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Silver and Rhodium Complexes of Stable, Monomeric Imidazolidin-2-ylidenes: Synthesis, Reactivity and Decomposition Pathway

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Silver(I) complexes of the freely stable carbenes 1,3-bis(2,4,6-trimethylphenyl)imidazolidin-2-ylidene (**3**) and 1,3-bis(2,6-diisopropylphenyl)imidazolidin-2-ylidene (**4**) were prepared from the imidazolinium chlorides **1** and **2**, respectively, and silver oxide. These two air-stable and light-sensitive carbene complexes [AgCl(**3**)] (**5**) and [AgCl(**4**)] (**6**) were characterized by NMR spectroscopy, and the molecular structure of **6** was confirmed by X-ray diffraction. The imidazolidin-2-thiones **7** and **8** were obtained by reaction of the silver carbene complexes **5** and **6**, respectively, with elemental sulfur at ambient temperature. Spectroscopic evidence for the formation of the rhodium(I) complex [(cod)Rh(Cl)(**10**)] (**11**) with the sterically demanding 1,3-di-*tert*-butyl-imidazolidin-2-ylidene ligand **10** obtained in situ from 1,3-di-*tert*-butyl-imidazolinium tetrafluoroborate **9** is presented. Because of the steric demand of the carbene ligand **10**, complex **11** decomposed rapidly in solutions of chlorinated or polar solvents.

Introduction

Metal complexes of N-heterocyclic carbenes have emerged as an important class of compounds with widespread applications in homogeneous catalysis.[1,2] For example, such complexes represent efficient catalysts for palladium-catalyzed carbon–carbon coupling reactions,[3,4] ruthenium-catalyzed olefin metathesis reactions,[5–7] or iridium-catalyzed transfer hydrogenation reactions.[8] In general, metal complexes of "saturated" (nonaromatic) imidazolidin-2-ylidenes[9] reveal higher catalytic activity than the analogous complexes of "unsaturated" (aromatic) imidazolin-2-ylidenes[10] or benzannulated benzimidazol-2-ylidenes.[11] This is regarded as a consequence of the stronger basicity and nucleophilicity of the nonaromatically stabilized carbene ligands. However, in contrast to unsaturated N-heterocyclic carbenes, imidazolidin-2-ylidenes can occur as carbene dimers (enetetramines) if the steric demand of their *N*-substituents is small (e.g. *N*-methyl,[12] *N*-ethyl,[12] and *N*-phenyl[13]) and the kinetic barrier for dimerization is low. Imidazolidin-2-ylidenes with bulky *N*-substituents [e.g. *N*-*tert*-butyl,[12] *N*-(2,4,6-trimethylphenyl),[14] and *N*-(2,6-diisopropylphenyl)[14]] showed no tendency to dimerize and could be isolated and characterized as monomeric compounds. Recently, a simple procedure for the formation of unsymmetrical *N*,*N'*-substituted imidazolidin-2-ylidenes was described, and it was demonstrated that only one sterically demanding *N*-substituent is sufficient to prevent the dimerization of the carbene.[15]

Initially, transition metal complexes with imidazolidin-2-ylidene ligands were synthesized by cleavage of the enetetramines under forceful conditions.[16,17] The direct formation of such carbene-metal complexes by utilization of monomeric saturated carbenes is less attractive since the free ligands are extremely sensitive towards oxygen and moisture. However, preparation of the free carbenes by in situ deprotonation of imidazolinium salts with strong bases and subsequent reaction with suitable transition-metal precursors produced an improvement. In contrast to this, transmetalation has emerged as an interesting alternative for the synthesis of numerous transition-metal carbene complexes.[18] Silver(I)-carbene complexes have turned out to be the transmetalation agent of choice and were first employed by Wang and Lin in order to prepare rhodium and palladium complexes of benzimidazol-2-ylidene ligands.[19] The analogous silver complexes of imidazolidin-2-ylidene ligands were prepared by Pytkowicz et al. from silver(I) oxide and imidazolinium salts.[20]

In this contribution we report on the preparation and characterization of silver complexes **5** and **6** (Scheme 1), along with the sterically demanding imidazolidin-2-ylidene ligands **3** and **4**. We demonstrate that complexes **5** and **6** do not react in the transmetalation reaction with PdI_2 and [(*p*-cymene)RuCl(μ-Cl)]$_2$, most likely because of the steric demand of the carbene ligands, which shows the limitations of the transmetalation reaction. Furthermore, the rhodium

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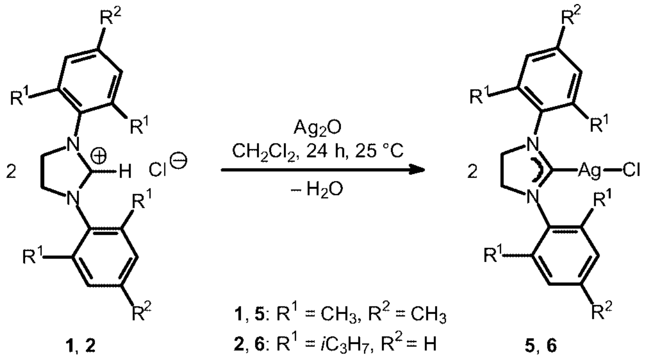
complex **11** with the *N*-*tert*-butyl-substituted carbene **10** is described (Scheme 3). These three complexes contain ligands that are also stable as monomeric imidazolidin-2-ylidenes when they are not coordinated to a metal center. In addition, the reaction of the complexes **5** and **6** with elemental sulfur to give imdazolidin-2-thiones is described (Scheme 2).

Results and Discussion

The preparation of the silver complexes **5** and **6** was carried out in an analogous procedure to that described by Wang and Lin for the preparation of silver complexes with benzimidazolin-2-ylidene ligands.[19] The reaction of the imidazolinium salts **1** and **2** with 0.5 equiv. silver oxide in dichloromethane afforded the monocarbene complexes after a reaction time of 24 h (Scheme 1).



Scheme 1. Preparation of the silver carbene complexes **5** and **6**.

During the reaction, the dark suspension of silver oxide and the imidazolidinium salt became a clear and colorless solution as the silver oxide was consumed. The reaction did not require an exclusion of oxygen or moisture. This represents a substantial advantage compared with the complex synthesis using air-sensitive free carbenes and silver(I) precursors. However, complexes **5** and **6** decompose under the influence of light, as expected for silver complexes, giving the free carbenes **3** and **4** and silver chloride. Nevertheless, both novel silver carbene complexes could be fully characterized by NMR and mass spectroscopy.

Single crystals of $\mathbf{6}\cdot 4CH_2Cl_2$ suitable for an X-ray diffraction analysis were obtained by layering *n*-pentane over a saturated dichloromethane solution of complex **6**. The molecular structure of the silver carbene complex **6** is depicted in Figure 1.[21] The X-ray diffraction data led, even after application of an absorption correction,[22–25] only to a poor structure model which, however, confirmed the overall composition and geometry of **6**. The quality of the X-ray data does not allow a detailed discussion of molecular parameters of **6**. Complex **6** resides on a crystallographic twofold axis that bisects the C4–C4* bond. The Ag–C2 bond in complex **6** [2.059(9) Å] is slightly shorter than the analogous bond in the silver(I) bromide complex with an *N*,*N*′-benzyl-substituted imidazolidin-2-ylidene ligand [2.09(2) Å].[20] However, the Ag–C2 bond length in **6** has a value that is similar to that found for the complex [AgCl(NHC)] (NHC = imidazolin-2-ylidene) [2.056(7) Å].[26]

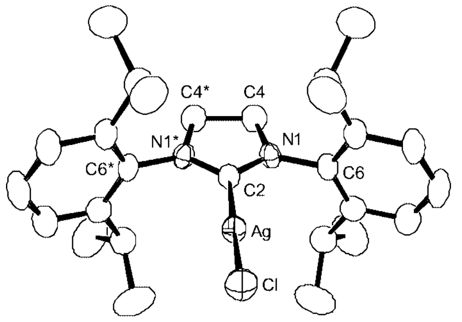
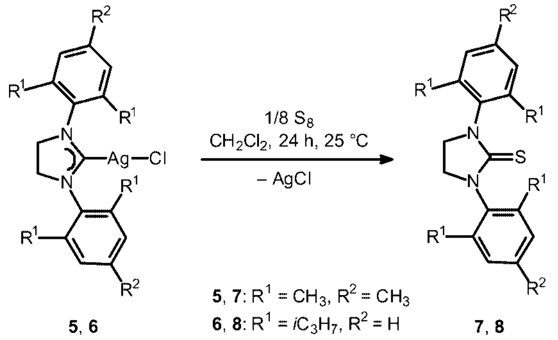


Figure 1. Molecular structure of one molecule of **6** in crystals of $\mathbf{6}\cdot 4CH_2Cl_2$. Hydrogen atoms and solvent molecules have been omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Ag–Cl 2.306(2), Ag–C2 2.059(9), N1–C2 1.324(7), N1–C4 1.457(8), C4–C4* 1.538(14); C2–Ag–Cl 173.5(2), C2–N1–C4 114.2(6), C2–N1–C6 123.1(5), Ag–C2–N1 125.9(4), N1–C2–N1* 107.8(8).

The transmetalation reactions with selected complexes of ruthenium and palladium {PdI_2, [(*p*-cymene)RuCl(μ-Cl)]$_2$} that use **5** and **6** as transmetalation agents were unsuccessful, most likely owing to the steric demand of the carbene ligands. We also studied the reactions of the complexes **5** and **6** with elemental sulfur. The imidazolidin-2-thiones **7** and **8** were obtained by simple addition of sulfur to a solution of the silver carbene complexes **5** and **6**, respectively, in dichloromethane at ambient temperature (Scheme 2).



Scheme 2. Preparation of the thiones **7** and **8**.

The formation of a carbene intermediate during the reaction of complexes **5** and **6** with sulfur is very likely. This transformation represents the reverse reaction of the sequence thione reduction[27] and reaction of the free carbene with a transition metal to give transition-metal carbene complexes. The ^{13}C NMR spectrum of **8** reveals the characteristic resonance signal for the carbon atom of the thiocarbonyl group at $\delta = 184.1$ ppm. Furthermore, the spectrum shows the resonance signal for the methylene carbon atom of the *N*-heterocyclic ring at $\delta = 50.2$ ppm. The cyclic thioureas **7** and **8** were characterized by X-ray diffraction to confirm the assigned structures. Crystals of **7** and **8** were obtained by diffusion of *n*-hexane into saturated dichloromethane solutions of the thiones. Figure 2 (**7**) and Figure 3 (**8**) depict the molecular structures of the thiones.[21–25]

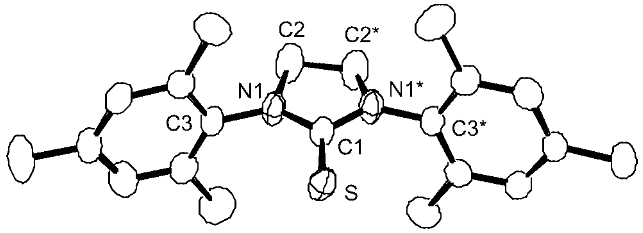


Figure 2. Molecular structure of one molecule of **7** in the crystal. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: S–C1 1.666(2), N1–C1 1.355(2), N1–C2 1.460(2), N1–C3 1.428(2), C2–C2* 1.513(4); C1–N1–C2 112.3(1), C1–N1–C3 125.3(1), C2–N1–C3 121.96(12), S–C1–N1 126.12(9), N1–C1–N1* 107.8(2).

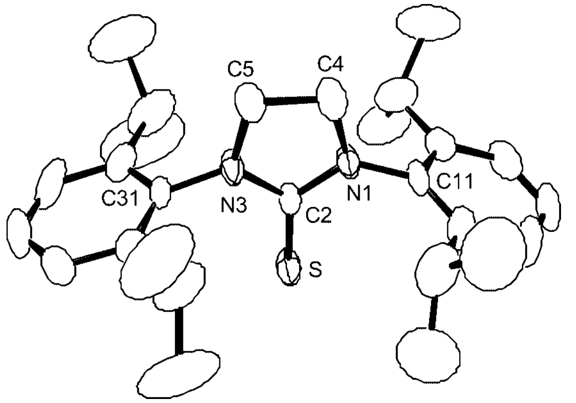
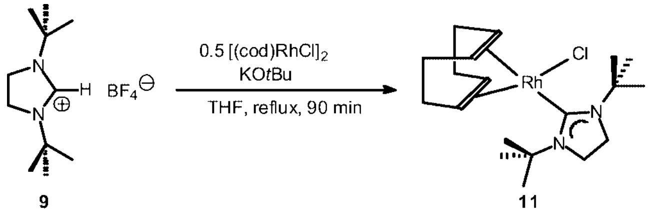


Figure 3. Molecular structure of one molecule of **8** in the crystal. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: S–C2 1.6611(15), N1–C2 1.347(2), N1–C4 1.453(2), N1–C11 1.440(2), N3–C2 1.353(2), N3–C5 1.457(2), N3–C31 1.425(2), C4–C5 1.495(3); C2–N1–C4 112.61(13), C2–N1–C11 124.75(13), C4–N1–C11 122.63(13), C2–N3–C5 112.45(13), C2–N3–C31 126.25(13), C5–N3–C31 121.15(12), S–C2–N1 126.54(11), S–C2–N3 125.77(11), N1–C2–N3 107.69(13).

The carbon–sulfur bond lengths in both thioureas are similar to those reported for symmetrically *N,N′*-substituted[28] or unsymmetrically substituted spirocyclic imidazolidin-2-thiones.[15b] The N–C–N angles in thiones **7** and **8** are similar to those observed in the carbene complexes.[15]

Imidazolidin-2-thiones can act as ligands by using the sulfur atom for coordination. The molecular structure of the complex *cis*-[PdCl$_2$(**7**)$_2$] has been determined. The structure analysis reveals that coordination of the thiourea to a transition metal leaves the C–S bond length as well as the N–C–N angles of the ligand unchanged within experimental error.[29]

Complexes with *N*-*tert*-butyl-substituted imidazolidin-2-ylidenes are rare because of the steric demand of the *N*-substituents of the carbene ligand that hampers coordination and facilitates ligand dissociation from the metal center.[30] However, we found that the rhodium carbene complex **11** can be synthesized from the imidazolidinium tetrafluoroborate **9**, potassium *tert*-butoxide, and the dinuclear complex [(cod)Rh(Cl)]$_2$ by heating to reflux in THF (Scheme 3).



Scheme 3. Synthesis of the carbene complex **11**.

The rhodium atom in **11** is coordinated by carbene ligand **10**, which is stable in the free state and was previously isolated as such by Denk et al.[12] The *N,N′*-*tert*-butyl-substituted imidazolinium salt **9** is easily obtained from *N,N′*-di-*tert*-butylethylenediamine, triethylorthoformate, and ammonium tetrafluoroborate.[31] The ^{13}C NMR spectrum of **11** exhibits a resonance signal for the carbene carbon atom at δ = 212.1 ppm with a ^{103}Rh-^{13}C coupling constant of $^1J_{\mathrm{Rh,C}}$ = 45 Hz. This constitutes clear evidence for complex formation. Both spectroscopic parameters are in good agreement with the analogous parameters for rhodium cod [(1*Z*,5*Z*)-1,5-cyclooctadiene] complexes with unsymmetrically *N,N′*-substituted carbene ligands.[15a] In comparison with rhodium complexes with benzannulated[32] and "unsaturated" (imidazolin-2-ylidene)[33] carbene ligands, the carbene carbon resonance in the ^{13}C NMR spectrum of **11** is shifted to a lower field, whereas compared to acyclic carbene ligands,[34] a small upfield shift is observed for the carbene carbon resonance in **11**. This corroborates the expectation that the σ-donor capability of carbenes with a saturated five-membered ring is higher than that for unsaturated carbenes of the imidazolin-2-ylidene type.

Complex **11** exhibits only two resonance signals for the olefinic carbon atoms of the cod ring (δ = 68.7 ppm, $^1J_{\mathrm{Rh,C}}$ = 15 Hz, and δ = 93.0 ppm, $^1J_{\mathrm{Rh,C}}$ = 8 Hz). In contrast to this, the ^{13}C NMR spectra of the rhodium complexes with unsymmetrically *N,N′*-substituted imidazolidin-2-ylidene ligands exhibit four signals for the olefinic carbon atoms of the cod ring, each with a ^1J coupling to the ^{103}Rh nucleus.[15a] This is attributed to the loss of symmetry in the rhodium(I) complexes with unsymmetrically *N,N′*-substituted carbene ligands.

Rhodium complex **11** is air stable when stored as a solid, but it decomposes in solutions of dichloromethane. This lability can be rationalized by the weak bond between the rhodium atom and the carbene carbon atom, which is presumably caused by the steric demand of the *N*-*tert*-butyl substitutents of the carbene ligand. Similar observations have been made with nickel complexes of ligand **10**.[30]

Conclusions

We have prepared the silver(I) complexes **5** and **6** along with the two monomeric imidazolidin-2-ylidenes **3** and **4**[14] starting from the imidazolinium salts **1** and **2**, respectively. The reaction of the silver complexes **5** and **6** with elemental sulfur gave the imidazolidin-2-thiones **7** and **8**, respectively. These thioureas were characterized by X-ray diffraction analysis. It was shown that the rhodium(I) complex with the *N*,*N′*-*tert*-butyl-substituted imidazolidin-2-ylidene ligand **10** can be synthesized in spite of the steric bulk of this carbene ligand.

Experimental Section

General: Reactions with air- and moisture-sensitive compounds or reagents were carried out in dry argon by using Schlenk and vacuum techniques. Solvents were dried by standard methods and freshly distilled prior to use. NMR spectra were recorded with a Bruker AC 200 (200 MHz) spectrometer and are reported relative to TMS as an internal standard. Mass spectra (EI) were measured with a Varian MAT 212 or a Bruker Reflex IV (MALDI) instrument. Elemental analyses (C, H, N) were obtained by using a Vario EL III elemental analyzer at the Westfälische Wilhelms-Universität Münster. The following compounds were prepared according to published procedures: 1,3-bis(2,4,6-trimethylphenyl)imidazolinium chloride (**1**),[14] 1,3-bis(2,6-diisopropylphenyl)imidazolinium chloride (**2**),[14] 1,3-di-*tert*-butyl-imidazolinium-tetrafluoroborate (**9**),[31] and {[(cod)Rh(Cl)]$_2$}.[35] All other compounds were used as purchased without further purification.

[AgCl(3)] (5): Silver(I) oxide (0.348 g, 1.5 mmol) was added to a solution of the imidazolinium salt **1** (1.029 g, 3.0 mmol) in dichloromethane (50 mL). The mixture was stirred at room temperature until the solid was completely consumed (24 h). The resulting solution was filtered through Celite and concentrated under vacuum. After recrystallization from dichloromethane/*n*-hexane, the silver carbene complex was obtained as a colorless solid (1.28 g, 95%). $C_{21}H_{26}N_2AgCl$ (449.8): calcd. C 56.08, H 5.83, N 6.23; found C 55.77, H 5.95, N 6.38. ^1H NMR (200.1 MHz, CD_3CN): δ = 2.31 (s, 12 H, *o*-Ar–CH_3), 2.37 (s, 6 H, *p*-Ar–CH_3), 4.05 (s, 4 H, NCH_2CH_2N), 6.90, 7.08 (2×s, 4 H, Ar–H) ppm. ^{13}C NMR (50.3 MHz, CD_3CN): δ = 18.1 (*o*-Ar–CH_3), 21.1 (*p*-Ar–CH_3), 51.8 (NCH_2), 130.1, 135.6, 137.0, 139.2 (Ar–C) ppm. The resonance for the carbene carbon atom was not observed. MS (MALDI): *m*/*z* = 719 [Ag(**3**)$_2$]$^+$.

[AgCl(4)] (6): Silver(I) oxide (0.348 g, 1.5 mmol) was added to a solution of **2** (1.281 g, 3.0 mmol) in dichloromethane (50 mL). The mixture was stirred at room temperature until the solid was completely consumed (24 h). It was then filtered through Celite and concentrated under vacuum. After recrystallization from dichloromethane/*n*-hexane, the silver carbene complex was obtained as a colorless solid (1.47 g, 92%). $C_{27}H_{38}N_2AgCl$ (533.9): calcd. C 60.74, H 7.17, N 5.25; found C 60.51, H 7.29, N 5.43. ^1H NMR (200.1 MHz, CD_3CN): δ = 1.19, 1.27 [2×d, ^3J(H,H) = 6.6, 7.6 Hz, 24 H, CH(CH_3)$_2$], 3.17 [sept, 4 H, CH(CH_3)$_2$], 4.11 (s, 4 H, NCH_2CH_2N), 7.31–7.46 (m, 6 H, Ar–H) ppm. ^{13}C NMR (50.3 MHz, CD_3CN): δ = 23.9, 25.5 [CH(CH_3)$_2$], 29.2 [CH(CH_3)$_2$], 54.7 (NCH_2), 125.4, 130.7, 134.4, 148.1 (Ar–C) ppm. The resonance for the carbene carbon atom was not observed.

1,3-Bis(2,4,6-trimethylphenyl)imidazolidin-2-thione (7): A mixture of the silver complex **5** (0.450 g, 1 mmol) and sulfur (0.032 g, 1 mmol) was suspended in dichloromethane (50 mL) and stirred for 24 h at room temperature. After removal of silver chloride by filtration, the solvent was evaporated in vacuo. The crude product was purified chromatographically [silica gel, *n*-hexane/diethyl ether (5:1, v:v)] to give a yellow solid (0.269 g, 80%). $C_{21}H_{26}N_2S$ (338.5): calcd. C 74.51, H 7.74, N 8.28; found C 75.32, H 7.48, N 8.29. ^1H NMR (200.1 MHz, $CDCl_3$): δ = 2.25 (s, 18 H, *p*-Ar–CH_3, *o*-Ar–CH_3), 4.00 (s, 4 H, NCH_2CH_2N), 6.99 (s, 4 H, Ar–H) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 17.5 (*o*-Ar–CH_3), 21.0 (*p*-Ar–CH_3), 47.5 (NCH_2), 129.3, 134.4, 136.3, 138.0 (Ar–C), 180.8 (C=S). MS (EI, 70 eV): *m*/*z* (%) = 338 (48) [M]$^+$.

1,3-Bis(2,6-diisopropylphenyl)imidazolidin-2-thione (8): A mixture of the silver complex **6** (0.534 g, 1 mmol) and sulfur (0.032 g, 1 mmol) was suspended in dichloromethane (50 mL) and stirred for 24 h at room temperature. After removal of silver chloride by filtration, the solvent was evaporated in vacuo. The crude product was purified chromatographically [silica gel, *n*-hexane/diethyl ether (5:1, v:v)] to give a yellow solid (0.262 g, 62%). $C_{27}H_{38}N_2S$ (422.7): calcd. C 76.73, H 9.06, N 6.63; found C 76.99, H 8.68, N 6.65. ^1H NMR (200.1 MHz, $CDCl_3$): δ = 1.33, 1.37 [2×d, $^3J_{H,H}$ = 4.4, 5.2 Hz, 24 H, CH(CH_3)$_2$], 3.10 [sept, 4 H, CH(CH_3)$_2$], 4.05 (s, 4 H, NCH_2CH_2N), 7.24–7.41 (m, 6 H, Ar–H) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 24.3 [CH(CH_3)$_2$], 28.9 [CH(CH_3)$_2$], 50.2 (NCH_2), 124.2, 129.1, 134.7, 147.3 (Ar–C), 184.1 (C=S) ppm. MS (EI, 70 eV): *m*/*z* (%) = 422 (85) [M]$^+$, 407 (6) [M – CH_3]$^+$.

[(cod)Rh(Cl)(10)] (11): A solution of {[(cod)Rh(Cl)]$_2$} (0.098 g, 0.20 mmol) in THF (20 mL) was added to a suspension of the imidazolinium tetrafluoroborate **9** (0.108 g, 0.40 mmol) and potassium *tert*-butoxide (0.045 g, 0.40 mmol) in THF (20 mL). The resulting mixture was heated under reflux for 90 min. After cooling and evaporation of the solvent, the residue was suspended in toluene (10 mL) and filtered. The solvent of the filtrate was removed under vacuum, and the crude product was purified chromatographically [silica gel, hexane/ethyl acetate (5:1, v:v)] to give a yellow solid (0.067 g, 78%). $C_{19}H_{34}N_2RhCl$ (428.9): calcd. C 53.21, H 7.99, N 6.53; found C 53.56, H 7.78, N 6.59. ^1H NMR (200.1 MHz, $CDCl_3$): δ = 1.64–1.93 [m, 8 H, cod(CH_2)], 1.84 (s, 18 H, CH_3), 3.61 (s, 4 H, NCH_2CH_2N), 3.43–3.61 [m, 2 H, cod(CH)], 4.85 [m, 2 H, cod(CH)] ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 28.2 [cod(CH_2)], 30.8 (CH_3), 31.8 [cod(CH_2)], 45.6 (NCH_2CH_2N), 57.4 [C(CH_3)$_3$], 68.7 [d, $^1J_{Rh,C}$ = 15 Hz, cod(CH)], 93.0 [d, $^1J_{Rh,C}$ = 8 Hz, cod(CH)], 212.1 (d, $^1J_{Rh,C}$ = 45 Hz, NCN) ppm.

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[21] X-ray crystal structure analysis for **6**·$4CH_2Cl_2$: formula $C_{27}H_{38}N_2AgCl\cdot4CH_2Cl_2$, $M = 873.62\ \mathrm{g\,mol^{-1}}$, yellow crystal $0.20\times0.10\times0.05$ mm, $a = 9.760(1)$, $b = 16.286(1)$, $c = 10.980(1)$ Å, $\beta = 103.38(1)°$, $V = 1697.9(3)$ Å^3, $\rho_{\mathrm{calcd.}} = 1.709\ \mathrm{g\,cm^{-3}}$, $\mu = 1.329\ \mathrm{mm^{-1}}$, $Z = 2$, monoclinic, space group $P2_1/m$ (no. 11), Mo-K_α radiation, $\lambda = 0.71073$ Å, $T = 198$ K, 7976 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.66$ Å^{-1}, 5162 independent ($R_{\mathrm{int}} = 0.044$) and 3448 observed reflections $[I \geq 2\sigma(I)]$, 204 refined parameters, $R = 0.088$, $wR^2 = 0.287$, max. residual electron density 2.78 (–2.34) e Å^{-3} (near disordered chlorine atoms of solvent molecules). X-ray crystal structure analysis for **7**: formula $C_{21}H_{26}N_2S$, $M = 338.50\ \mathrm{g\,mol^{-1}}$, colorless crystal, $0.40\times0.25\times0.20$ mm, $a = 16.046(1)$, $b = 7.357(1)$, $c = 16.170(1)$ Å, $V = 1908.9(3)$ Å^3, $\rho_{\mathrm{calcd.}} = 1.178\ \mathrm{g\,cm^{-3}}$, $\mu = 1.513\ \mathrm{mm^{-1}}$, $Z = 4$, orthorhombic, space group *Pbcn* (no. 60), Cu-K_α radiation, $\lambda = 1.54178$ Å, $T = 223$ K, 1938 reflections collected ($-h$, $-k$, $+l$), $[(\sin\theta)/\lambda] = 0.62$ Å^{-1}, 1938 independent and 1739 observed reflections $[I \geq 2\sigma(I)]$, 114 refined parameters, $R = 0.043$, $wR^2 = 0.136$, max. residual electron density 0.27 (–0.23) e Å^{-3}. X-ray crystal structure analysis for **8**: formula $C_{27}H_{38}N_2S$, $M = 422.65\ \mathrm{g\,mol^{-1}}$, colorless crystal, $0.50\times0.50\times0.30$ mm, $a = 19.354(1)$, $b = 6.920(1)$, $c = 20.788(1)$ Å, $\beta = 106.98(1)$, $V = 2662.8(4)$ Å^3, $\rho_{\mathrm{calcd.}} = 1.054\ \mathrm{g\,cm^{-3}}$, $\mu = 1.167\ \mathrm{mm^{-1}}$, $Z = 4$, monoclinic, space group $P2_1/n$ (no. 14), Cu-K_α radiation, $\lambda = 1.54178$ Å, $T = 223$ K, 15515 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.59$ Å^{-1}, 4389 independent ($R_{\mathrm{int}} = 0.031$) and 3874 observed reflections $[I \geq 2\sigma(I)]$, 279 refined parameters, $R = 0.048$, $wR^2 = 0.142$, max. residual electron density 0.29 (–0.23) e Å^{-3}. Data sets were collected with Enraf–Nonius CAD4 and Nonius KappaCCD diffractometers, the latter was equipped with a rotating anode generator. Programs used: absorption correction for CCD data, SORTAV[22] and Denzo;[23] structure solution, SHELXS-97;[24] structure refinement, SHELXL-97.[25] CCDC-282505 (**6**·$4CH_2Cl_2$), CCDC-282503 (**7**) and CCDC-282504 (**8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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