N-Heterocyclic Carbenes: Synthesis, Structures, and Electronic Ligand Properties[†,‡]

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N-Heterocyclic carbene (NHC) rhodium(I) complexes of general formula Rh(COD)X(NHC) are synthesized and structurally characterized (spectroscopy, X-ray diffraction). The relative σ-donor/π-acceptor quality of various NHC ligands was examined and classified by means of IR spectroscopy at the corresponding $Rh(CO)_2I(NHC)$ complexes. The first single-crystal X-ray diffraction studies of rhodium pyrazolin- and tetrazolinylidene complexes are reported. A wide variety of different azolium salts was applied to obtain rhodium and iridium complexes with two and four carbene ligands.

Introduction

The discovery of transition metal complexes of *N*-heterocyclic carbenes (NHC) by Wanzlick and Schönherr[1] and by Öfele[2] in 1968 and the isolation of the first free stable carbenes in 1991 by Arduengo et al.[3] paved the way for NHCs to become universal ligands in organometallic and inorganic coordination chemistry. Many catalyst systems with NHC spectator ligands have been described in the last decade.[4]

NHC ligands are two-electron σ-donors with little π-accepting ability.[5] We pointed out in 1993 that *N*-heterocyclic carbenes display ligand properties that resemble trialkylphosphines very much,[6] and shortly later we presented evidence of their specific use in organometallic catalysis.[7,8] An ever-increasing research activity has been documented in the literature.[7,9−11] *N*-Heterocyclic carbenes have the advantageous property of forming strong bonds to metal centers, with little tendency of dissociation.[6,12] This is particularly beneficial in their use as ligands in organometallic catalysts.[4] The σ-donor strength varies with the constitution of the respective derivative. In the present paper

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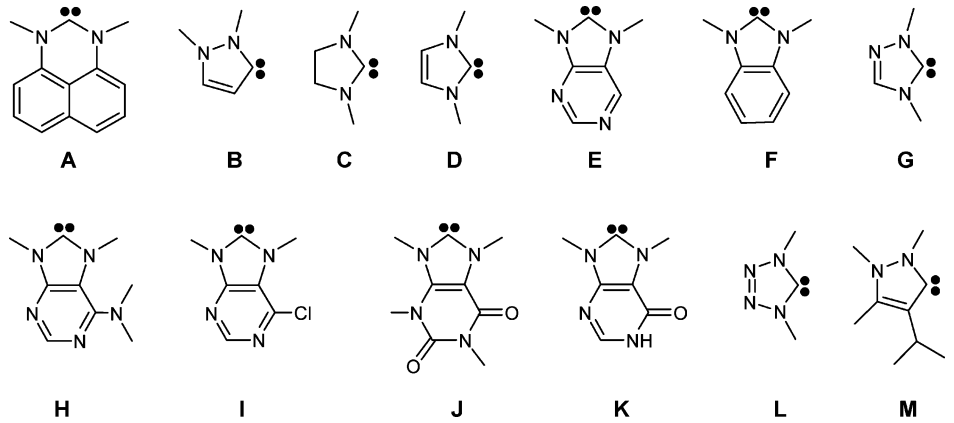


Figure 1. Carbene ligands in rhodium complexes **1** and **2**. The standard carbenes being used most frequently in the literature reports are **C** (1,3-dimethylimidazolidin-2-ylidene) and **D** (1,3-dimethylimidazolin-2-ylidene).

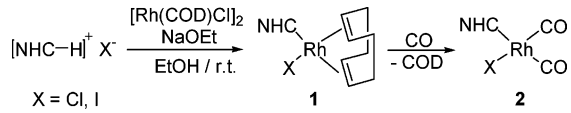
we used complexes of type $Rh(CO)_2(Cl/I)$(carbene) to obtain an estimate of the electronic properties of the carbenes.[13]

Results and Discussion

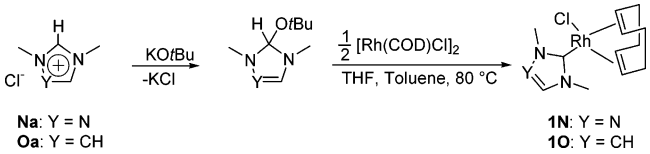
By means of theoretical data, IR spectroscopy, and X-ray diffraction data it is possible to compare the electronic properties of NHC ligands, e.g., the σ-donor/π-acceptor quality. One possibility to judge the σ-donor strength of carbene ligands is the pK_a value of the corresponding acid, the azolium salt. High pK_a values suggest strong donors. Some pK_a values of NHCs were theoretically derived[14] {**C**, [28.5 (H_2O),[14a] 22.3 (DMSO)[14a]]; **D**, [27.4 (H_2O)[14a] and 23.0 (H_2O),[14b] 21.1 (DMSO)[14a]]; **F**, 21.6 (H_2O)[14b] (see Figure 1)}; others are based on experimental data.[15,16] Besides the influence on the pK_a values of substituents in α-position to the acidic proton, there was limited investigation on the effect of the pK_a values for different *N*-heterocycles.[14] In comparison to imidazolin-2-ylidenes, their CC-saturated analogues and acyclic carbenes revealed that the latter are the most basic carbenes, whereas imidazolidin-2-ylidines are only slightly more basic than imidazolin-2-ylidenes.

For the experimental determination of the relative σ-donor strength this method is quite extensive. A simple and relatively precise method is the indirect measurement of the σ-donor strength by IR spectroscopy.[17] The basicity of a carbene ligand is evaluated by the comparison of the ν(CO) infrared data in $Rh(CO)_2X$(carbene) complexes.[13a,d] A σ-basic carbene ligand is related to a low stretching frequency (wavenumber) of the carbon monoxide opposite the carbene.[5a,18]

Scheme 1. Synthesis of Rhodium-NHC Complexes 1 and 2



Scheme 2. Synthesis of Rhodium Complexes 1N and 1O



To examine the ligand properties of various NHCs, halogeno(η^4-1,5-COD)(azolinylidene)rhodium(I) complexes **1** were synthesized and transformed to their corresponding dicarbonyl complexes **2** (Scheme 1).

The synthesis of the iodo complexes **1**(**A**−**M**) followed established procedures of monocarbene complexes of rhodium(I) with in situ deprotonation of the azolium salts.[19] Substitution of the chloro bridge in the dimeric precursor $[Rh(COD)Cl]_2$ by an ethoxy bridge allows the coordinated base to

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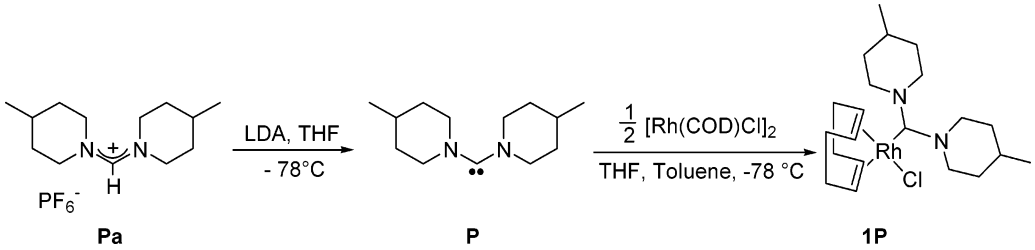
Scheme 3. Synthesis of Rhodium Complex 1P



deprotonate the azolium salt in situ, leading to the desired complexes **1**(**A**−**M**).

To avoid any possible influence on the electronic properties of the CO ligands by steric factors in the complexes **2**, NHC ligands with methyl substituents in α-position to the carbene center were chosen (**A**−**L**). Figure 1 shows a list of all carbene ligands in rhodium complexes **1**(**A**−**M**) and **2**(**A**−**L**). These were synthesized in situ from the corresponding azolium salts.

The rhodium carbonyl complexes **2** were obtained by passing carbon monoxide through a solution of the iodo complexes **1** in dichloromethane at room temperature for 30 min, which was observed by a color change from light to dark yellow. Due to the strong donor capability of the NHC ligands, the cyclooctadiene ligand can be completely substituted by the stronger acceptor ligand carbon monoxide.[20]

Furthermore the rhodium complexes (**2A**−**2L**) that bear iodide ligands were compared with the purpose of avoiding an influence on the electronic properties of the CO ligands by different halogenide ligands. To the precursors of carbene ligands **H**, **I**, **J**, and **L** with weak coordinating anions as tetrafluoroborate or perchlorate, sodium iodide was added to the reaction mixture (Scheme 1).

The chloro complexes **1N** and **1O** were prepared following a different approach (Scheme 2).[21] The azolium salt is transferred into an alkoxy-protected carbene via the addition of potassium *tert*-butanolate. The alcoholate adduct is removed in situ, and therefore after the addition of bis[μ-chloro(η^4-1,5-COD)rhodium] the formation of the desired complexes **1N** and **1O** was observed. The formed potassium salt is almost insoluble in ethanol and THF and can be removed by filtration of the suspension.

Another method for the synthesis of carbene-substituted rhodium (COD) complexes via the free carbene is shown in Scheme 3. Complex **1P** was first mentioned from our group[22] and was prepared according to a procedure published recently.[13a]

There are transition metal complexes with coordinating purine bases reported in the literature. In most of the cases the bases are coordinated via the N(9) nitrogen atom.[23] Only a few examples with a C(8) coordinated purine were observed.[23a,b,24] In very recent publications, alkylated purines coordinating at C(8) such as 1,3,7,9-tetramethylxanthine-8-ylidene,[25,26] 1,3-dimethylxanthine-8-ylidene,[27] 7,9-dimethylhypoxanthine-8-ylidene,[25,26] and 6-chloro-7,9-dimethylpurine-8-ylidene[28] resemble NHC ligands based on purine bases. Herein it was not only possible to elucidate the structure of complex **1J** with a caffeine-based ligand but also to obtain the first 6-(dimethylamino)-7,9-dimethylpurine-8-ylidene transition metal complex **1H**. All purine-based carbene complexes were obtained in yields higher than 60% as yellow solids that are soluble in polar solvents such as chloroform, dichloromethane, or DMSO. Suitable pale yellow crystals of complex **1J** for X-ray single-crystal diffraction were obtained from a DMSO/*n*-pentane solution at ambient temperature. The X-ray single-crystal diffraction study of **1J** reveals a slightly distorted square-planar structure (Figure 2).

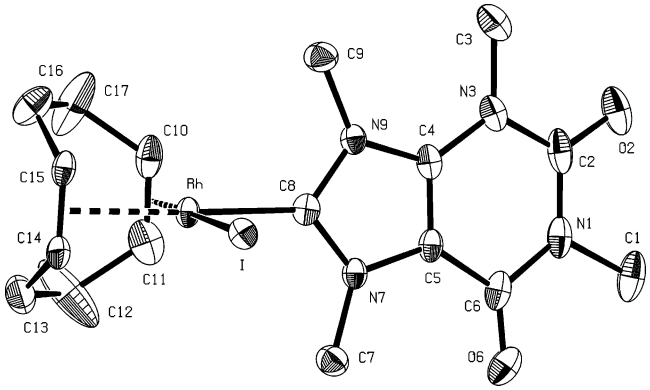


Figure 2. ORTEP style plot of compound **1J** in the solid state. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [deg]: Rh−C8 2.011(3), Rh−I 2.6738(3), Rh−C10 2.129(3), Rh−C11 2.126(4), Rh−C14 2.241(3), Rh−C15 2.219(3); I−Rh−C8 88.30(8), N7−C8−N9 105.6(2).

All carbene ligands of Figure 1 except of **A** (perimidin-2-ylidene) are restricted to five-membered heterocyclic rings. The steric properties of the methyl groups in a six-membered ring differ significantly from those of a five-membered ring. Richeson first synthesized a perimidin-2-ylidene complex.[29] In this work it was possible to obtain a perimidin-2-ylidene complex

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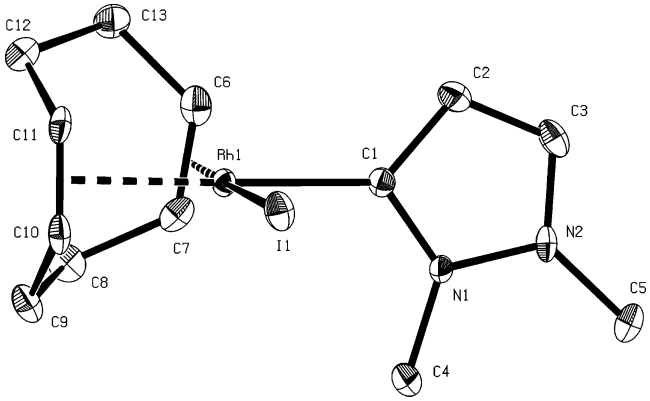

Figure 3. ORTEP style plot of compound **1B** in the solid state. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [deg]. The corresponding values of a second, crystallographically independent molecule of **1B** are given in italics: Rh1−C1 2.034(5) *2.024(5)*, Rh1−I1 2.6757(6) *2.6956(6)*, Rh1−C6 2.109(5) *2.113(5)*, Rh1−C7 2.131(5) *2.120(6)*, Rh1−C10 2.207(5) *2.204(5)*, Rh1−C11 2.228(5) *2.224(5)*; I1−Rh1−C1 86.9(1) *87.6(1)*, N1−C1−C2 104.7(4) *104.9(4)*.

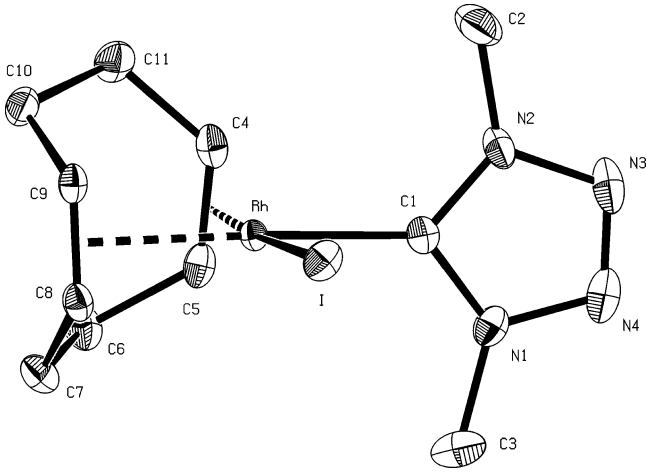

Figure 4. ORTEP style plot of compound **1L** in the solid state. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [deg]: Rh−C1 2.009(3), Rh−I 2.6757(3), Rh−C4 2.119(3), Rh−C5 2.138(3), Rh−C8 2.209(3), Rh−C9 2.226(3); I−Rh−C1 86.76(7), N1−C1−N2 101.3(2).

with methyl groups adjacent to the carbene center. The low yield of 16% is due to the poor solubility of the 1,3-dimethylperimidinium iodide **A** in commonly used solvents.

Complexes **1B**, **1D**, **1F**, and, **1G** were synthesized according to the literature.[19] However, for the first time it was possible to obtain an X-ray single-crystal structure of a pyrazolin-2-ylidene rhodium complex (Figure 3).

It was Öfele who obtained the first tetrazolinylidene and pyrazolin-3-ylidene complexes.[30] These were solely carbonyl complexes of group 6 metals and of iron. Twenty years later, a pyrazolin-3-ylidene complex of copper was reported by Raubenheimer.[31] To react the pyrazolium salt precursor of **B** with the rhodium precursor, a large excess of 1,2-dimethylpyrazolium iodide, slightly higher reaction temperatures, and far longer reaction times (7 days) are necessary. Studies on the acidity of pyrazolium salts compared to tetrazolium and imidazolium salts showed that the azolium salt of **B** is less acidic than the corresponding salts of **D** and **L**.[32] This is consistent with the lower reactivity during the in situ deprotonation of pyrazolium salts.

Complex **1C** is the first iodo complex with a saturated NHC. Chloro(η^4-1,5-COD)(1,3-di-R-imidazolidin-2-ylidene)rhodium-(I) was prepared from electron-rich olefins by Lappert et al.[33] The synthesis of **1C** followed the procedure of the before described azolinylidene complexes.

The iron and chromium complexes of tetrazolinylidene, synthesized by Öfele, have remained the only examples of this ligand.[30] The synthesis of complex **1L** could not follow the conventional route for azolium salts due to the strong basic conditions. The intermediate tetrazolinylidene decomposes in the presence of a base to the corresponding carbodiimide and nitrogen (Scheme 4).[34]

To avoid a free base, it is imperative to exclude an excess of sodium ethanolate in the reaction mixture. The isolation of bis-[μ-ethoxy-(η^4-1,5-COD)rhodium] instead of the common in situ

Scheme 4. Base-Catalyzed Decomposition of Tetrazolium Ions

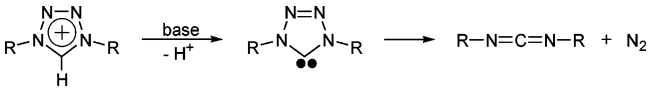

Table 1. ^{13}C NMR Chemical Shifts δ and Rh−C$_{Carbene}$ Coupling Constants J of Rh(COD)(Cl,I)(NHC) Complexes 1

complex	δ C$_{carbene}$ [ppm]	J(Rh−C$_{carbene}$) [Hz]	yield [%]
1A	200.4	51.1	16
1B	181.8	42.6	56
1C	211.0	50.8	51
1D	180.1	53.3	71
1E	181.2	50.1	61
1F	194.8	48.5	79
1G	183.9	48.8	79
1H	200.0	46.7	95
1I	198.2	68.0	77
1J	189.6	52.2	88
1K	188.1	52.9	89
1L	180.6	50.9	90
1M	187.0	49.8	56
1N	183.8	50.6	71
1O	179.6	51.1	60
1P	232.6		71

preparation of this complex avoids any free base during the synthesis of **1L**.[19] Pale yellow crystals of complex **1L** suitable for single X-ray diffraction were obtained from a dichloromethane/*n*-pentane solution at ambient temperature. The solid-state structure of **1L** reveals a slightly distorted square-planar coordination (Figure 4).

The chemical shifts of the carbene carbons and the coupling constants J(Rh−C) in the ^{13}C NMR of complexes **1** do not show systematic order for an estimation of the σ-donor strength of the carbene ligands (Table 1). Therefore the syntheses of complexes **2** and the determination of the CO-stretching frequencies were necessary to evaluate the electronic properties of the NHC ligands.

There was no considerable difference observed in the chemical shift of the carbene carbon and the rhodium−carbene coupling constant by varying the halogenide of complex **1G** to **1N** or complex **1D** to **1O**.

Crystal Structure Discussion. The molecular structures of the complexes **1B**, **1J**, and **1L** in the solid state are depicted in

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Table 2. Selected Bond Distances (Å) and Bond and Torsion Angles (deg) for Complexes 1B, 1J, and 1L

complex	Rh−$C_{carbene}$	N/C−$C_{carbene}$−N	$C_{carbene}$−Rh−I	N−$C_{carbene}$−Rh−I
1B	2.034(5)	104.7(4)	86.9(1)	−82.7(4)
	2.024(5)	*104.9(4)*	*87.6(1)*	*78.1(4)*
1J	2.011(3)	105.6(2)	88.30(8)	87.2(2)
1L	2.009(3)	101.3(2)	86.76(7)	88.4(2)

Table 3. Carbonyl Stretching Frequencies ν in Dichloromethane, ^{13}C NMR Chemical Shifts δ, and Rh−$C_{carbene}$ Coupling Constants J of the Carbene Carbon of the Complexes RhI(CO)$_2$NHC (2) in d_6-DMSO

complex	ν(CO) sym. [cm^{-1}]	ν(CO) asym. [cm^{-1}]	δ $C_{carbene}$ [ppm]	J(Rh−$C_{carbene}$) [Hz]	yield [%]
2A	2061	1994	185.0	41.0	99
2B	2066	1993	169.2	35.8	100
2C	2072	1999	195.2		100
2D	2073	2000	168.9	40.8	99
2E	2069	2006	181.9		100
2F	2075	2001	180.8	40.5	100
2G	2078	2006	174.2	42.6	83
2H	2077	2008	189.3		99
2I	2078	2008	180.7		100
2J	2080	2009	178.2	50.7	100
2K	2084	2015	183.1		100
2L	2086	2015	168.9	42.0	100

Figures 2, 3, and 4. A selection of characteristic bond angles and bond distances are given in Table 2. Crystal data and details of the structure determination of the three crystal structures are presented in Table 4.

All complexes favor a slightly disturbed square-planar coordination sphere of the rhodium center. The rhodium−carbene bond length does not differ in the range of the standard deviation for all complexes. This bond length is not an indication for the donor strength of the carbene ligand due to the similar properties of these ligands. In all three complexes the N/C−C−N angles of the carbene ligands are in accordance with coordinated azole rings reported in the literature.[26,35] The angles between the coordination plane of the complex and the carbene ligand changes in accordance with the symmetry of the carbene. For an asymmetric substituted ligand such as 1,2-dimethylpyrazolinylidene the angle varies most from the ideal 90° perpendicular coordination. The different *trans*-influences of the carbene and iodide ligands lead to different distances between the coordinated COD carbon atoms and the rhodium or iridium (**7G**) atoms. As a result of the longer distance to the metal, the C═C double bond *trans* to the NHC ligand is shorter, owing to reduced back-donation from the metal to its π^* orbitals (see also Figures 8 and 9).

Carbene Donor Strength. The IR and NMR spectra consistently indicate the *cis*-conformation of both carbonyl ligands in the complexes **2**(**A**−**L**). The IR spectra exhibit two strong ν(CO) bands. The ^{13}C NMR spectra have three doublets between δ = 165 and 220 ppm for both carbonyl carbons and the carbene carbon. All complexes **2**(**A**−**L**) are air-stable but decompose in solution under air within 1 to 4 h. They are all soluble in polar solvents such as chloroform, dichloromethane, DMSO, and THF and less soluble in less polar solvents such as diethyl ether, *n*-hexane, and *n*-pentane.

The CO-stretching frequencies of each complex **2** were recorded in dichloromethane solution and are listed in Table 3. Steric, electronic, and solvent influences are excluded by using identical sets of *N*-substituents (CH_3) and counterions (I^-) as well as the same solvent (CH_2Cl_2). Previous comparisons presented by different authors varied at least one of these parameters.[13a,c,36]

The relevant IR data differ by 20−25 wavenumbers. The carbene ligands in **2A** and **2B** are among the strongest σ-donors of this comparison, whereas the tetrazolinylidene ligand represents the weakest donor of this table. This result demonstrates that the carbene ligands in complexes **2A** and **2B** induce a much higher electron density at the metal atom by simultaneous stronger back-donation from the metal center to the carbonyls than for example the tetrazolinylidene ligand. This small difference in the wavenumbers (20−25 cm^{-1}) can give only a direction of the σ-donor abilities of the different carbenes. The data also show that the chemical shift of the carbene carbon in the respective rhodium complexes **2** does not correlate with the donor strength of the NHC ligand, as mentioned before for complexes **1**.[13a,20,22,35i,37] The rhodium center of the complexes **2** couples with the carbene and carbonyl carbon (three doublets in the ^{13}C NMR spectra). However, since not all complexes are soluble in chlorinated solvents, d_6-DMSO was used as the standard NMR solvent. This resulted in some cases in broad signals for these atoms. Therefore coupling constants could not be obtained for all complexes **2**. In addition, the chemical shifts of these three doublets appear close together. To allow a differentiation between them, complexes **2B**, **2D**, and **2F** were also prepared with 99% enriched ^{13}CO. Figure 5 shows that both low-field signals (187.5 ppm, $^1J_{Rh-C}$ = 52.6 Hz and 182.2 ppm) correspond to the ^{13}C marked carbonyl ligands of complex **2D**, whereas the carbene signal appears at 169.0 ppm ($^1J_{Rh-C}$ = 40.8 Hz). The row of carbene ligands ordered by their σ-donor strength correlate very well with the pK_a values calculated for some of the corresponding carbene ligands (**C**, **D**, **F**).[14−16]

Rhodium NHC Complexes with More Than One NHC Ligand. Cationic NHC rhodium complexes with two NHC equivalents per rhodium center can be generated from [Rh(COD)Cl]$_2$. A few examples of Rh(L)$_2$(NHC)$_2$ complexes have been known.[25,38] In principle it should also be possible to generate a rhodium center with four NHC ligands to obtain an ionic complex. As a matter of fact, a tetrakis-NHC rhodium complex was recently reported.[39] However, NHC-silver precursors are necessary to transfer the carbene to the rhodium center. It is possible to follow the known procedure for the preparation

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(36) See for example: (a) Lavallo, V.; Mafhouz, J.; Canac, Y.; Donnadieu, B.; Schoeller, W. W.; Bertrand, G. *J. Am. Chem. Soc.* **2004**, *126*, 8670. (b) Doyle, M. J.; Lappert, M. F.; Pye, P. L.; Terreros, P. *J. Chem. Soc., Dalton Trans.* **1984**, *11*, 2355.
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Table 4. Crystallographic Data for Compounds 1B·(CH_2Cl_2), 1J, 1L, 6G, and 7G

	1B·(CH_2Cl_2)	**1J**	**1L**	**6G**	**7G**
formula	$C_{14}H_{22}Cl_2IN_2Rh$	$C_{17}H_{24}IN_4O_2Rh$	$C_{11}H_{18}IN_4Rh$	$C_{16}H_{26}IrN_6$	$C_{12}H_{19}IrN_3$
fw	519.05	546.21	436.10	621.55	524.42
color/habit	yellow/needle	pale yellow/plate	pale yellow/fragment	orange/fragment	yellow/plate
cryst dimens (mm^3)	0.05 × 0.05 × 0.46	0.18 × 0.48 × 0.51	0.23 × 0.29 × 0.44	0.36 × 0.38 × 0.51	0.05 × 0.25 × 0.81
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/n$ (no. 14)	$C2/c$ (no. 15)	$P2_1/n$ (no. 14)
a, Å	24.9166(2)	11.5467(1)	7.4133(1)	29.0510(2)	7.3634(2)
b, Å	7.1008(1)	12.0211(1)	16.1728(1)	10.0355(1)	16.0249(4)
c, Å	22.5135(2)	13.7354(1)	11.6507(1)	28.0782(2)	11.7962(3)
β, deg	116.8930(4)	95.6384(3)	95.7301(4)	92.2956(2)	93.2966(10)
V, $Å^3$	3552.49(7)	1897.30(3)	1389.87(2)	8179.39(11)	1389.62(6)
Z	8	4	4	16	4
T, K	123	123	123	173	123
D_{calcd}, g cm^{-3}	1.941	1.912	2.084	2.019	2.507
μ, mm^{-1}	2.993	2.545	3.435	8.049	11.813
F(000)	2016	1072	840	4704	968
θ range, deg	1.81−25.37	1.77−25.38	2.16−25.32	1.40−25.37	2.15−25.32
index ranges (h, k, l)	±29, ±8, ±27	±13, ±14, ±16	±8, ±19, ±14	±34, ±12, ±33	±8, ±19, ±14
no. of reflns collected	65 917	44 339	30 447	73 769	28 259
no. of indep reflns/R_{int}	6529/0.070	3490/0.051	2525/0.044	7486/0.053	2521/0.067
no. of obsd reflns ($I > 2\sigma(I)$)	5968	3280	2502	7167	2353
no. of data/restraints/params	6529/0/365	3490/0/230	2525/0/157	7486/0/441	2521/0/157
R1/wR2 ($I > 2\sigma(I)$)[a]	0.0422/0.0605	0.0225/0.0559	0.0190/0.0478	0.0235/0.0570	0.0231/0.0620
R1/wR2 (all data)[a]	0.0495/0.0621	0.0245/0.0569	0.0192/0.0479	0.0249/0.0576	0.0253/0.0633
GOF (on F^2)[a]	1.273	1.054	1.218	1.144	1.056
largest diff peak and hole (e $Å^{-3}$)	+0.67/−0.84	+0.54/−0.55	+0.53/−0.58	+0.84/−1.40	+1.13/−0.91

[a] $R1 = \sum(||F_o| - |F_c||)/\sum|F_o|$; $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$; $GOF = \{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$.

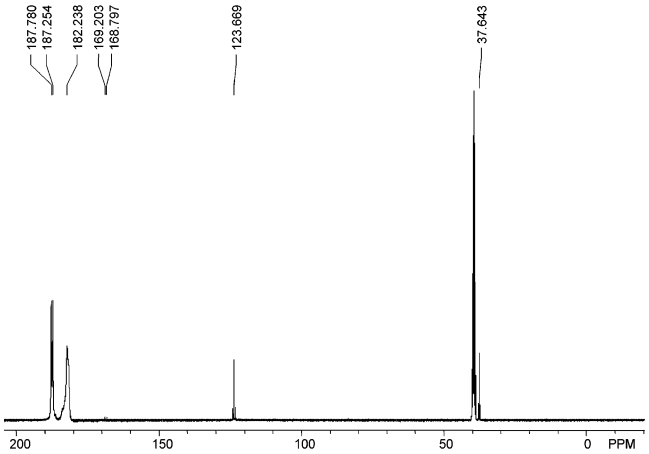


Figure 5. ^{13}C NMR spectra of RhI($^{13}CO)_2$NHC (**2D**) in d_6-DMSO.

of the complexes **1**(**A**−**M**), but instead of using just 1 equiv of azolium salt, at least 4 equiv are essential. Also the reaction conditions need to be more rigorous: The reaction time and temperature are increased up to several days and 40 °C depending on the reactivity of the azolium salt. Triazolium salts are easily available and more acidic, hence more reactive than ordinary imidazolium salts. They were used in order to show the principle way for this preparation method (Scheme 5). Both bridged and unbridged azolium salts form air- and moisture-stable tetrakis-NHC rhodium complexes.

Suitable crystals of complex **4G** for single X-ray diffraction were obtained from a dichloromethane/*n*-pentane solution at ambient temperature. The solid-state structure of **4G** reveals a slightly distorted square-planar coordination (Figure 6).

However, for some azolium salts even rigorous reaction conditions do not result in a quadruple coordination of the ligand. η^4-1,5-Cyclooctadiene binds too strongly to the rhodium center to be replaced for instance by 1,3,7,9-tetramethylxanthine-8-ylidene. Therefore η^2-cyclooctene was used as a weaker coordinating ligand than η^4-1,5-cyclooctadiene for the rhodium precursor (Scheme 6).

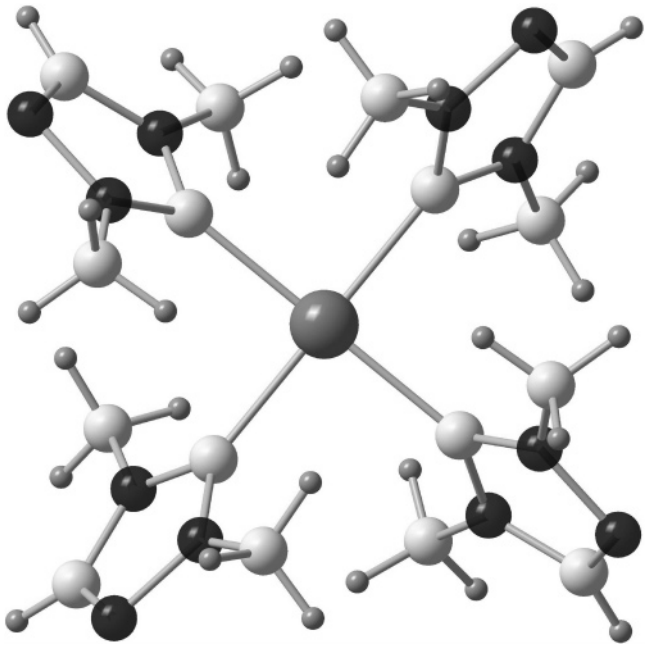


Figure 6. Ball-and-stick model of compound **4G** in the solid state. For details see the Experimental Section.

The 1,3,7,9-tetramethylxanthinium tetrafluoroborate can be applied in a great excess because the azolium salt **Ja** is soluble in water in contrast to the complex **4J** and can be removed by washing the crude product.

To date, only cyclic bridged carbene ligands were successfully applied in the synthesis of transition metal complexes. For acyclic bridged carbene ligands not even a corresponding salt was known. However, forming an acyclic bridged carbene complex **4U** from an acyclic bridged salt **Ua** (Scheme 7) was not successful. A reason for this could be the bulkiness and high basicity of the acyclic carbene.

Iridium NHC Complexes. The organometallic chemistry of rhodium and iridium is relatively similar.[10] With three examples

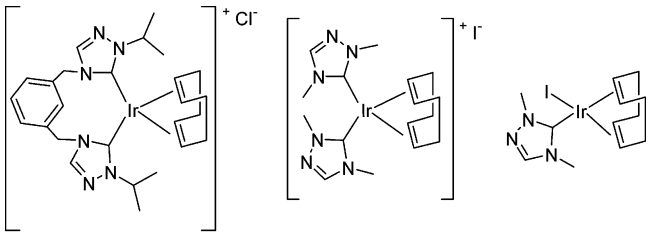


Figure 7. Synthesized iridium NHC complexes.

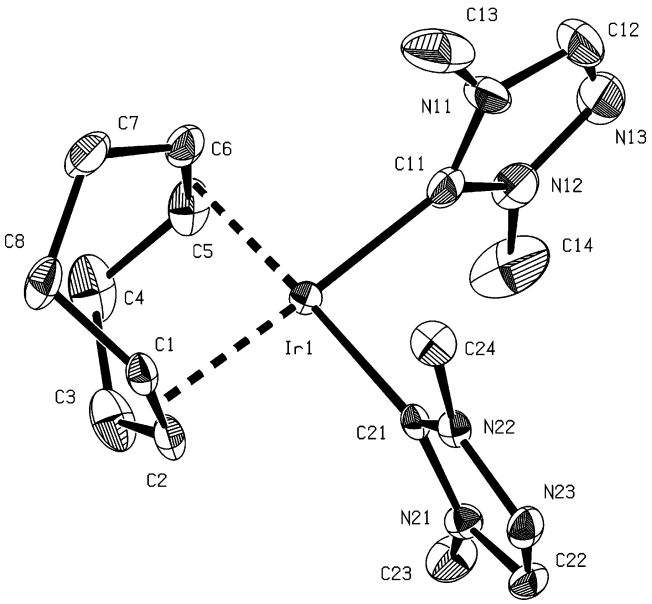


Figure 8. ORTEP style plot of compound **6G** in the solid state. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [deg]. The corresponding values of a second, crystallographic independent molecule of **1G** are given in italics: Ir1−C11 2.038(5) *2.031(4)*, Ir1−C21 2.038(4) *2.036(4)*, Ir1−C1 2.211(4) *2.195(4)*, Ir1−C2 2.192(5) *2.185(5)*, Ir1−C5 2.193(4) *2.197(4)*, Ir1−C6 2.183(5) *2.188(4)*; C11−Ir1−C21 92.2(2) *91.9(2)*, N11−C11−N12 103.2(4) *103.1(4)*, N21−C21−N22 102.7(3) *102.8(3)*.

for iridium complexes we showed the principle application of a variety of azolium salts in this work for both rhodium and iridium NHC complexes. Again, bridged and unbridged azolium salts were applied to obtain the complexes **5T**, **6G**, and **7G** (Scheme 8, Figure 7). The syntheses followed the same procedures as for the above-mentioned rhodium NHC complexes. Compared to the analogous rhodium complexes, no unexpected results were obtained.

Suitable crystals for single X-ray diffraction were obtained for both complexes **6G** and **7G** from a concentrated dichloromethane solution at ambient temperature (Figure 8 and Figure 9). Crystal data and details of the structure determination of both crystal structures are presented in Table 4.

In the solid-state structures of **6G** and **7G** the carbene−Ir bond distances [**6G**, 2.038(5) *2.031(4)* and 2.038(4) *2.036(4)* Å; **7G**, 2.021(5) Å] as well as the N−C−N angles of the carbenes [**6G**, 103.2(4)° *103.1(4)*°, 102.7(3)° *102.8(3)*°; **7G**, 102.6(4)°] are equal within esd's.

Conclusion

CO-stretching frequencies of CO-substituted Rh-NHC complexes allow a good estimation of the relative σ-donor/π-acceptor properties for *N*-heterocyclic carbenes. Perimidin-2-ylidene is so far one of the most σ-basic NHC ligands known, and tetrazolinylidene is the weakest one. In light of the data analysis, the most frequently used imidazolin-2-ylidene and imidazolidin-2-ylidene hardly differ in their electronic ligand properties. These two NHC derivatives belong to the more electron-rich C-donors among the congeners hitherto known.

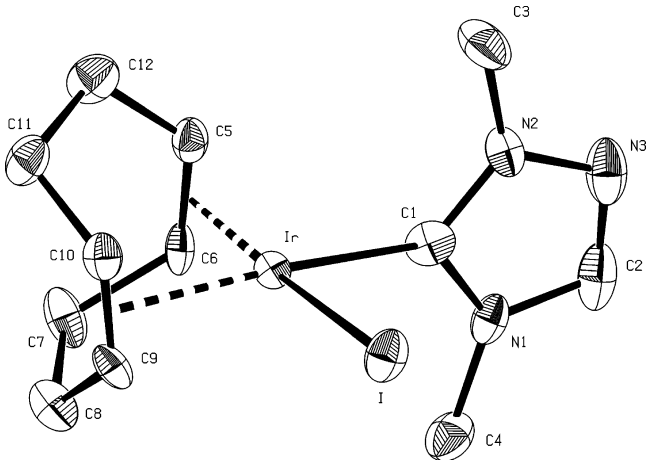
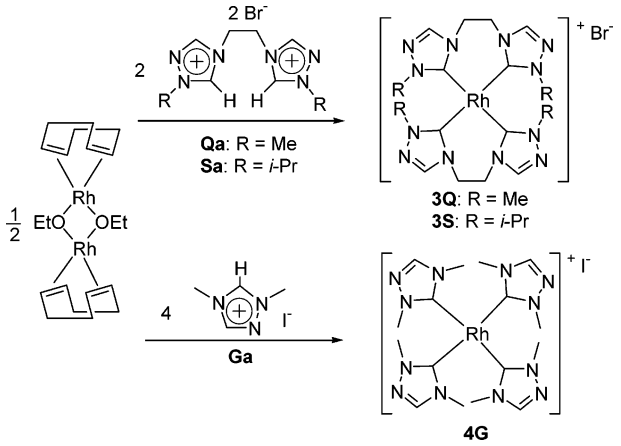
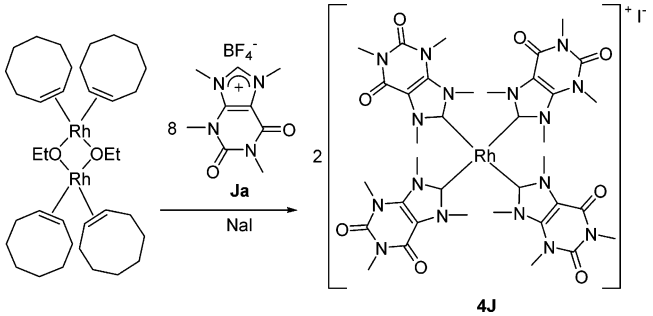


Figure 9. ORTEP style plot of compound **7G** in the solid state. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [deg]: Ir−C1 2.021(5), Ir−I 2.6524(4), Ir−C5 2.116(5), Ir−C6 2.122(5), Ir−C9 2.186(5), Ir−C10 2.216(5); I−Ir−C1 88.1(1), N1−C1−N2 102.6(4).

Scheme 5. Preparation of Tetrakistriazolin-5-ylidene Rhodium Complexes



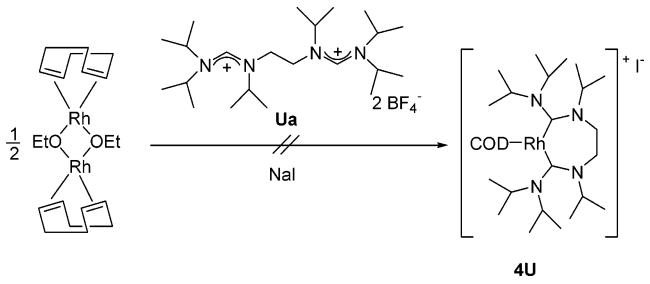
Scheme 6. Preparation of a Tetrakisxanthine-8-ylidene Complex



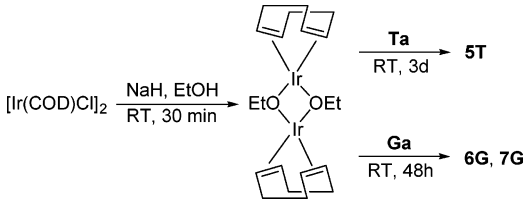
Experimental Section

General Considerations. The azolium salts, the precursors 1-methyl-1*H*-1,2,4-triazole, and 1-isopropyl-1*H*-1,2,4-triazole were

Scheme 7. Attempted Preparation of Acyclic-Bridged Bis-carbene Complex 4U



Scheme 8. Preparation of Iridium Carbene Complexes 5T, 6G, and 7G



prepared according to reported procedures.[25,28,40,41,42] The rhodium dimer precursor [(Rh(COD)Cl)$_2$] was synthesized as reported in the literature.[19,43] Iodo(η^4-1,5-COD)(1,2-dimethylpyrazolin-3-ylidene)rhodium(I) (**1B**),[19,44] iodo(η^4-1,5-COD)(1,3-dimethylimidazolin-2-ylidene)rhodium(I) (**1D**),[19,44] iodo(η^4-1,5-COD)(1,3-dimethylbenzimidazolin-2-ylidene)rhodium(I) (**1F**),[19] iodo(η^4-1,5-COD)(1,4-dimethyl-4,5-dihydro-1*H*-1,2,4-triazolin-5-ylidene)rhodium(I) (**1G**),[19] iodo(η^4-1,5-COD)(1,3,7,9-tetramethylxanthine-8-ylidene)rhodium(I) (**1J**), iodo(η^4-1,5-COD)(7,9-dimethylhypoxanthine-8-ylidene)rhodium(I) (**1K**),[25] chloro(η^4-1,5-COD)(1,3-dimethylimidazolin-2-ylidene)rhodium(I) (**1O**),[20] iododicarbonyl-(1,2-dimethylpyrazolin-3-ylidene)rhodium(I) (**2B**), iododicarbonyl-(1,3-dimethylimidazolin-2-ylidene)rhodium(I) (**2D**),[44] iododicarbonyl(1,3,7,9-tetramethylxanthine-8-ylidene)rhodium(I) (**2J**), and iododicarbonyl(7,9-dimethylhypoxanthine-8-ylidene)rhodium(I) (**2K**) were prepared as reported in the literature.[25]

^{1}H and ^{13}C NMR spectra were recorded on a JEOL-JMX-GX 270 or 400 MHz spectrometer at room temperature and referenced to the residual ^{1}H and ^{13}C signals of the solvents. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, hept = heptet, m = multiplet, br = broad signal. Coupling constants *J* are given in Hz. IR spectra were recorded on a FTS 575C BIO-RAD spectrometer. Elemental analyses were carried out by the Microanalytical Laboratory at the TU München. Mass spectra were performed at the TU München Mass Spectrometry Laboratory on a Finnigan MAT 90 spectrometer using the CI or FAB technique.

1,2,3-Trimethyl-4-isopropylpyrazolium Iodide (Ma). Iodomethane (0.42 mL, 29.9 mmol) was added to 3-methyl-4-isopropylpyrazole (660 mg, 5.32 mmol) in methanol (0.76 mL, 4.23 mmol). The solution was stirred for 13 h in an autoclave at 130 °C. The volatiles were removed in vacuo and the remaining solid recrystallized in 2-propanol and diethyl ether. Yield: 13%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (1H, s, CC*H*N), 4.40 (3H, s, NCH_3), 4.21 (3H, s, NCH_3), 2.84 (1H, hept, $^3J_{H-H}$ = 6.8 Hz, C*H*Me$_2$), 2.44 (3H, s, CCH_3), 1.18 (6H, d, $^3J_{H-H}$ = 6.8 Hz, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (100.5 MHz, $CDCl_3$): δ 131.9 (MeN*C*C*i*Pr), 129.0 (C=C), 123.3 (C=C), 37.0 (NCH_3), 34.6 (NCH_3), 26.0 (CCH_3), 22.9 (*C*HMe$_2$), 18.5 (CH(*C*H$_3$)$_2$).

(4-Methyl)piperidine-1-ylmethylidene-(4′-methyl)piperidinium Hexafluorophosphate (Pa). 4-Methylpiperidine (2.00 g, 20.2 mmol) and *N*,*N*,*N*′,*N*′-tetramethylformamidinium chloride (1.22 g, 10.0 mmol) were dissolved in 2 mL of ethanol and stirred for 4 h under reflux at 100 °C. The emerging gas was led through diluted acid, to neutralize the formed dimethylamine. Afterward the solution was cooled to ambient temperature; the reaction mixture was mixed with approximately 25 mL of ice-cold water and an ice-cold solution of approximately 2 equiv of NH_4PF_6. The emerging precipitate was filtered, washed twice with 10 mL of ice-cold water and diethyl ether, and dried in vacuo. Yield: 93%. Mp: 179 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (1H, s, NC*H*N), 3.95 (1H, br s, C*H*), 3.70 (1H, br s, C*H*), 3.33 (4H, m, NCH_2), 1.78 (4H, d, $^3J_{H-H}$ = 11.2 Hz, CH_2), 1.66 (4H, m, CH_2), 1.35 (4H, m, CH_2), 0.95 (6H, d, $^3J_{H-H}$ = 6.4 Hz, CH_3). ^{13}C{^{1}H} NMR (100.5 MHz, $CDCl_3$): δ 154.4 (s, N*C*HN), 46.0 (*C*HCH$_3$), 39.7 (*C*HCH$_3$), 33.6, 33.3 (N*C*H$_2$), 29.7, 29.4 (*C*H$_2$), 21.1 (*C*H$_3$). ^{31}P{^{1}H} NMR (161.8 MHz, $CDCl_3$): δ −143.8 (hept, *J* = 712 Hz). MS (FAB) *m*/*z*: 209.2 (M^+). Anal. Calc for $C_{13}H_{25}N_2F_6P$ (354.32 g mol^{-1}): C, 44.07; H, 7.11; N, 7.91. Found: C, 44.31; H, 6.89; N, 8.25.

Di(4-methyl)-*N*-piperidylmethylidene (P). A suspension of ligand **Pa** (425 mg, 1.20 mmol) in 10 mL of THF was mixed at −78 °C with a solution of LDA (135 mg, 1.26 mmol) in 5 mL of THF. After removing the cooling bath the solution was stirred for 45 min at room temperature. A clear light yellow solution was observed. All volatile compounds were removed in vacuo. Afterward the residual solid was extracted three times with 15 mL of *n*-hexane. After removing the solvent in vacuo and sublimation of the free carbene bis(dialkylamino)carbene was obtained as a colorless crystalline solid. Yield: 69%. ^{1}H NMR (400 MHz, C_6D_6): δ 3.17 (8H, s, NCH_2), 1.53 (8H, s, CH_2), 1.19 (2H, br s, C*H*), 0.73 (6H, s, CH_3). ^{13}C{^{1}H} NMR (100.5 MHz, C_6D_6): δ 237.4 (s, N*C*N), 50.8 (s, NCH_2), 46.0 (s, *C*H), 31.39, 26.04 (*C*H$_2$), 22.7 (*C*H$_3$).

1,2-Bis[1-methyl-4,5-dihydro-1*H*-1,2,4-triazolium]ethylene Dibromide (Qa). In a high-pressure tube 1-methyl-4,5-dihydro-1*H*-1,2,4-triazole (1100 mg, 13.2 mmol) and 1,2-dibromoethane (1200 mg, 6.39 mmol) in 5 mL of THF were heated at 130 °C for 72 h. The suspension was filtered and washed three times with 20 mL of diethyl ether. Yield: 53%. ^{1}H NMR (400 MHz, $(CD_3)_2SO$): δ 10.22 (2H, s, CH$_3$NC*H*NCH$_2$), 9.23 (2H, s, NC*H*NCH$_2$), 4.87 (4H, s, CH_2), 4.09 (6H, s, CH_3). ^{13}C{^{1}H} NMR (100.5 MHz, $(CD_3)_2$SO): δ 144.5 (CH$_3$N*C*HNCH$_2$), 143.3 (N*C*HNCH$_2$), 46.5 (*C*H$_2$), 38.9 (*C*H$_3$).

1,2-Bis[1-isopropyl-4,5-dihydro-1*H*-1,2,4-triazolium]ethylene Dibromide (Sa). In a high-pressure tube 1-isopropyl-4,5-dihydro-1*H*-1,2,4-triazole (1500 mg, 13.5 mmol) and 1,2-dibromoethane (1210 mg, 6.43 mmol) were heated at 130 °C for 40 h. The reaction mixture was suspended in diethyl ether, filtered, and washed three times with 10 mL of diethyl ether. Yield: 78%. ^{1}H NMR (400 MHz, $(CD_3)_2SO$): δ 10.97 (2H, s, CHNC*H*NCH$_2$), 9.61 (2H, s, NC*H*NCH$_2$), 5.59 (4H, s, CH_2), 4.83 (2H, hept, $^3J_{H-H}$ = 6.5 Hz, C*H*(CH$_3$)$_2$), 1.51 (12H, d, $^3J_{H-H}$ = 6.5 Hz, CH_3). ^{13}C{^{1}H} NMR (100.5 MHz, $(CD_3)_2SO$): similar to **Qa**.

α,α′-Bis[1-isopropyl-4,5-dihydro-1*H*-1,2,4-triazolium]*m*-xylene Dichloride (Ta). In a high-pressure tube 1-isopropyl-4,5-dihydro-1*H*-1,2,4-triazole (946 mg, 8.5 mmol) and α,α′-dichloro-*m*-xylene (720 mg, 6.52 mmol) were dissolved in 5 mL of THF and heated at 100 °C for 80 h. The reaction mixture was suspended in diethyl ether, filtered, and washed three times with 15 mL of diethyl ether. Yield: 53%. ^{1}H NMR (400 MHz, $(CD_3)_2SO$): δ 10.87 (2H, s, CHNC*H*NCH$_2$), 9.54 (2H, s, NC*H*NCH$_2$), 7.94 (1H, s, Ar−H), 7.60−7.50 (3H, m, Ar−H), 5.57 (4H, s, CH_2), 4.82 (2H, hept, $^3J_{H-H}$ = 6.4 Hz, C*H*(CH$_3$)$_2$), 1.51 (12H, d, $^3J_{H-H}$ = 6.4 Hz, CH_3).

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$^{13}C\{^1H\}$ NMR (100.5 MHz, $(CD_3)_2SO$): δ 144.5 ($CH_3NCHNCH_2$), 141.7 ($NCHNCH_2$), 134.5, 129.8, 129.7, 129.6 (Ar−C), 55.3 ($CH(CH_3)_2$), 50.1 (CH_2), 21.2 (CH_3).

α,α′-Bis[1-isopropyl-4,5-dihydro-1*H*-1,2,4-triazolium]*m*-xylene ditetrafluoroborate (Tb). Ammonium tetraflurorоborate (500 mg, 4.77 mmol) was dissolved in 5 mL of water and added to a solution of 600 mg (1.5 mmol) of α,α′-bis[1-isopropyl-1,2,4-triazolium]*m*-xylene dichloride (**Ta**) in 5 mL of water. The solution was stirred for 15 min at room temperature. The precipitate was filtered and washed twice with 4 mL of water and once with 20 mL of diethyl ether. Yield: 69%. ^1H NMR (400 MHz, $(CD_3)_2SO$): δ 10.18 (2H, s, $CHNCHNCH_2$), 9.22 (2H, s, $NCHNCH_2$), 7.59 (1H, s, Ar−H), 7.53 (3H, s, Ar−H), 5.49 (4H, s, CH_2), 4.77 (2H, hept, $^3J_{H-H} = 6.4$ Hz, $CH(CH_3)_2$), 1.51 (12H, d, $^3J_{HH} = 6.8$ Hz, CH_3).$^{13}C\{^1H\}$ NMR (100.5 MHz, $(CD_3)_2SO$): δ 143.8 ($CH_3NCHNCH_2$), 140.7 ($NCHNCH_2$), 133.5, 129.3, 128.8, 128.5 (Ar−C), 54.8 ($CH(CH_3)_2$), 49.6 (CH_2), 20.5 (CH_3). MS (FAB) *m*/*z* (%): 413.0 (87, $[M - BF_4^-]$), 325.0 (100). Anal. Calcd for $C_{18}H_{26}N_6B_2F_8$ (500.05 g mol^{-1}): C, 43.23; H, 5.24; N, 16.81. Found: C, 43.00; H, 5.10; N, 17.15.

***N,N′*-Bis{[di(1-methylethyl)amino]methylene}-*N,N′*-di(1-methylethyl)-1,2-ethylendiamine Ditetrafluoroborate (Ua).** A solution of $POCl_3$ (3.2 mL, 34.5 mmol) in 20 mL of diethyl ether was added to a solution of diisopropylformamide (5 mL, 34.5 mmol) in 50 mL of diethyl ether. After stirring the combined solution for 1.5 h at room temperature, the solvent was removed by filtration. The residue was washed twice with 20 mL of diethyl ether. Afterward the residue was dissolved in 30 mL of dichloromethane and cooled to −30 °C. To this solution *N,N′*-diisopropylethylenediamin (3.0 mL, 16.5 mmol) was added, and the mixture was stirred for 45 min at 25 °C. To this solution 100 mL of diethyl ether was added to precipitate a white crystalline product. The precipitate was extracted with acetone and to the acetone solution diethyl ether was added to precipitate the product. The precipitate was dissolved in 25 mL of water, and a solution of ammonium tetrafluoroborate (3.45 g, 38 mmol) in 30 mL of water was added. After stirring for 2 h the product was obtained as a white product. Yield: 14%. ^1H NMR (270 MHz, $(CD_3)_2SO$): δ 7.87 (2H, s, C*H*), 4.05 (6H, sept, $^3J_{H-H} = 5.5$ Hz, $CH(CH_3)_2$), 3.76 (4H, br s, $NCH(CH_3)CH_2$), 1.33 (36H, d, $^3J_{H-H} = 6.2$ Hz, CH_3). $^{13}C\{^1H\}$ NMR (67.9 MHz, $(CD_3)_2SO$): δ 155.0 (N*C*HN), 55.5 (*C*H), 52.6 (*C*H), 49.4 (CH_2), 22.9 (CH_3), 19.9 (CH_3). MS (FAB) *m*/*z* (%): 454.7 (67, $[M - BF_4^-]$), 324.8 (34), 255.8 (100). Anal. Calcd for $C_{22}H_{48}N_4B_2F_8$ (542.25 g mol^{-1}): C, 48.73; H, 8.92; N, 10.33. Found: C, 48.26; H, 8.40; N, 10.26.

Preparation of Complexes 1A, 1C, 1E, 1H, 1I, and 1L. Bis-[μ-chloro-(η^4-1,5-COD)rhodium] (148 mg, 0.30 mmol) was suspended in 10 mL of ethanol. NaH (30 mg, 1.25 mmol) in 5 mL of ethanol was slowly added. The reaction mixture was stirred for 30 min at room temperature. After the addition of the azolium salt (0.66 mmol) and in case of tetrafluoroborate and perchlorate salts of sodium iodide (0.75 mmol), the suspension was stirred for 24−60 h at room temperature. The isolation of the complex was conducted for each complex according to its properties.

Iodo(η^4-1,5-COD)(1,3-dimethylperimidin-2-ylidene)rhodium(I) (1A). The solvent was removed in vacuo and the remaining solid washed three times with 5 mL of *n*-hexane. Yield: 16%. ^1H NMR (400 MHz, $(CD_3)_2SO$): δ 7.26 (2H, dd, $^3J_{H-H} = 7.6$ Hz, $^3J_{H-H} = 8.0$ Hz, CHC*H*CH), 7.10 (2H, d, $^3J_{H-H} = 8.0$ Hz, CHC*H*C), 6.28 (2H, d, $^3J_{H-H} = 7.6$ Hz, CC*H*CH), 4.66 (2H, br, COD_{vinyl}), 4.13 (2H, br, COD_{vinyl}), 2.90 (6H, s, CH_3), 2.36 (4H, br, COD_{allyl}), 1.92 (4H, m, COD_{allyl}). $^{13}C\{^1H\}$ NMR (100.5 MHz, $(CD_3)_2SO$): δ 200.4 (d, $^1J_{Rh-C} = 51.1$ Hz, N*C*N), 145.1 (Ar), 134.8 (Ar), 129.0 (*C*H), 117.0 (*C*H), 114.7 (Ar), 103.3 (*C*H), 89.1 (br, COD_{vinyl}), 69.8 (COD_{vinyl}), 40.8 (CH_3), 36.8 (COD_{allyl}), 30.9 (COD_{allyl}). Anal. Calcd for $C_{21}H_{24}N_2IRh$ (534.24 g mol^{-1}): C, 47.21; H, 4.53; N, 5.24. Found: C, 42.09; H, 4.60; N, 5.11.

Iodo(η^4-1,5-COD)(1,3-dimethylimidazolidin-2-ylidene)rhodium(I) (1C). The solvent was removed in vacuo and the remaining solid washed three times with 5 mL of *n*-hexane. Yield: 51%. ^1H NMR (400 MHz, $(CD_3)_2SO$): δ 4.68 (2H, br, COD_{vinyl}), 4.47 (2H, br, COD_{vinyl}), 3.47 (6H, s, CH_3), 3.37 (4H, s, CH_2) 2.23 (4H, br, COD_{allyl}), 1.81 (4H, m, COD_{allyl}). $^{13}C\{^1H\}$ NMR (100.5 MHz, $(CD_3)_2SO$): δ 211.0 (d, $^1J_{Rh-C} = 50.8$ Hz, N*C*N), 87.7 (d, $^1J_{Rh-C} = 10.1$ Hz, COD_{vinyl}), 78.5 (br, COD_{vinyl}), 50.8 (CH_2), 36.7 (COD_{allyl}), 36.5 (CH_3), 30.9 (COD_{allyl}). Anal. Calcd for $C_{13}H_{22}N_2IRh$ (436.14 g mol^{-1}): C, 35.80; H, 5.08; N, 6.42. Found: C, 35.83; H, 5.21; N, 6.55.

Iodo(η^4-1,5-COD)(7,9-dimethylpurine-8-ylidene)rhodium(I) (1E). Half of the solvent was removed in vacuo and the remaining suspension filtered at −60 °C. The yellow solid was washed once with 8 mL of ethanol at −60 °C and three times with 10 mL of diethyl ether at room temperature. Yield: 61%. ^1H NMR (400 MHz, $(CD_3)_2SO$): δ 8.07 (1H, s, NC*H*N), 7.20 (1H, s, C(6)*H*), 5.22 (2H, br, COD_{vinyl}), 4.24 (3H, s, CH_3), 4.08 (3H, s, CH_3), 3.83 (2H, br, COD_{vinyl}), 2.46 (4H, br, COD_{allyl}), 1.86 (4H, m, COD_{allyl}). $^{13}C\{^1H\}$ NMR (100.5 MHz, $(CD_3)_2SO$): δ 181.2 (d, $^1J_{Rh-C} = 50.1$ Hz, carbene), 166.6 (*C*(2)H), 154.5 (*C*(6)H), 150.3 (*C(4)*═C(5)), 134.6 (C(4)═*C(5)*), 98.2 (br, COD_{vinyl}), 74.0 (br, COD_{vinyl}), 35.2 (CH_3), 31.2 (CH_3), 30.5 (br, COD_{allyl}), 29.0 (br, COD_{allyl}). Anal. Calcd for $C_{15}H_{20}N_4IRh$ (486.16 g mol^{-1}): C, 37.06; H, 4.15; N, 11.52. Found: C, 36.84; H, 4.46; N, 11.27.

Iodo(η^4-1,5-COD)(6-(dimethylamino)-7,9-dimethylpurin-8-ylidene)rhodium(I) (1H). The employed azolium salt is 6-(dimethylamino)-7,9-dimethylpurinium perchlorate. The suspension was filtered at 0 °C and washed once with 10 mL of ethanol and once with 10 mL of diethyl ether at 0 °C. Yield: 95%. ^1H NMR (270 MHz, CD_2Cl_2): δ 8.30 (NC*H*N), 4.35 (3H, s, NCH_3), 4.12 (3H, s, NCH_3), 3.48 (4H, br, COD_{vinyl}), 3.06 (6H, s, $N(CH_3)_2$), 2.04 (4H, m, COD_{allyl}), 1.85 (4H, m, COD_{allyl}). $^{13}C\{^1H\}$ NMR (100.5 MHz, CD_2Cl_2): δ 200.0 (d, $^1J_{Rh-C} = 46.7$ Hz, carbene), 152.9, 152.7 (*C(4)*═C(5) and *C*NMe_2), 150.9 (N*C*HN), 116.1 (C(4)═*C(5)*), 98.5 (d, $^1J_{Rh-C} = 6.4$ Hz, COD_{vinyl}−Rh), 73.6 (d, $^1J_{Rh-C} = 14.6$ Hz, COD_{vinyl}−Rh), 41.6, 39.3, 33.3 (NCH_3), 32.4, 32.1, 29.6, 29.4 (COD_{allyl}). MS (FAB) *m*/*z*: 529 [M^+], 402 [$M^+ - I$], 211 [$M^+ - (I^- + \text{carbene})$], 192 [carbene]. Anal. Calcd for $C_{17}H_{25}N_5IRh$ (529.23 g mol^{-1}): C, 38.58; H, 4.76; N, 13.23. Found: C, 38.71; H, 4.68; N, 12.90.

Iodo(η^4-1,5-COD)(6-chloro-7,9-dimethylpurin-8-ylidene)rhodium(I) (1I). The employed azolium salt is 6-chloro-7,9-dimethylpurinium perchlorate. The suspension was filtered at 0 °C and washed once with 10 mL of ethanol and twice with 10 mL of diethyl ether at 0 °C. Yield: 77%. ^1H NMR (270 MHz, $(CD_3)_2SO$): δ 8.49 (1H, s, NC*H*N), 4.33 (3H, s, CH_3), 4.15 (3H, s, CH_3), 3.49 (4H, br, COD_{vinyl}), 2.60 (4H, m, COD_{allyl}), 1.93 (4H, m, COD_{allyl}). $^{13}C\{^1H\}$ NMR (100.5 MHz, $(CD_3)_2SO$): δ 198.2 (d, $^1J_{Rh-C} = 68.0$ Hz, carbene), 154.4 (N*C*HN), 152.8 (*C*Cl), 152.1 (*C(4)*═C(5)), 113.6 (C(4)═*C(5)*), 99.7 (br, COD_{vinyl}−Rh), 71.4 (d, $^1J_{Rh-C} = 13.0$ Hz, COD_{vinyl}−Rh), 38.1, 33.0, 32.9, 29.0, 28.9, 19.1 (NCH_3, COD_{allyl}). Anal. Calcd for $C_{15}H_{19}N_4ClIORh$ (520.61 g mol^{-1}): C, 34.61; H, 3.68; N, 10.76. Found: C, 33.89; H, 3.91; N, 10.11.

Iodo(η^4-1,5-COD)(1,3-dimethyltetrazolin-2-ylidene)rhodium(I) (1L). 1,3-Dimethyltetrazolium tetrafluoroborate (**La**) (105 mg, 0.57 mmol) was added to a vigorously stirred suspension of bis-[μ-ethoxy-(η^4-1,5-COD)rhodium] (140 mg, 0.26 mmol) in 10 mL of ethanol. The solution was stirred for 20 h at room temperature. Afterward 8 mL of the ethanol was removed in vacuo, and the precipitate was filtered at −40 °C and washed three times with 5 mL of diethyl ether. Yield: 90%. ^1H NMR (400 MHz, $(CD_3)_2SO$): δ 5.00 (2H, br, COD_{vinyl}), 4.27 (6H, s, CH_3), 3.57 (2H, br, COD_{vinyl}), 2.35 (4H, br, COD_{allyl}), 1.89 (4H, br, COD_{allyl}). $^{13}C\{^1H\}$ NMR (100.5 MHz, $(CD_3)_2SO$): δ 180.6 (d, $^1J_{Rh-C} = 50.9$ Hz, N*C*N), 97.9 (br, COD_{vinyl}), 71.5 (br, COD_{vinyl}), 37.8 (CH_3), 32.6 (br,

COD_{allyl}), 29.4 (br, COD_{allyl}). Anal. Calcd for $C_{11}H_{18}N_4IRh$ (436.10 g mol^{-1}): C, 30.30; H, 4.16; N, 12.85. Found: C, 30.15; H, 4.00; N, 12.77.

Iodo(η^4-1,5-COD)(1,2,3-trimethyl-4-isopropylpyrazolin-5-ylidene)rhodium(I) (1M). NaH (30 mg, 3.24 mmol) was suspended in 5 mL of ethanol and added dropwise to a solution of bis[μ-chloro-(η^4-1,5-COD)rhodium] (150 mg, 0.30 mmol) in 10 mL of ethanol. After stirring 20 min at room temperature 1,2,3-trimethyl-4-isopropylpyrazolium iodide (**Ma**) (90 mg, 0.68 mmol) dissolved in 15 mL of ethanol was added, and the mixture was heated for 7 days at 40 °C. The suspension was filtered and the remaining solid washed with 10 mL of methanol and diethyl ether. The product was dissolved in 5 mL of dichloromethane and filtered through Celite. After removing the solvent a yellow solid was obtained. Yield: 56%. ^{1}H NMR (400 MHz, $(CD_3)_2SO$): δ 4.42 (3H, s, CH_3), 4.12 (3H, s, CH_3), 4.03 (2H, br, COD_{vinyl}), 4.01 (3H, s, NCH_3), 3.99 (2H, br, COD_{vinyl}), 3.94 (3H, s, NCH_3), 2.90 (1H, hept, $^3J_{HH}$ = 6.7 Hz, CH(CH_3)$_2$), 2.68 (3H, s, CCH_3), 2.55 (4H, br, COD_{allyl}), 2.11 (4H, m, COD_{allyl}), 1.05 (6H, d, $^3J_{HH}$ = 6.7 Hz, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (100.5 MHz, $(CD_3)_2SO$): δ 187.0 (d, $^1J_{Rh-C}$ = 49.8 Hz, carbene), 129.7 (C═C), 126.1 (C═C), 84.3 (d, $^1J_{Rh-C}$ = 10.4 Hz, COD_{vinyl}), 77.8 (d, $^1J_{Rh-C}$ = 14.7 Hz, COD_{vinyl}), 37.1 (NCH_3), 32.9 (NCH_3), 30.6 (COD_{allyl}), 28.5 (COD_{allyl}), 26.5 (CCH_3), 22.7 (CH(CH_3)$_2$), 18.6 (CH(CH_3)$_2$).

Chloro(η^4-1,5-COD)(1,4-dimethyl-4,5-dihydro-1*H*-1,2,4-triazolin-5-ylidene)rhodium(I) (1N). KO*t*-Bu (168 mg, 1.50 mmol) was dissolved in 10 mL of THF, and the solution was added dropwise to a suspension of 1,4-dimethyltriazolium iodide (**Ga**) (299 mg, 1.33 mmol) in 20 mL of THF. The suspension was stirred for 30 min at room temperature. After addition of bis[μ-chloro-(η^4-1,5-COD)rhodium] (330 mg, 0.67 mmol) and 20 mL of toluene the solution was heated for 1 h at 80 °C. The solvent was removed in vacuo, and the product was extracted three times with a 1:1 mixture of toluene/THF (10 mL). Yield: 71%. ^{1}H NMR (400 MHz, $(CD_3)_2SO$): δ 8.56 (1H, s, NCH), 4.86 (2H, br, COD_{vinyl}), 4.05 (3H, s, CH_3), 3.91 (3H, s, CH_3), 3.39 (2H, br, COD_{vinyl}), 2.30 (4H, br, COD_{allyl}), 1.87 (4H, br, COD_{allyl}). ^{13}C{^{1}H} NMR (100.5 MHz, $(CD_3)_2SO$): δ 183.8 (d, $^1J_{Rh-C}$ = 50.6 Hz, NCN), 144.2 (NCHN), 96.9 (br, COD_{vinyl}), 68.8 (br, COD_{vinyl}), 38.4 (CH_3), 33.9 (CH_3), 31.6 (COD_{allyl}), 28.0 (COD_{allyl}).

Chloro(η^4-1,5-COD)[di(4-methyl)-*N*-piperidylmethylidene]-rhodium(I) (1P). The free carbene **P** (173 mg, 0.82 mmol) was added to a stirred solution of bis[μ-chloro-(η^4-1,5-COD)rhodium] (202 mg, 0.41 mmol) in 15 mL of anhydrous THF at −78 °C. A color change was observed from light to dark yellow. After the reaction mixture was stirred for 6 h at room temperature, the solvent was removed in vacuo. The precipitate was washed twice with *n*-hexane and diethyl ether (10 mL). After the solvent was decanted, the resulting solid was dried in vacuo. Yield: 264 mg, 71%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.39 (2H, COD_{vinyl}), 4.16 (2H, COD_{vinyl}), 3.61 (8H, br s, NCH_2), 3.07 (2H, CH), 2.20 (4H, br, COD_{allyl}), 1.71 (4H, br, COD_{allyl}), 1.58 (8H, br s, CH_2), 1.29 (8H, br, CH_3). ^{13}C{^{1}H} NMR (100.5 MHz, $CDCl_3$): δ 232.6 (NCN), 89.0 (COD_{vinyl}), 86.2 (COD_{vinyl}), 63.2, 51.5 (CH_2N), 49.5 (CH), 33.6, 31.4 (COD_{allyl}), 29.8, 26.0 (CH_2), 23.1 (CH_3). Anal. Calcd for $C_{21}H_{36}N_2ClRh$ (454.89 g mol^{-1}): C, 55.45; H, 7.98; N, 6.16. Found: C, 55.84; H, 8.12; N, 6.37.

Preparation of Complexes 2A, 2C, 2E−2I, and 2L. Iodo(η^4-1,5-COD)(azolinylidene)rhodium(I) (0.36 mmol) was dissolved in 10 mL of dichloromethane, and carbon monoxide was bubbled 30 min through the solution. The isolation of the complex was conducted for each complex according to its properties.

Iododicarbonyl(1,3-dimethylperimidinin-2-ylidene)rhodium-(I) (2A). Carbon monoxide was passed through the reaction mixture until the solvent evaporated. The residue was washed three times with 5 mL of *n*-pentane. Yield: 99%. ^{1}H NMR (400 MHz, $(CD_3)_2$-SO): δ 7.25 (2H, dd, $^3J_{H-H}$ = 8.0 Hz, $^3J_{H-H}$ = 7.6 Hz, CHCHCH), 7.12 (2H, d, $^3J_{H-H}$ = 8.0 Hz, CHCHC), 6.29 (2H, d, $^3J_{H-H}$ = 7.6 Hz, CCHCH), 2.89 (6H, s, CH_3). ^{13}C{^{1}H} NMR (100.5 MHz, $(CD_3)_2SO$): δ 194.4 (d, $^1J_{Rh-C}$ = 59.2 Hz, *C*O), 187.1 (d, $^1J_{Rh-C}$ = 41.0 Hz, N*C*N), 185.0 (br, *C*O), 145.1 (Ar), 134.7 (Ar), 129.0 (*C*H), 117.0 (*C*H), 114.7 (Ar), 103.3 (*C*H), 36.8 (*C*H_3). IR (CH_2Cl_2): ν [cm^{-1}] 2075.3 (s), 2004.1 (s).

Iododicarbonyl(1,3-dimethylimidazolidin-2-ylidene)rhodium-(I) (2C). Carbon monoxide was passed through the reaction mixture until the solvent evaporated. The residue was washed three times with 5 mL of *n*-pentane. Yield: 100%. ^{1}H NMR (400 MHz, $(CD_3)_2$-SO): δ 3.41 (6H, s, CH_3), 3.39 (4H, s, CH_2). ^{13}C{^{1}H} NMR (100.5 MHz, $(CD_3)_2SO$): δ 214.9 (br, *C*O), 204.7 (br, *C*O), 200.5 (br, N*C*N), 52.0 (*C*H_2), 36.7(*C*H_3). IR (CH_2Cl_2): ν [cm^{-1}] 2073.0 (s), 1999.8 (s).

Iododicarbonyl(7,9-dimethylpurine-2-ylidene)rhodium(I) (2E). The solvent was removed in vacuo and the residue washed three times with 5 mL of *n*-hexane. Yield: 100%. ^{1}H NMR (400 MHz, $(CD_3)_2SO$): δ 8.10 (1H, s, NCHN), 7.36 (1H, s, C(6)H), 4.04 (3H, s, CH_3), 3.36 (3H, s, CH_3). ^{13}C{^{1}H} NMR (100.5 MHz, $(CD_3)_2SO$): δ 192.3 (br, *C*O), 181.9 (br, *C*O), 179.7 (br, carbene), 160.1 (*C(2)*H), 154.4 (*C(6)*H), 147.4 (*C(4)*═C(5)), 136.3 (C(4)═*C(5)*), 29.3 (*C*H_3), 27.4 (*C*H_3). IR (CH_2Cl_2): ν [cm^{-1}] 2069.2 (s), 2006.3 (s).

Iododicarbonyl(1,3-dimethylbenzimidazolin-2-ylidene)rhodium(I) (2F). The solvent was removed in vacuo and the residue washed three times with 5 mL of *n*-pentane. Yield: 100%. ^{1}H NMR (400 MHz, $(CD_3)_2SO$): δ 7.71 (2H, dd, $^3J_{H-H}$ = 5.9 Hz, $^5J_{H-H}$ = 3.0 Hz, CHCHCH), 7.41 (2H, dd, $^3J_{H-H}$ = 5.9 Hz, $^5J_{H-H}$ = 2.9 Hz, CHCHCN), 3.97 (6H, s, CH_3). ^{13}C{^{1}H} NMR (100.5 MHz, $(CD_3)_2SO$): δ 188.0 (d, $^1J_{Rh-C}$ = 52.9 Hz, *C*O), 182.3 (d, $^1J_{Rh-C}$ = 40.5 Hz, N*C*N), 180.9 (br, *C*O), 134.6 (N*C*−*C*N), 123.3 (CH*C*HCH), 110.9 (CH*C*HCN), 35.0 (*C*H_3). IR (CH_2Cl_2): ν [cm^{-1}] 2061.4 (s), 1994.0 (s).

Iododicarbonyl(1,4-dimethyl-4,5-dihydro-1*H*-1,2,4-triazolin-5-ylidene)rhodium(I) (2G). The reaction was conducted at −10 °C. Carbon monoxide was passed through the reaction mixture until the solvent evaporated. The residue was washed three times with 6 mL of *n*-pentane at −78 °C under CO atmosphere. Yield: 83%. ^{1}H NMR (400 MHz, $(CD_3)_2SO$): δ 8.81 (1H, s, N*C*H), 3.91 (3H, s, CH_3), 3.75 (3H, s, CH_3). ^{13}C{^{1}H} NMR (100.5 MHz, $(CD_3)_2SO$): δ 187.7 (d, $^1J_{Rh-C}$ = 54.0 Hz, *C*O), 181.1 (d, $^1J_{Rh-C}$ = 79.9 Hz, *C*O), 174.1 (d, $^1J_{Rh-C}$ = 42.6 Hz, N*C*N), 145.2 (N*C*HN), 39.9 (*C*H_3), 35.2 (*C*H_3). IR (CH_2Cl_2): ν [cm^{-1}] 2077.8 (s), 2006.4 (s).

Iododicarbonyl(6-(dimethylamino)-7,9-dimethylpurin-8-ylidene)rhodium(I) (2H). The solvent was removed in vacuo and the residue washed twice with 15 mL of *n*-hexane. Yield: 99%. ^{1}H NMR (270 MHz, $(CD_3)_2SO$): δ 8.41 (NCHN), 4.48 (3H, s, NCH_3), 4.35 (3H, s, NCH_3), 3.14 (6H, s, N(CH_3)$_2$). ^{13}C{^{1}H} NMR (100.5 MHz, $(CD_3)_2SO$): δ 195.2 (br, *C*O), 191.1 (br, *C*O), 189.3 (br, carbene), 153.2, 153.0 (*C(4)*═C(5) and *C*NMe_2), 151.5 (N*C*HN), 116.8 (C(4)═*C(5)*), 41.7, 39.6, 33.5 (NCH_3). IR (CH_2Cl_2): ν [cm^{-1}] 2077.3 (s), 2008.1 (s).

Iododicarbonyl(6-chloro-7,9-dimethylpurin-8-ylidene)rhodium(I) (2I). The solvent was removed in vacuo and the residue washed twice with 10 mL of *n*-hexane at 0 °C. Yield: 100%. ^{1}H NMR (270 MHz, $(CD_3)_2SO$): δ 8.56 (1H, s, NCHN), 4.40 (3H, s, CH_3), 4.22 (3H, s, CH_3). ^{13}C{^{1}H} NMR (100.5 MHz, $(CD_3)_2SO$): δ 196.2 (br, *C*O), 190.6 (br, *C*O), 189.7 (br, carbene), 154.4 (N*C*HN), 153.0 (*C*Cl), 152.8 (*C(4)*═C(5)), 114.9 (C(4)═*C(5)*), 38.4, 33.2, (NCH_3). IR (CH_2Cl_2): ν [cm^{-1}] 2078.4 (s), 2007.8 (s).

Iododicarbonyl(1,3-dimethyltetrazolin-2-ylidene)rhodium-(I) (2L). The solvent was removed in vacuo and the residue washed three times with 5 mL of *n*-hexane at 0 °C. Yield: 100%. ^{1}H NMR (400 MHz, $(CD_3)_2SO$): δ 4.33 (6H, s, CH_3). ^{13}C{^{1}H} NMR (100.5 MHz, $(CD_3)_2SO$): δ 187.7 (br, *C*O), 183.3 (d, $^1J_{Rh-C}$ = 40.8 Hz,

*C*O), 178.8 (d, $^1J_{Rh-C}$ = 42.0 Hz, N*C*N), 37.6 (*C*H_3). IR (CH_2Cl_2): ν [cm^{-1}] 2086.1 (s), 2014.7 (s).

Bis[1,2-bis(1-methyl-4,5-dihydro-1*H*-1,2,4-triazolin-5-ylidene)ethylene]rhodium(I) Bromide (3Q). NaH (100 mg, 4.17 mmol) was dissolved in 8 mL of ethanol and slowly added to a suspension of bis[μ-chloro-(η^4-1,5-COD)rhodium] (250 mg, 0.51 mmol) in 10 mL of ethanol. After stirring for 30 min at room temperature 1,2-bis[1-methyltriazolium]ethylene dibromide (**Qa**) (900 mg, 2.54 mmol) was added. The mixture was heated for 48 h at 40 °C. The solvent was reduced to 6 mL, and the suspension was filtered. The remaining precipitate was washed three times with 5 mL of diethyl ether. Yield: 76%. ^{1}H NMR (400 MHz, $(CD_3)_2SO$): δ 8.75 (4H, s, C*H*), 4.87 (8H, s, CH_2), 1.76 (12H, s, CH_3). $^{13}C\{^1H\}$ NMR (100.5 MHz, $(CD_3)_2SO$): δ 190.0 (d, $^1J_{Rh-C}$ = 43.6 Hz, carbene), 143.3 (N*C*N), 45.6 (*C*H_2), 27.5 (*C*H_3). MS (FAB) *m*/*z*: 487 [M^+], 295 [M^+ − biscarbene], 176 [biscarbene − CH_3].

Bis[1,2-bis(1-isopropyl-4,5-dihydro-1*H*-1,2,4-triazolin-5-ylidene)ethylene]rhodium(I) Bromide (3S). NaH (78 mg, 3.25 mmol) was dissolved in 10 mL of ethanol and slowly added to a suspension of bis[μ-chloro-(η^4-1,5-COD)rhodium] (175 mg, 0.35 mmol) in 10 mL of ethanol. After stirring for 30 min at room temperature 1,2-bis[1-isopropyltriazolium]ethylene dibromide (**Sa**) (594 mg, 1.44 mmol) was added. The solvent was reduced in vacuo to 8 mL and the remaining reaction mixture stirred for 5 days at room temperature. The suspension was filtered and the precipitate was washed twice with 5 mL of diethyl ether. Yield: 68%. ^{1}H NMR (400 MHz, $(CD_3)_2SO$): δ 8.33 (4H, s, C*H*), 4.99 (8H, s, CH_2), 4.99 (4H, hept., $^3J_{H-H}$ = 6.1 Hz, C*H*CH_3), 1.76 (24H, d, $^3J_{H-H}$ = 6.1 Hz, CH_3). $^{13}C\{^1H\}$ NMR (100.5 MHz, $(CD_3)_2SO$): δ 189.8 (d, $^1J_{Rh-C}$ = 43.2 Hz, N*C*N), 144.0 (N*C*HN), 48.5 (*C*H_2), 47.2 (*C*H$(CH_3)_2$), 22.8 (*C*H_3). Anal. Calcd for $C_{24}H_{48}N_{12}IRh$ (734.53 g mol^{-1}): C, 39.24; H, 6.59; N, 22.88. Found: C, 38.98; H, 6.39; N, 23.11.

Tetrakis(1,4-dimethyl-4,5-dihydro-1*H*-1,2,4-triazolin-5-ylidene)rhodium(I) Iodide (4G). NaH (105 mg, 4.38 mmol) was dissolved in 10 mL of ethanol and slowly added to a suspension of bis[μ-chloro-(η^4-1,5-COD)rhodium] (280 mg, 0.57 mmol) in 10 mL of ethanol. After stirring for 30 min at room temperature 1,4-dimethyltriazolium iodide (**Ga**) (1022 mg, 4.54 mmol) was added. The solvent was reduced to 8 mL and the remaining reaction mixture stirred for 48 h at room temperature. The suspension was filtered at 0 °C, and the solid was washed three times with 10 mL of diethyl ether. Yield: 75%. ^{1}H NMR (400 MHz, $(CD_3)_2SO$): δ 8.75 (4H, s, C*H*), 3.60 (3H, s, CH_3), 3.41 (3H, s, CH_3). $^{13}C\{^1H\}$ NMR (100.5 MHz, $(CD_3)_2SO$): δ 191.4 (d, $^1J_{Rh-C}$ = 43.6 Hz, carbene), 143.0 (N*C*N), 38.5 (*C*H_3), 27.4 (*C*H_3). MS (FAB) *m*/*z*: 491 [M^+], 394 [M^+ − carbene], 297 [M^+ − 2*carbene], 200 [M^+ − 3*carbene]. Anal. Calcd for $C_{16}H_{28}N_{12}IRh$ (618.31 g mol^{-1}): C, 31.08; H, 4.56; N, 27.19. Found: C, 30.83; H, 4.98; N, 27.07.

Tetrakis(1,3,7,9-tetramethylxanthin-8-ylidene)rhodium(I) Bromide (4J). NaH (170 mg, 7.08 mmol) was dissolved in 10 mL of ethanol and slowly added to a suspension of bis[μ-chlorobis(η^2-cyclooctene)rhodium] (250 mg, 0.35 mmol) in 10 mL of ethanol. After stirring for 30 min at room temperature 1,3,7,9-tetramethylxanthinium tetrafluoroborate (**Ja**) (1651 mg, 5.58 mmol) and NaI (860 mg, 5.74 mmol) were added. The suspension was stirred for 60 h at room temperature. The solvent was removed in vacuo and the remaining solid dissolved in dichloromethane. The solution was filtered over Celite and the solvent was removed in vacuo. 1,3,7,9-Tetramethylxanthinium tetrafluoroborate was removed by extraction with 3 × 3.5 mL of water. The residue was washed at −30 °C with 4 mL of ethanol and at room temperature with 5 mL of diethyl ether. Yield: 31%. ^{1}H NMR (400 MHz, $(CD_3)_2SO$): δ 4.60 (3H, s), 4.32 (3H, s), 3.74 (3H, s), 3.20 (3H, s, CH_3). $^{13}C\{^1H\}$ NMR (67.9 MHz, $(CD_3)_2SO$): δ 192.8 (d, $^1J_{Rh-C}$ = 46.7 Hz, carbene), 152.4 (*C(6)*O), 150.3 (*C(2)*O), 140.7 (*C(4)*═C(5)), 109.1 (C(4)═*C(5)*), 38.0, 31.5, 31.4, 28.0 (N*C*H_3). MS (FAB) *m*/*z*: 935 [M^+], 727 [M^+ − carbene], 519 [M^+ − 2*carbene], 208 [carbene].

α,α′-Bis(1-isopropyl-4,5-dihydro-1*H*-1,2,4-triazolin-5-ylidene)*m*-xylene(η^4-1,5-COD)iridium(I) Chloride (5T). NaH (29 mg, 1.21 mmol) was dissolved in 10 mL of ethanol and slowly added to a suspension of bis[μ-chloro-(η^4-1,5-COD)iridium] (236 mg, 0.60 mmol) in 10 mL of ethanol. The reaction mixture was stirred for 30 min at room temperature, and 1,2-bis[1-isopropyl-4,5-dihydro-1*H*-1,2,4-triazolium]*m*-xylene dichloride (**Ta**) (160 mg, 0.24 mmol) was added. After stirring for 3 days at room temperature the solvent was reduced to one-third in vacuo. The suspension was filtered and the solvent was removed in vacuo. Yield: 69%. ^{1}H NMR (400 MHz, $(CD_3)_2SO$): δ 8.84 (2H, s, C*H*), 7.52−7.05 (4H, m, Ar−H), 5.47 (4H, s, CH_2), 4.84 (4H, hept, $^3J_{H-H}$ = 5.9 Hz, C*H*CH_3), 4.06 (4H, br, COD_{vinyl}), 2.29 (4H, br, COD_{vinyl}), 1.73 (4H, br, COD_{allyl}), 1.41 (12H, d, $^3J_{H-H}$ = 5.9 Hz, CH_3). $^{13}C\{^1H\}$ NMR (100.5 MHz, $(CD_3)_2SO$): δ 176.6 (N*C*N), 144.0 (N*C*HN), 135.8, 129.8, 128.3, 126.4 (Ar−*C*), 83.1 (COD_{vinyl}), 79.3 (COD_{vinyl}), 55.9 (*C*H_2), 50.1 (*C*H$(CH_3)_2$), 27.5 (*C*H_3), 25.0, 22.7 (COD_{allyl}). Anal. Calcd for $C_{26}H_{36}N_6ClIr$ (660.28 g mol^{-1}): C, 47.30; H, 5.50; N, 12.73. Found: C, 46.81; H, 5.17; N, 13.07.

Bis(1,4-dimethyl-4,5-dihydro-1*H*-1,2,4-triazolin-5-ylidene)(η^4-1,5-COD)iridium(I) Iodide (6G). NaH (110 mg, 4.58 mmol) was dissolved in 10 mL of ethanol and slowly added to a suspension of bis[μ-chloro-(η^4-1,5-COD)iridium] (300 mg, 0.45 mmol) in 15 mL of ethanol. The reaction mixture was stirred for 30 min at room temperature, and 1,4-dimethyl-4,5-dihydro-1*H*-1,2,4-triazolium iodide (**Ga**) (800 mg, 3.56 mmol) was added. After stirring for 48 h at room temperature the solvent was reduced to one-third in vacuo. The suspension was filtered at 0 °C, and the remaining solid was washed three times with 5 mL of diethyl ether. Yield: 88%. ^{1}H NMR (400 MHz, $(CD_3)_2SO$): δ 8.69 (2H, s, N*C*H), 4.02 (6H, s, CH_3), 3.90 (4H, br, COD_{vinyl}), 3.85 (6H, s, CH_3), 2.29 (4H, br, COD_{vinyl}), 1.96 (4H, br, COD_{allyl}). $^{13}C\{^1H\}$ NMR (100.5 MHz, $(CD_3)_2SO$): δ 179.3 (N*C*N), 145.7 (N*C*HN), 78.2 (COD_{vinyl}), 77.7 (COD_{vinyl}), 35.5 (*C*H_3), 31.7 (COD_{allyl}), 31.3 (*C*H_3), 31.0 (COD_{allyl}). Anal. Calcd for $C_{16}H_{26}N_6IIr$ (621.55 g mol^{-1}): C, 30.92; H, 4.22; N, 13.52. Found: C, 30.31; H, 4.00; N, 13.62.

Iodo(η^4-1,5-COD)(1,4-dimethyl-4,5-dihydro-1*H*-1,2,4-triazolin-5-ylidene)iridium(I) (7G). NaH (45 mg, 1.89 mmol) was dissolved in 10 mL of ethanol and slowly added to a suspension of bis[μ-chloro-(η^4-1,5-COD)iridium] (300 mg, 0.45 mmol) in 20 mL of ethanol. After stirring for 30 min at room temperature 1,4-dimethyl-4,5-dihydro-1*H*-1,2,4-triazolium iodide (**Ga**) (221 mg, 0.98 mmol) was added. The solvent was reduced to 10 mL, and the suspension was stirred for 48 h at room temperature. The suspension was filtered at −40 °C, and the precipitate was washed at −40 °C with 10 mL of ethanol and 20 mL of diethyl ether. Yield: 90%. ^{1}H NMR (400 MHz, $(CD_3)_2SO$): δ 8.60 (1H, s, N*C*H), 4.60 (2H, br, COD_{vinyl}), 3.91 (3H, s, CH_3), 3.77 (3H, s, CH_3), 3.05 (2H, br, COD_{vinyl}), 2.11 (4H, br, COD_{vinyl}), 1.73 (2H, br, COD_{allyl}), 1.36 (2H, br, COD_{allyl}). $^{13}C\{^1H\}$ NMR (100.5 MHz, $(CD_3)_2SO$): δ 181.3 (N*C*N), 144.4 (N*C*HN), 82.1 (COD_{vinyl}), 81.9 (COD_{vinyl}), 39.7 (*C*H_3), 34.2 (*C*H_3), 32.3 (COD_{allyl}), 29.8 (COD_{allyl}). Anal. Calcd for $C_{12}H_{19}N_3IIr$ (524.42 g mol^{-1}): C, 27.48; H, 3.65; N, 8.01. Found: C, 27.83; H, 3.91; N, 7.59.

Single-Crystal X-ray Structure Determination of Compounds 1B, 1J, 1L, 4G, 6G, and 7G. General. Crystal data and details of the structure determination are presented in Table 4. Suitable single crystals for the X-ray diffraction study were grown with standard cooling techniques. Crystals were stored under perfluorinated ether, transferred in a Lindemann capillary, fixed, and sealed. Preliminary examination and data collection were carried out on an area detecting system (NONIUS, MACH3, κ-CCD) at the window of a rotating anode (NONIUS, FR591) and graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The unit cell parameters were obtained by full-matrix least-squares refinements during the scaling

procedure. Data collection was performed at low temperatures (Oxford Cryosystems); each crystal was measured with a couple of data sets in rotation scan modus with $\Delta\varphi/\Delta\omega = 1.0$. Intensities were integrated and the raw data were corrected for Lorentz, polarization, and, arising from the scaling procedure for latent decay, absorption effects. The structures were solved by a combination of direct methods and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic displacement parameters. The methyl hydrogen atoms were refined as part of rigid groups, with $d_{C-H} = 0.98$ Å and $U_{iso(H)} = 1.5U_{eq(C)}$. All other hydrogen atoms were placed in calculated positions and refined using a riding model, with d_{C-H} distances of 0.95 and 0.99 Å, and $U_{iso(H)} = 1.2U_{eq(C)}$. Full-matrix least-squares refinements were carried out by minimizing $\sum w(F_o^2 - F_c^2)^2$ with the SHELXL-97 weighting scheme and stopped at shift/err < 0.001. The final residual electron density maps showed no remarkable features. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from International Tables for Crystallography. All calculations were performed on an Intel Pentium II PC, with the STRUX-V system, including the programs PLATON, SIR92, and SHELXL-97.[45] *Special observations*: **1B**: Compound **1B** cocrystallizes with one molecule of the solvent CH_2Cl_2. The unit cell contains two crystallographically independent molecules. **1J**: Large anisotropic displacement parameters for the COD-ring atoms C12 and C17 are indicative for disorder; attempts to refine such a model failed. **4G**: $C_{16}H_{28}IN_{12}Rh$, $M_r = 618.31$, yellow fragment, monoclinic, $P2/c$ (No. 13), $a = 8.7860(1)$ Å, $b = 8.6851(1)$ Å, $c = 17.5697(2)$ Å, $\beta = 90.0058(6)°$, $V = 1340.70(3)$ Å^3, $Z = 2$, $d_{calc} = 1.532$ g cm^{-3}, $F_{000} = 612$, $\mu = 1.813$ mm^{-1}. Only a basic substructure could be refined. All crystals show strong diffuse streaks in the reciprocal space. The almost tetragonal metric of the unit cell suggests unresolvable twin problems. Additional, very weak peaks are observed that could be indexed based on a supercell with a doubled *a*- and *b*-axis. **6G**: Compound **6G** cocrystallizes with half a molecule of the solvent C_2H_5OH. The highly disordered alcohol molecule could not be modeled satisfactorily. The problem was solved with the PLATON Calc Squeeze procedure. The unit cell contains two crystallographically independent molecules. The assignment of the C versus N atoms in the NHC ligand is proved by difference Fourier syntheses. **7G**: A disorder (0.58(5):0.42(5)) of the C versus N atoms in the NHC ligand backbone is observed and could be modeled clearly. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-602421 (**1B**), CCDC-602425 (**1J**), CCDC-602424 CCDC-602422 (**6G**), and CCDC-602423 (**7G**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Supporting Information Available: Tables of crystallographic data, atomic coordinates, atomic displacement parameters, bond distances, and bond angles for complexes **1B**, **1J**, **1L**, **6G**, and **7G**. Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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