirring the reaction mixture at rt for 18 h, the reaction mixture was filtered and the filtrate transferred to a Schlenk tube containing $[Rh(cod)Cl]_2$ or $[Ir(cod)Cl]_2$ (0.23−0.24 mmol). THF (10 mL) was added, and the reaction mixture was stirred at reflux for 18 h. After cooling, the mixture was filtered through a pad of Celite, concentrated *in vacuo*, and purified using flash column chromatography (pentane/DCM = 4:1, gradient).

General Procedure IV for the Synthesis of M(cod)X(NHC) Complexes. Reactions were carried out at a concentration of 0.04 M of imdazol(in)ium salt in dry THF. A Schlenk tube was charged with imidazol(in)ium salt (1 equiv), KO^{t}Bu (1 equiv), $[Rh(cod)Cl]_2$ or $[Ir(cod)Cl]_2$ (0.95 equiv), and KI (3 equiv). THF was added and the reaction mixture was stirred at rt for 18 h. Then, the mixture was filtered through a pad of Celite, concentrated *in vacuo*, and purified using flash column chromatography (pentane/DCM = 4:1, gradient).

Rh−NHC Complex 35. Method A. According to General Procedure III, reaction between imidazolinium iodide **23** (209 mg, 0.5 mmol), NaH (12 mg, 0.5 mmol), $[Rh(cod)Cl]_2$ (113 mg, 0.23 mmol), and KI (249 mg, 1.5 mmol), followed by flash column chromatography, afforded **35** (150 mg, 52%) as an orange-yellow solid.

Method B. According to General Procedure IV, reaction between imidazolinium iodide **23** (209 mg, 0.5 mmol), KO^{t}Bu (56 mg, 0.5 mmol), $[Rh(cod)Cl]_2$ (113 mg, 0.23 mmol), and KI (249 mg, 1.5 mmol), followed by flash column chromatography, afforded **35** (238 mg, 82%) as an orange-yellow solid. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) 7.86−7.83 (m, 1H), 7.71−7.66 (m, 2H), 7.47−7.23 (m, 5H), 5.22 (br s, 2H), 4.08 (d, J = 10.8 Hz, 1H), 3.96 (d, J = 10.8 Hz, 1H), 3.65 (br s, 2H), 3.19 (s, 3H), 2.37−2.21 (m, 3H), 2.15−2.07 (m, 2H), 1.90 (s, 9H), 1.82−1.73 (m, 3H). ^{13}C NMR (63 MHz, $CDCl_3$): δ (ppm) 213.3 (d, J = 43.5 Hz, C), 145.7 (C), 145.1 (C), 140.5 (C), 139.4 (C), 129.5 (CH), 129.4 (CH), 129.0 (CH), 128.3 (CH), 125.0 (CH), 122.8 (CH), 120.3 (CH), 120.0 (CH), 95.2 (d, J = 6.9 Hz, CH), 93.5 (d, J = 6.7 Hz, CH), 74.2 (C), 74.0 (d, J = 15.4 Hz, CH), 70.4 (d, J = 14.0 Hz, CH), 59.7 (CH_2), 56.6 (C), 35.3 (CH_3), 33.9 (CH_2), 30.9 (CH_2), 30.2 (3×CH_3), 30.2 (CH_2), 27.9 (CH_2). IR (neat): 1475 (s), 1433 (s). HRMS (EI, 70 eV): calcd for $C_{28}H_{34}IN_2Rh$ (M^+) 628.0822, found 628.0820. Crystals suitable for X-ray crystal structure determination were obtained by the slow diffusion of pentane into a saturated solution of **75** in DCM. Mp: 230−233 °C.

Ir−NHC Complex 36. Method A. According to General Procedure III, reaction between imidazolinium iodide **23** (209 mg, 0.5 mmol), NaH (12 mg, 0.5 mmol), $[Ir(cod)Cl]_2$ (154 mg, 0.23

mmol), and KI (249 mg, 1.5 mmol), followed by flash column chromatography, afforded **36** (182 mg, 55%) as an orange solid.

Method B. According to General Procedure IV, reaction between imidazolinium iodide **23** (209 mg, 0.5 mmol), KO^{t}Bu (56 mg, 0.5 mmol), $[Ir(cod)Cl]_2$ (154 mg, 0.23 mmol), and KI (249 mg, 1.5 mmol), followed by flash column chromatography, afforded **36** (209 mg, 63%) as an orange solid, which could be recrystallized by the slow diffusion of pentane into a saturated solution of the complex in DCM. Mp: 236−238 °C (dec). ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) 7.88−7.85 (m, 1H), 7.72−7.67 (m, 2H), 7.49−7.29 (m, 5H), 4.83−4.72 (m, 2H), 4.13 (d, J = 10.9 Hz, 1H), 4.04 (d, J = 10.9 Hz, 1H), 3.25−3.13 (m, 2H), 3.02 (s, 3H), 2.34−2.24 (m, 1H), 2.18−1.84 (m, 4H), 1.81 (s, 9H), 1.56−1.29 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 209.0 (C), 145.7 (C), 145.1 (C), 140.5 (C), 139.6 (C), 129.53 (CH), 129.50 (CH), 129.0 (CH), 128.4 (CH), 124.8 (CH), 122.9 (CH), 120.9 (CH), 120.0 (CH), 80.5 (CH), 79.7 (CH), 74.4 (C), 60.1 (CH_2), 56.94 (C), 56.93 (CH), 54.3 (CH), 35.0 (CH_3), 34.4 (CH_2), 31.5 (CH_2), 30.8 (CH_2), 30.6 (3×CH_3), 28.6 (CH_2). IR (neat) 1473 (s), 1448 (s), 1429 (s), 1304 (s). HRMS (EI, 70 eV) calcd for $C_{28}H_{34}IIrN_2$ (M^+) 718.1396, found 718.1370. Anal. Calcd for $C_{28}H_{34}IIrN_2$ (%): C 46.86, H 4.77, N 3.90. Found: C 46.62, H 4.78, N 3.87.

Rh−NHC Complex 37. Method A. According to General Procedure III, reaction between imidazolinium iodide **30** (201 mg, 0.5 mmol), NaH (12 mg, 0.5 mmol), $[Rh(cod)Cl]_2$ (113 mg, 0.23 mmol), and KI (249 mg, 1.5 mmol), followed by flash column chromatography, afforded **37** (143 mg, 51%) as a 89:11 mixture of rotamers as an orange-yellow solid.

Method B. According to General Procedure IV, reaction between imidazolinium iodide **30** (300 mg, 0.75 mmol), KO^{t}Bu (84 mg, 0.75 mmol), $[Rh(cod)Cl]_2$ (176 mg, 0.35 mmol), and KI (374 mg, 2.25 mmol), followed by flash column chromatography, afforded **37** (271 mg, 63%) as a 78:22 mixture of rotamers as a yellow solid. Main isomer: ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) 7.47−7.33 (m, 5H), 5.22−5.19 (m, 2H), 4.41 (d, J = 11.3 Hz, 1H), 3.92 (s, 3H), 3.78 (d, J = 11.3 Hz, 1H), 3.72−3.60 (m, 1H), 3.69 (s, 3H), 3.48−3.41 (m, 1H), 2.55−2.37 (m, 2H), 2.29−2.04 (m, 3H), 1.94−1.88 (m, 1H), 1.82 (s, 9H), 1.77−1.64 (m, 2H). ^{13}C NMR (63 MHz, $CDCl_3$): δ (ppm) 213.3 (d, J = 43.8 Hz, C), 171.7 (C), 137.8 (C), 129.1 (2×CH), 128.6 (CH), 126.7 (2×CH), 95.3 (d, J = 7.0 Hz, CH), 93.4 (d, J = 6.7 Hz, CH), 74.9 (C), 73.9 (d, J = 15.3 Hz, CH), 70.8 (d, J = 14.0 Hz, CH), 60.9 (CH_2), 56.8 (C), 52.8 (CH_3), 37.8 (CH_3), 33.9 (CH_2), 30.9 (CH_2), 30.1 (3×CH_3), 30.0 (CH_2), 27.9 (CH_2). IR (neat): 1739 (s), 1475 (m), 1433 (s), 1221 (s). HRMS (EI, 70 eV): calcd for $C_{24}H_{34}IN_2O_2Rh$ (M^+) 612.0720, found 612.0739. Anal. Calcd for $C_{24}H_{34}IN_2O_2Rh$ (%): C 47.07, H 5.60, N 4.57. Found: C 46.46, H 5.45, N 4.63.

Ir−NHC Complex 38. Method A. According to General Procedure III, reaction between imidazolinium iodide **30** (201 mg, 0.5 mmol), NaH (12 mg, 0.5 mmol), $[Ir(cod)Cl]_2$ (154 mg, 0.23 mmol), and KI (249 mg, 1.5 mmol), followed by flash column chromatography, afforded two rotamers of **38** (least polar fraction **38a**: 88 mg, 27%; most polar fraction **38b**: 81 mg, 25%) as orange solids.

Method B. According to General Procedure IV, reaction between imidazolinium iodide **30** (201 mg, 0.5 mmol), KO^{t}Bu (56 mg, 0.5 mmol), $[Ir(cod)Cl]_2$ (154 mg, 0.23 mmol), and KI (249 mg, 1.5 mmol), followed by flash column chromatography, afforded two rotamers of **38** (least polar fraction **38a**: 91 mg, 28%; most polar fraction **38b**: 67 mg, 21%) as orange solids.

Method C. According to General Procedure IV, reaction between imidazolinium iodide **30** (201 mg, 0.5 mmol), KO^{t}Bu (56 mg, 0.5 mmol), $[Ir(cod)Cl]_2$ (154 mg, 0.23 mmol), and KI (249 mg, 1.5 mmol) in refluxing THF, followed by flash column chromatography, afforded two rotamers of **38** (least polar fraction **38a**: 122 mg, 38%; most polar fraction **38b**: 60 mg, 19%) as orange solids. **38a**: ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) 7.39−7.27 (m, 5H), 4.70−4.64 (m, 2H), 4.40 (d, J = 11.3 Hz, 1H), 3.84 (s, 3H), 3.72 (d, J = 11.3 Hz, 1H), 3.43 (s, 3H), 3.17−3.14 (m, 1H), 2.90−2.88 (m, 1H), 2.19−1.82 (m, 5H), 1.64 (s, 9H), 1.56−1.35 (m, 2H), 1.22−1.20 (m, 1H). ^{13}C NMR (63 MHz, $CDCl_3$): δ (ppm) 208.8 (C), 171.2 (C), 137.7 (C), 129.1 (2×CH), 128.7 (CH), 126.7 (2×CH), 80.7 (CH), 79.9 (CH), 74.9 (C), 61.3 (CH_2), 57.1 (C), 56.9 (CH), 54.7 (CH), 52.9 (CH_3), 37.6 (CH_3), 34.4 (CH_2), 31.5 (CH_2), 30.6 (CH_2), 30.5 (3×CH_3), 28.5 (CH_2). IR (neat) 1738 (s), 1238 (m). HRMS (EI, 70 eV) calcd for $C_{24}H_{34}IIrN_2O_2$ (M^+) 702.1294, found 702.1289. Crystals suitable for X-ray crystal structure determination were obtained by the slow diffusion of pentane into a saturated solution of **38a** in dichloromethane (DCM). Mp 177−179 °C. **38b**: ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) 7.38−7.30 (m, 3H), 7.16−7.13 (m, 2H), 4.70 (br s, 2H), 4.54 (d, J = 11.1 Hz, 1H), 3.86 (s, 3H), 3.54 (d, J = 11.1 Hz, 1H), 3.42 (s, 3H), 3.12−3.10 (m, 1H), 3.03−3.00 (m, 1H), 2.18−1.80 (m, 5H), 1.63 (s, 9H), 1.39−1.20 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 209.2 (C), 170.6 (C), 137.4 (C), 129.0 (2×CH), 128.6 (CH), 126.2 (2×CH), 80.9 (CH), 79.7 (CH), 75.6 (C), 60.9 (CH_2), 56.9 (C), 56.0 (CH), 54.5 (CH), 52.9 (CH_3), 37.8 (CH_3), 34.1 (CH_2), 31.11 (CH_2), 31.06 (CH_2), 30.6 (3×CH_3), 28.9 (CH_2); IR (neat) 1736 (s), 1217 (m); HRMS (EI, 70 eV) calcd for $C_{24}H_{34}IIrN_2O_2$ (M^+) 702.1294, found 702.1276. Crystals suitable for X-ray crystal structure determination were obtained by the slow diffusion of pentane into a saturated solution of **38b** in DCM. Mp 178−180 °C.

2-Imidazolinium Hexafluorophosphate 39. $AgPF_6$ (384 mg, 1.52 mmol) was added to a solution of imidazolinium iodide **30** (612 mg, 1.52 mmol) in DCM (12 mL). While stirring the reaction mixture at rt, a yellow precipitate was formed. After 15 min, the suspension was filtered and the filtrate concentrated *in vacuo* and washed with pentane to afford salt **39** as a white solid (611 mg, 96%). ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) 8.75 (s, 1H), 7.51−7.46 (m, 3H), 7.29−7.27 (m, 2H), 4.83 (d, J = 12.2 Hz, 1H), 4.02 (s, 3H), 3.96 (d, J = 12.2 Hz, 1H), 3.29 (s, 3H), 1.50 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 168.9 (C), 156.9 (CH), 134.0 (C), 130.1 (CH), 129.9 (2×CH), 126.1 (2×CH), 75.9 (C), 57.83 (C), 57.79 (CH_2), 54.0 (CH3), 33.1 (CH_3), 27.5 (3×CH_3). IR (neat) 1747 (s), 1641 (s), 1267 (m), 839 (s). HRMS (EI, 70 eV): calcd for $C_{16}H_{23}N_2O_2^+$ (cation) 275.1754, found 275.1745.

Rh−NHC Complex 40. A Schlenk tube was charged with imidazolinium salt **39** (210 mg, 0.5 mmol), KO^{t}Bu (56 mg, 0.5 mmol), $[Rh(cod)Cl]_2$ (106 mg, 0.215 mmol), and tetraethylammonium chloride (248 mg, 1.5 mmol). THF (10 mL) was added, and the reaction mixture was stirred at rt for 18 h. Then, the mixture was filtered through a pad of Celite, concentrated *in vacuo*, and purified using flash column chromatography (pentane/DCM = 1:2, DCM, DCM/EtOAc = 8:1) to afford **40** (175 mg, 79%) as a 78:22 mixture of rotamers as a yellow-orange solid. Main isomer: ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) 7.36−7.19 (m, 5H), 4.89 (br s, 2H), 4.29 (d, J = 11.3 Hz, 1H), 3.82 (s, 3H), 3.74 (s, 3H), 3.63 (d, J = 11.3 Hz, 1H), 3.49−3.38 (m, 1H), 3.23−3.17 (m, 1H), 2.47−2.13 (m, 4H), 1.94−1.83 (m, 2H), 1.74 (s, 9H), 1.73−1.63 (m, 2H). ^{13}C NMR (63 MHz, $CDCl_3$): δ (ppm) 213.8 (d, J = 45.9 Hz, C), 171.5 (C), 137.7 (C), 129.1 (2×CH), 128.6 (CH), 126.3 (2×CH), 97.4 (d, J = 7.0 Hz, CH), 95.1 (d, J = 6.2 Hz, CH), 75.0 (C), 70.9 (d, J = 15.5 Hz, CH), 67.3 (d, J = 14.5 Hz, CH), 60.6 (CH_2), 56.8 (C), 52.8 (CH_3), 37.3 (CH_3), 33.5 (CH_2), 31.3 (CH_2), 30.3 (3×CH_3), 29.4 (CH_2), 27.9 (CH_2). IR (neat): 1739 (s), 1475 (m), 1435 (m), 1223 (m). HRMS (EI, 70 eV): calcd for $C_{24}H_{34}ClN_2O_2Rh$ (M^+) 520.1364, found 520.1375.

2-Imidazolinium Tosylate 41. According to General Procedure II, alkylation of imidazoline **22** (203 mg, 0.74 mmol) with methyl tosylate (141 mg, 0.74 mmol), followed by washing with pentane, afforded salt **41** (336 mg, 99%) as a white solid. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) 9.70 (s, 1H), 7.75 (d, J = 8.1 Hz, 2H), 7.64 (d, J = 7.4 Hz, 2H), 7.54−7.33 (m, 6H), 7.06 (d, J = 8.0 Hz,

2H), 4.17 (s, 2H), 2.75 (s, 3H), 2.26 (s, 3H), 1.54 (s, 9H). ^{13}C NMR (63 MHz, $CDCl_3$): δ (ppm) 158.8 (CH), 143.9 (C), 141.9 (2×C), 140.2 (2×C), 138.9 (C), 131.0 (2×CH), 129.4 (2×CH), 128.5 (2×CH), 126.0 (2×CH), 124.1 (2×CH), 120.7 (2×CH), 74.8 (C), 57.6 (C), 56.7 (CH_2), 30.5 (CH_3), 28.0 (3×CH_3), 21.2 (CH_3). IR (neat): 1475 (s), 1433 (s). HRMS (EI, 70 eV): calcd for $C_{20}H_{23}N_2^+$ (cation) 291.1856, found 291.1849.

Rh−NHC Complex 42. A Schlenk tube was charged with imidazolinium salt **41** (231 mg, 0.5 mmol), KO^{t}Bu (56 mg, 0.5 mmol), $[Rh(cod)Cl]_2$ (123 mg, 0.25 mmol), and LiCl (64 mg, 1.5 mmol). THF (10 mL) was added and the reaction mixture was stirred at rt for 18 h. Then, the mixture was filtered through a pad of Celite and concentrated *in vacuo*. The residue was taken into DCM, washed with water, dried with Na_2SO_4, concentrated *in vacuo*, and purified using flash column chromatography (DCM, DCM/EtOAc = 20:1, gradient) to afford **40** (75 mg, 27%) as a yellow-orange solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.68−7.63 (m, 3H), 7.42−7.29 (m, 4H), 7.20 (d, J = 7.4 Hz, 1H), 4.99−4.94 (m, 2H), 4.01 (d, J = 10.8 Hz, 1H), 3.89 (d, J = 10.8 Hz, 1H), 3.44−3.40 (m, 2H), 3.28 (s, 3H), 2.45−2.33 (m, 3H), 2.23−2.20 (m, 1H), 1.97−1.91 (m, 2H), 1.88 (s, 9H), 1.86−1.75 (m, 2H). ^{13}C NMR (63 MHz, $CDCl_3$): δ (ppm) 214.0 (d, J = 45.6 Hz, C), 145.5 (C), 145.0 (C), 140.5 (C), 139.4 (C), 129.47 (CH), 129.45 (CH), 129.0 (CH), 128.3 (CH), 124.6 (CH), 122.8 (CH), 120.3 (CH), 120.0 (CH), 97.4 (d, J = 7.2 Hz, CH), 94.9 (d, J = 7.0 Hz, CH), 74.4 (C), 70.7 (d, J = 15.7 Hz, CH), 67.0 (d, J = 14.5 Hz, CH), 59.6 (CH_2), 56.7 (C), 34.6 (CH_3), 33.5 (CH_2), 31.5 (CH_2), 30.4 (3×CH_3), 29.4 (CH_2),28.0 (CH_2). IR (neat): 1473 (s), 1450 (s), 1435 (s). HRMS (EI, 70 eV): calcd for $C_{28}H_{34}ClN_2Rh$ (M^+) 536.1466, found 536.1473.

Rh−NHC Complex 43. A Schlenk tube was charged with imidazolinium chloride **24** (222 mg, 0.5 mmol), KO^{t}Bu (56 mg, 0.5 mmol), and $[Rh(cod)Cl]_2$ (118 mg, 0.24 mmol). THF (10 mL) was added, and the reaction mixture was stirred at rt for 18 h. Then, the mixture was filtered through a pad of Celite, concentrated *in vacuo*, and purified using flash column chromatography (DCM, DCM/EtOAc = 3:1) to afford **43** (170 mg, 54%) as a yellow-orange solid. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) 7.55 (d, J = 7.8 Hz, 1H), 7.41 (d, J = 7.4 Hz, 1H), 7.35−7.17 (m, 5H), 7.10−7.02 (m, 1H), 6.32 (br s, 1H), 6.19 (d, J = 14.3 Hz, 1H), 6.09 (br s, 1H), 5.31 (d, J = 14.2 Hz, 1H), 5.12−5.02 (m, 2H), 3.91 (d, J = 10.7 Hz, 1H), 3.78−3.73 (m, 2H), 3.77 (d, J = 10.7 Hz, 1H), 2.54−2.19 (m, 5H), 1.98 (s, 6H), 1.96 (s, 9H), 1.96 (br s, 3H), 1.70−1.64 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 217.8 (d, J = 46.2 Hz, C), 145.1 (C), 144.5 (C), 140.2 (C), 139.7 (C), 139.0 (C), 137.1 (C), 136.7 (C), 128.7 (CH), 128.4 (CH), 128.1 (C), 128.0 (CH), 127.5 (CH), 124.5 (CH), 123.7 (CH), 122.4 (CH), 119.9 (CH), 119.6 (CH), 119.3 (CH), 97.2 (d, J = 7.4 Hz, CH), 94.7 (d, J = 6.9 Hz, CH), 73.8 (C), 69.2 (d, J = 14.7 Hz, CH), 68.8 (d, J = 15.2 Hz, CH), 61.2 (CH_2), 57.3 (C), 50.4 (CH_2), 32.6 (CH_2), 32.3 (CH_2), 30.5 (3×CH_3), 28.7 (CH_2), 28.4 (CH_2), 27.4 (CH_3), 20.4 (CH_3), *p*-CH_3 of mesityl group could not be observed. IR (neat): 1691 (m), 1450 (s), 1200 (s). HRMS (EI, 70 eV): calcd for $C_{37}H_{44}ClN_2Rh$ (M^+) 654.2248, found 654.2250.

Rh−NHC Complex 44. According to General Procedure IV, reaction between imidazolinium bromide **26** (553 mg, 0.5 mmol), KO^{t}Bu (56 mg, 0.5 mmol), $[Rh(cod)Cl]_2$ (118 mg, 0.24 mmol), and KI (249 mg, 1.5 mmol), followed by flash column chromatography, afforded **44** (314 mg, 81%) as a 80:20 mixture of rotamers as a yellow solid. Main isomer: ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) 7.78 (d, J = 8.6 Hz, 2H), 7.54 (d, J = 7.5 Hz, 1H), 7.49−6.65 (m, 14H), 5.70 (d, J = 14.1 Hz, 1H), 5.37−5.22 (m, 2H), 4.74 (d, J = 14.7 Hz, 1H), 4.46 (d, J = 14.2 Hz, 1H), 4.04−3.93 (m, 1H), 3.92 (d, J = 4.1 Hz, 1H), 3.86−3.78 (m, 2H), 3.84 (s, 3H), 2.52−2.17 (m, 4H), 2.08−1.69 (m, 5H), 0.64 (d, J = 7.2 Hz, 3H), 0.48 (d, J = 7.0 Hz, 3H). ^{13}C NMR (63 MHz, $CDCl_3$): δ (ppm) 217.8 (d, J = 45.6 Hz, C), 159.2 (C), 147.2 (C), 142.0 (C), 140.7 (C), 138.6 (C), 135.7 (2×C), 130.5 (2×CH), 129.8 (2×CH), 129.5 (CH), 128.5 (CH), 127.9 (CH), 127.2 (2×CH), 127.1 (CH), 126.9 (CH), 126.5 (CH), 125.4 (CH), 120.2 (CH), 119.1 (CH), 113.8 (2×CH), 97.5 (d, J = 6.4 Hz, 2×CH), 79.3 (C), 73.6 (CH), 73.1 (d, J = 14.2 Hz, CH), 71.9 (d, J = 14.1 Hz, CH), 55.3 (CH_3), 53.5 (CH_2), 52.8 (CH_2), 32.5 (CH_2), 32.1 (CH_2), 29.39 (CH_2), 29.36 (CH_2), 28.7 (CH), 19.9 (CH_3), 18.0 (CH_3). IR (neat): 1512 (s), 1450 (s), 1248 (s). HRMS (EI, 70 eV): calcd for $C_{33}H_{32}N_2ORh$ ($M - (I + cod)^+$) 575.1570, found 575.1564 (the molecular ion is hardly detectable in the mass spectrometer). Crystals suitable for X-ray crystal structure determination were obtained by the slow diffusion of pentane into a saturated solution of **44** in DCM. Mp: 186−187 °C.

Rh−NHC Complex 45. According to General Procedure IV, reaction between imidazolinium iodide **28** (166 mg, 0.25 mmol), KO^{t}Bu (28 mg, 0.25 mmol), $[Rh(cod)Cl]_2$ (59 mg, 0.12 mmol), and KI (125 mg, 0.75 mmol), followed by flash column chromatography, afforded **45** (173 mg, 82%) as a 58:42 mixture of rotamers as an orange-yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.87−7.85 (m, 1H^B), 7.67−7.62 (m, 1H^A+2H^B), 7.55−7.34 (m, 7H^A+4H^B), 7.26−7.21 (m, 1H^B), 7.11−7.06 (m, 1H^B), 6.99−6.92 (m, 3H^A+1H^B), 6.91−6.88 (m, 1H^A+1H^B), 6.81 (d, J = 7.6 Hz, 1H^B), 6.54 (d, J = 16.9 Hz, 1H^A), 5.90 (d, J = 15.3 Hz, 1H^B), 5.81 (d, J = 17.0 Hz, 1H^A), 5.32 (s, 1H^A), 5.31−5.26 (m, 1H^B), 5.27 (d, J = 15.2 Hz, 1H^B), 5.23−5.13 (m, 2H^A+1H^B), 5.09 (s, 1H^B), 4.74 (br s, 1H^A), 4.14 (br s, 1H^A), 3.94 (br s, 1H^B), 3.83 (s, 3H^A), 3.81 (s, 3H^B), 3.76 (s, 5H^A), 3.77−3.75 (m, 1H^B), 3.75−3.72 (m, 1H^A), 3.68−3.59 (m, 2H^A+1H^B), 3.60 (s, 5H^B), 3.58−3.50 (m, 2H^B), 3.03 (br s, 1H^A), 3.01 (br s, 1H^B), 2.94 (s, 3H^A), 2.93 (s, 3H^B), 2.37−2.22 (m, 2H^A+1H^B), 2.21−2.12 (m, 3H^B), 2.06−1.92 (m, 1H^A+1H^B), 1.87−1.74 (m, 4H^A+2H^B), 1.56−1.47 (m, 1H^B). ^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 216.6 (d, J = 45.0 Hz, C^B), 216.4 (d, J = 44.7 Hz, C^A), 158.8 (C^B), 158.5 (C^A), 147.0 (C^A), 145.2 (C^B), 141.9 (C^B), 141.0 (C^B), 140.9 (C^A), 140.7 (C^B), 140.3 (C^A), 139.9 (C^A), 131.8 (C^A+C^B), 129.8 (CH^B), 129.6 (CH^A), 129.5 (CH^B), 129.2 (2×CH^B), 129.0 (CH^A), 128.70 (CH^B), 128.66 (CH^A), 128.2 (CH^A), 127.2 (CH^A), 127.0 (CH^B), 126.9 (2×CH^A), 125.9 (CH^B), 124.9 (CH^B), 122.2 (CH^A), 120.3 (CH^A), 120.1 (CH^B), 119.9 (CH^B), 119.3 (CH^A), 114.3 (2×CH^A), 113.6 (2×CH^B), 97.4 (d, J = 6.2 Hz, CH^B), 97.3 (d, J = 6.6 Hz, CH^B), 97.2 (d, J = 6.5 Hz, CH^A), 96.8 (d, J = 6.5 Hz, CH^A), 84.4 (C^A), 82.2 (C^A), 81.4 (C^B), 80.4 (C^B), 72.7 (d, J = 14.2 Hz, CH^A), 72.3 (d, J = 14.4 Hz, CH^B), 71.9 (d, J = 13.9 Hz, CH^A), 71.7 (d, J = 14.2 Hz, CH^B), 70.7 (CH^A), 70.2 (CH^B), 68.78 (CH^B), 68.75 (CH^A), 68.6 (5×CH^B), 68.5 (5×CH^A), 68.4 (CH^B), 67.9 (CH^A), 67.6 (CH^A), 67.0 (CH^B), 66.6 (CH^B), 66.4 (CH^A), 55.3 (CH$_3^A$+CH$_3^B$), 52.0 (CH$_2^B$), 51.5 (CH$_2^A$), 33.4 (CH$_3^B$), 33.2 (CH$_2^B$), 33.1 (CH$_3^A$), 32.9 (CH$_2^A$), 31.3 (CH$_2^A$+CH$_2^B$), 30.2 (CH$_2^B$), 30.0 (CH$_2^A$), 28.7 (CH$_2^A$), 28.5 (CH$_2^B$). IR (neat): 1612 (m), 1512 (s), 1489 (m), 1450 (s), 1246 (s). HRMS (EI, 70 eV): calcd for $C_{42}H_{42}FeIN_2ORh$ (M^+) 876.0746, found 876.0768.

Rh−NHC Complex 46. According to General Procedure IV, reaction between imidazolinium iodide **32** (208 mg, 0.5 mmol), KO^{t}Bu (56 mg, 0.5 mmol), $[Rh(cod)Cl]_2$ (118 mg, 0.24 mmol), and KI (249 mg, 1.5 mmol), followed by flash column chromatography, afforded **46** (238 mg, 79%) as a 82:18 mixture of rotamers as an orange-yellow solid. Main isomer: ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) 8.18 (d, J = 8.7 Hz, 2H), 7.68 (d, J = 8.7 Hz, 2H), 5.65−5.50 (m, 1H), 5.15−5.03 (m, 2H), 4.34 (d, J = 3.9 Hz, 1H), 3.74−3.65 (m, 1H), 3.60−3.42 (m, 2H), 3.25 (s, 3H), 2.28−2.11 (m, 4H), 2.05−1.69 (m, 5H), 1.31 (d, J = 7.0 Hz, 3H), 1.19 (d, J = 6.7 Hz, 3H), 0.89 (d, J = 6.9 Hz, 3H), 0.71 (d, J = 6.7 Hz, 3H). ^{13}C NMR (63 MHz, $CDCl_3$): δ (ppm) 213.7 (d, J = 44.5 Hz, C), 147.8 (C), 147.3 (C), 128.1 (2×CH), 124.5 (2×CH), 97.7 (d, J = 6.4 Hz, CH), 97.1 (d, J = 6.3 Hz, CH), 72.1 (d, J = 18.5 Hz, CH), 71.2 (d, J = 15.8 Hz, CH), 71.0 (CH), 66.3 (CH), 51.5 (CH), 35.9 (CH_3), 32.3 (CH_2), 32.2 (CH_2), 30.7 (CH), 29.4 (CH_2), 29.3

Table 6. Experimental Details about the X-ray Crystal Structure Determinations

	35	**38a**	**38b**	**44-I**	**44-II**	**46**	**47**
formula	$C_{28}H_{34}IN_2Rh$	$C_{24}H_{34}IIrN_2O_2$	$C_{24}H_{34}IIrN_2O_2$	$C_{41}H_{44}IN_2O_2ORh$	$C_{41}H_{44}IN_2ORh$	$C_{24}H_{35}lN_3O_2Rh$ + disordered solvent	$C_{24}H_{33}lN_3O_2Rh$
fw	628.38	701.63	701.63	810.59	810.59	627.36[a]	625.34
cryst color	yellow	yellow	yellow	yellow	yellow	yellow	yellow-orange
crystal size [mm^3]	0.39 × 0.39 × 0.30	0.60 × 0.30 × 0.30	0.24 × 0.18 × 0.06	0.39 × 0.30 × 0.12	0.39 × 0.30 × 0.12	0.60 × 0.24 × 0.12	0.33 × 0.33 × 0.12
temp [K]	150(2)	150(2)	150(2)	200(2)	110(2)	150(2)	150(2)
cryst syst	monoclinic	triclinic	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic
space group	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)	$P2_1/c$ (no. 14)	$P2_1/n$ (no. 14)	$P2_1$ (no. 4)	$C2/c$ (no. 15)	$Pbcn$ (no. 60)
a [Å]	11.7415(7)	9.0938(4)	10.1683(10)	10.7506(1)	10.7673(2)	39.766(2)	27.0390(9)
b [Å]	17.7220(8)	11.8189(5)	16.2203(4)	16.5547(2)	16.4575(2)	9.43481(18)	12.4877(4)
c [Å]	16.8036(7)	12.7235(4)	16.3588(8)	19.6785(2)	19.4919(2)	14.8167(3)	15.1739(4)
α [deg]		70.237(3)					
β [deg]	133.593(2)	82.611(1)	115.041(3)	91.2308(5)	93.6885(5)	97.424(2)	
γ [deg]		68.241(2)					
V [Å^3]	2532.4(2)	1195.26(9)	2444.5(3)	3501.43(6)	3446.86(8)	5512.4(3)	5123.5(3)
Z	4	2	4	4	4	8	8
d_{calc} [g/cm^3]	1.648	1.950	1.906	1.538	1.562	1.512[a]	1.621
μ [mm^{-1}]	1.912	6.899	6.747	1.404	1.426	1.762[a]	1.896
no. of reflns (coll/unique)	75 733/5804	38 713/5481	74 049/5615	50 732/7953	43 501/14 942	59 404/6335	101 661/5898
abs corr	multiscan	multiscan	multiscan	multiscan	multiscan	multiscan	multiscan
abs corr range	0.48−0.56	0.07−0.13	0.44−0.67	0.75−0.85	0.66−0.84	0.48−0.81	0.65−0.80
no. of params/restraints	341/0	296/0	300/0	438/0	836/1	301/0	301/0
R1/wR2 [$I > 2\sigma(I)$]	0.0150/0.0364	0.0152/0.0356	0.0190/0.0364	0.0315/0.0798	0.0266/0.597	0.0167/0.0380	0.0224/0.0487
R1/wR2 [all reflns]	0.0180/0.0376	0.0175/0.0361	0.0280/0.0382	0.0370/0.0824	0.0299/0.0618	0.0217/0.0394	0.0280/0.0511
S	1.091	1.078	1.033	1.144	1.016	1.068	1.076
res density [e/Å^3]	−0.54/0.38	−0.86/1.12	−0.59/0.85	−0.64/1.21	−0.49/1.44	−0.53/0.52	−0.76/0.80

[a] Derived parameters do not contain the contribution of the disordered solvent.

(CH_2), 23.1 (CH_3), 20.3 (CH_3), 18.3 (CH_3), 13.6 (CH_3). IR (neat): 1523 (s), 1446 (m), 1346 (s), 1188 (m). HRMS (EI, 70 eV): calcd for $C_{24}H_{35}IN_3O_2Rh$ (M^+) 627.0829, found 627.0803. Crystals suitable for X-ray crystal structure determination were obtained by the slow diffusion of pentane into a saturated solution of **46** in DCM. Mp: 136−139 °C.

Rh−NHC Complex 47. According to General Procedure IV, reaction between imidazolium iodide **34** (112 mg, 0.27 mmol), KO^t-Bu (31 mg, 0.28 mmol), $[Rh(cod)Cl]_2$ (67 mg, 0.135 mmol), and KI (135 mg, 0.81 mmol), followed by flash column chromatography, afforded **47** (80 mg, 46%) as an orange-yellow solid. ^{1}H NMR (250 MHz, $CDCl_3$): δ (ppm) 8.25 (d, J = 7.5 Hz, 2H), 7.43 (d, J = 7.4 Hz, 2H), 6.19−5.96 (m, 1H), 5.23−5.04 (m, 2H), 3.55 (s, 3H), 3.52−3.40 (m, 2H), 3.29−3.08 (m, 1H), 2.36−2.11 (m, 4H), 1.95−1.63 (m, 4H), 1.62 (d, J = 7.9 Hz, 3H), 1.58 (d, J = 9.6 Hz, 3H), 1.04−0.83 (m, 6H). ^{13}C NMR (63 MHz, $CDCl_3$): δ (ppm) 180.0 (d, J = 48.8 Hz, C), 148.3 (C), 137.1 (C), 137.0 (C), 132.6 (2×CH), 129.3 (C), 123.7 (2×CH), 96.2 (d, J = 6.8 Hz, CH), 95.7 (d, J = 6.8 Hz, CH), 71.5 (d, J = 14.4 Hz, CH), 70.8 (d, J = 14.0 Hz, CH), 54.0 (CH), 35.9 (CH_3), 32.4 (CH_2), 32.1 (CH_2), 29.7 (CH_2), 29.4 (CH_2), 25.4 (CH), 23.1 (CH_3), 22.8 (CH_3), 22.6 (CH_3), 21.8 (CH_3). IR (neat): 1522 (s), 1342 (s). HRMS (EI, 70 eV): calcd for $C_{24}H_{33}IN_3O_2Rh$ (M^+) 625.0672, found 625.0653. Crystals suitable for X-ray crystal structure determination were obtained by the slow diffusion of pentane into a saturated solution of **47** in DCM. Mp: 223−225 °C (dec).

Crystal Structure Determinations. X-ray intensities were measured on a Nonius KappaCCD diffractometer with rotating anode (graphite monochromator, λ = 0.71073 Å) up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.65 Å^{-1}. The structures were solved with automated Patterson methods[33] and refined with SHELXL-97[34] against F^2 of all reflections. Non hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were introduced in calculated positions (**44-II**) or located in the difference Fourier map (all other structures). Geometry calculations and checking for higher symmetry was performed with the PLATON program.[35] Further experimental details are given in Table 6. In **35** the H atoms of the cod ligand were refined freely with isotropic displacement parameters; all other H atoms were refined with a riding model. In **38a** and **38b** the H atoms at C3 and at the cod double bonds were refined freely with isotropic displacement parameters; all other H atoms were refined with a riding model. Data sets for **44-I** and **44-II** were measured on the same crystal at different temperatures. While over a wide temperature range (110−250 K) both phases are present, at 200 K the $P2_1/n$ phase (**44-I**) has higher intensity and at 110 K the $P2_1$ phase (**44-II**). Only these major components were integrated using the HKL2000 software.[36] **44-II** was refined in a nonstandard setting of space group $P2_1$ with an origin shift of (0.25, 0, 0.25) to obtain consistent coordinates with respect to the high-temperature phase $P2_1/n$ of **44-I** (group/subgroup relationship of the phase transition). In **44-I** the H atoms at C3 and at the cod double bonds were refined freely with isotropic displacement parameters; all other H atoms were refined with a riding model. In **44-II** all H atoms were refined with a riding model. **44-II** was refined as an inversion twin resulting in a Flack parameter x = 0.183(9).[37] The crystal structure of **46** contains large voids (596.4 Å^3/unit cell) filled with disordered solvent molecules. Their contribution to the structure factors was secured by back-Fourier transformation using the SQUEEZE routine of the program PLATON,[35] accounting for 137 electrons/unit cell. The H atoms at the cod double bonds were refined freely with isotropic displacement parameters; all other H atoms were refined with a riding model. In **47** the H atoms at the cod double bonds were refined freely with isotropic displacement parameters; all other H atoms were refined with a riding model. For crystallographic data see also CCDC 612936 (**35**), 612937 (**38a**), 612938 (**38b**), 612939 (**44-I**), 612940 (**44-II**), 612941 (**46**), and 612942 (**47**).

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Supporting Information Available: Full crystallographic data for compounds **35**, **38a**, **38b**, **44-I**, **44-II**, **46**, and **47** are available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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