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Copper(I) Complexes of Phenanthro-Annulated N-Heterocyclic Carbenes: Synthesis and Transmetalation Reactions

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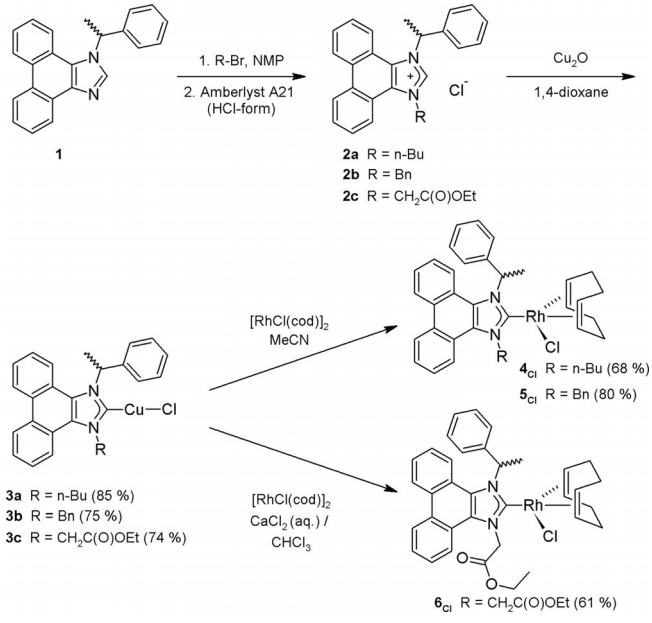
Copper(I) complexes with phenanthro-annulated N-heterocyclic carbene ligands were prepared by reaction of imidazolium salts with copper(I) oxide. Transmetalation of the copper complexes with $[RhCl(cod)]_2$ in usual solvents like CH_2Cl_2 led to an equilibrium between the reactants and the products. For rhodium complexes **4** and **5** this equilibrium could be shifted to the product side by carrying out the reaction in acetonitrile. The ester functionalized rhodium complex **6** was prepared in a two phase mixture of chloroform and aqueous $CaCl_2$ starting from copper complex **3c**. The rhodium complexes were characterized by NMR and X-ray measurements.

Introduction

Since the synthesis of the first stable N-heterocyclic carbene (NHC) in 1991 by Arduengo and co-workers significant progress has been made in this field.[1] In the last 20 years many groups have explored new procedures for the synthesis of NHC metal complexes. Thus, a variety of methods are now established. For instance, the use of free carbenes or reaction of imidazolium salts with basic metal precursors are well known.[2–11] Consequently, NHC complexes of almost every transition metal are known and widely used in homogeneous catalysis.[12–14] A mild and therefore very important route to NHC metal complexes involves the use of silver complexes as transmetalation agents; this approach was developed by Wang and Lin in 1998.[15] The silver complexes are most often obtained by reacting imidazolium salts with silver(I) oxide.[16–22] The first NHC copper complex was prepared by Arduengo et al. in 1993 by reacting a free carbene with copper(I) triflate.[23] In 2001 Danopoulos and co-workers showed that NHC copper complexes can be prepared by reacting an imidazolium salt with copper(I) oxide.[24] The first application of copper complexes as transmetalation agents was published in 2009 by Albrecht and co-workers.[25] Accordingly, there are now several reports about the transmetalation with copper NHC complexes.[26–29] Recently, we reported a simple synthesis of chiral phenanthro-annulated imidazolium salts and their conversion to silver(I) and ruthenium(II) complexes.[30,31] Here we describe the preparation of similar copper(I) complexes and their transmetalation with $[RhCl(cod)]_2$.

Results and Discussion

Imidazolium chlorides **2a** and **2b** were prepared according to our published procedure.[30,31] Imidazolium salt **2c** was analogously obtained by alkylation of imidazole derivative **1** with ethyl 2-bromoacetate (Scheme 1). To avoid problems with different types of anions in transmetalation reactions the anion was exchanged to chloride by the use



Scheme 1. Synthesis of compounds **2a**–**c**, **3a**–**c**, $\mathbf{4}_{Cl}$, $\mathbf{5}_{Cl}$ and $\mathbf{6}_{Cl}$.

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of a commercially available ion exchange resin (Amberlyst A21).[32,33]

Copper complexes **3a**–**c** were prepared in high yield by reaction of the imidazolium salts **2a**–**c** with copper(I) oxide in 1,4-dioxane. As reported for our silver(I) complexes, the NMR spectra of copper(I) complexes **3a**–**c** also showed strongly broadened signals, probably because of hindered rotation of the chiral 1-phenylethyl substituent about the exocyclic C–N bond. The signals for the carbene carbon atoms could be detected by HMBC NMR spectroscopy (**3a**: 182.9 ppm, **3b**: 184.4 ppm, **3c**: 184.8 ppm). Notably, these chemical shifts are higher than those for copper complexes with imidazolin-2-ylidene ligands but lower than those with saturated imidazolidin-2-ylidene ligands.[34]

Initial transmetalation experiments of the copper complexes with $[RhCl(cod)]_2$ in CD_2Cl_2 were characterized by a fast reaction towards the desired rhodium complexes. Unfortunately, the conversion did not proceed to completion. Rather, the transmetalation was found to cease at an equilibrium of about 1:3 (reactants:products). We envisioned that the noted equilibrium might be a result of the better solubility of copper chloride, versus silver chloride, in organic solvents. Consequently, we tried different common solvents for the transmetalation reaction (CH_2Cl_2, THF, 1,4-dioxane, $CHCl_3$). We have yet to find a solvent in which copper(I) chloride is insoluble but the desired rhodium complex is soluble. Fortunately, rhodium NHC complexes $\mathbf{4}_{Cl}$ and $\mathbf{5}_{Cl}$ were found to be poorly soluble in acetonitrile. Hence, these complexes could be prepared in acetonitrile and separated from the soluble copper chloride by simple filtration.

Rhodium complex **4** could be crystallized with bromide or iodide anions ($\mathbf{4}_{Br}$ and $\mathbf{4}_{I}$, Figures 1 and 2) and rhodium complex **5** was crystallized with a chloride/ bromide mixture ($\mathbf{5}_{Cl/Br}$, Figure 3). These crystals were obtained during our first experiments in which we used imidazolium bromides and iodides and did not exchange any anions to chloride.

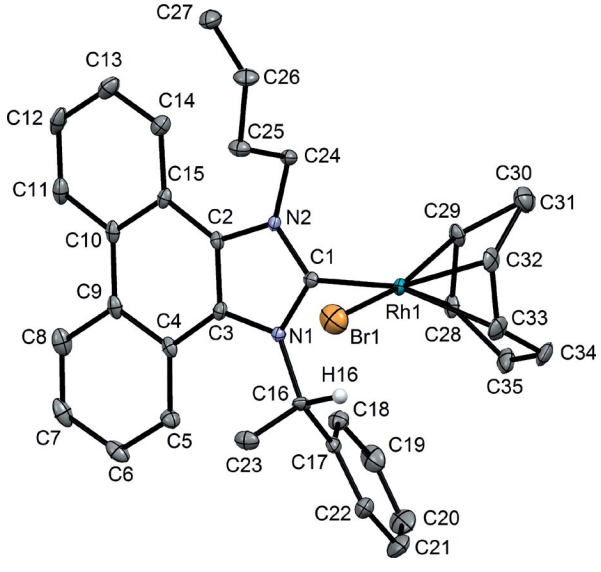

Figure 1. Molecular structure of complex $\mathbf{4}_{Br}$ (*S*-enantiomer) showing 50% probability ellipsoids. Most hydrogen atoms have been omitted for clarity.

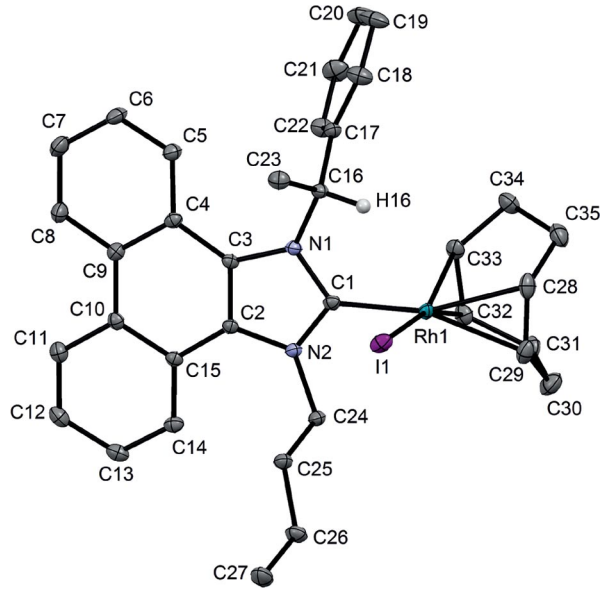

Figure 2. Molecular structure of complex $\mathbf{4}_{I}$ (*R*-enantiomer) showing 50% probability ellipsoids. Most hydrogen atoms have been omitted for clarity.

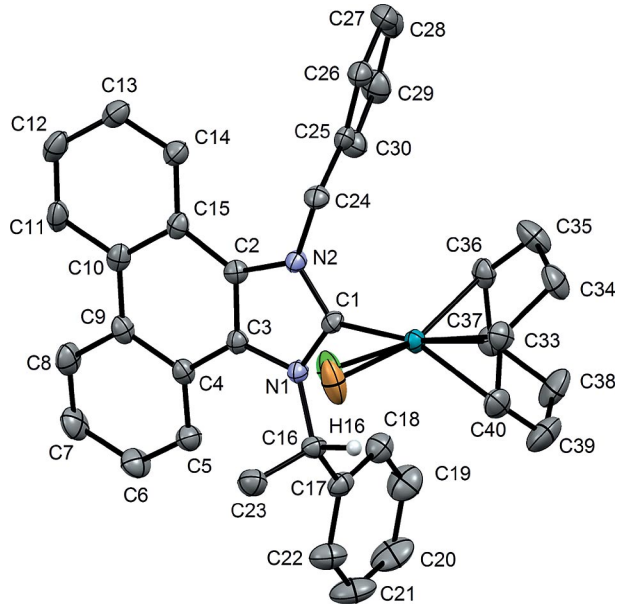

Figure 3. Molecular structure of complex $\mathbf{5}_{Cl/Br}$ (*S*-enantiomer) showing 50% probability ellipsoids. Most hydrogen atoms have been omitted for clarity.

In all structures the coordination sphere around the rhodium atom is square planar. The distances between rhodium and the carbene carbon atom are in the typical range for similar rhodium NHC complexes (see Supporting Information for selected bond lengths and angles).[24,35–42] The proton at the chiral center (H16) always points towards the metal atom leading to short Rh–H16 distances of about 2.5 Å. In the ^{1}H NMR spectra, this proton is shifted down-

field by more than 1.5 ppm compared with the respective copper complexes. This shift probably is the result of an electrostatic ("anagostic")[43] interaction of the proton with the metal center and indicates that the position of the 1-phenylethyl substituent is retained in solution and that no rotation of the chiral substituent about the C–N bond occurs on the NMR timescale.[44] Since we detected four olefinic signals for the cod ligand in the ^{1}H and ^{13}C NMR spectra it appears that rotation about the Rh–C1 bond is also hindered.

The chemical shifts for the carbene carbon atom in the ^{13}C NMR spectra are 193.0 ppm ($\mathbf{4}_{Cl}$) and 194.6 ppm ($\mathbf{5}_{Cl}$) with characteristic coupling constants ($^1J_{RhC}$) of about 52 Hz, and are therefore similar to data from rhodium complexes with benzimidazoline-2-ylidene ligands.[34]

In the developed procedure the equilibrium is shifted by precipitation of the rhodium complex from acetonitrile. Analogue experiments with ester functionalized copper complex **3c** failed because the rhodium complex did not precipitate during the reaction. Thus, a more general route needed to be established. Copper(I) chloride is almost completely insoluble in water but shows good solubility in aqueous alkali and alkaline earth metal salt solutions. Therefore, we carried out the transmetalation reaction in a two-phase mixture of chloroform and aqueous $CaCl_2$ (Scheme 1). Vigorous stirring allowed the copper chloride to be transferred into the aqueous phase, whereas rhodium complex $\mathbf{6}_{Cl}$ remained in the organic phase and could ultimately be obtained in an acceptable yield of about 60%.

Crystallographically suitable single crystals of $\mathbf{6}_{Cl}$ were obtained by slow evaporation of a saturated diethyl ether solution (Figure 4). The bond lengths and angles for complex $\mathbf{6}_{Cl}$ were found to be similar to those of rhodium complexes $\mathbf{4}_{Br}$, $\mathbf{4}_{I}$ and $\mathbf{5}_{Cl/Br}$. Again, the proton at the chiral center (H16) points towards the rhodium atom and again, this proton is shifted downfield by over 1.5 ppm relative to that of copper complex **3c**. The carbene carbon atom resonates as a doublet at δ = 194.8 ppm ($^1J_{RhC}$ = 51.3 Hz).

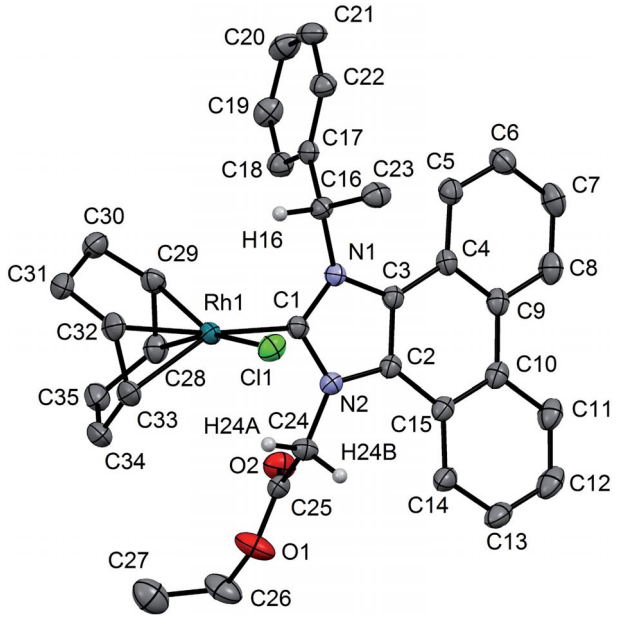

Figure 4. Molecular structure of complex $\mathbf{6}_{Cl}$ (*S*-enantiomer) showing 50% probability ellipsoids. Most hydrogen atoms have been omitted for clarity.

Conclusions

In summary, we have shown the synthesis of three different copper(I) complexes with N-heterocyclic carbene ligands. Initial transmetalation reactions with a rhodium(I) precursor led to an equilibrium between the copper and the rhodium complexes. To avoid this problem we developed two different procedures. First, the equilibrium can be shifted to the product side by precipitation of the desired rhodium complex from acetonitrile, the reaction solvent. When the product does not precipitate from acetonitrile, the rhodium complex can be prepared in a two-phase mixture of chloroform and aqueous $CaCl_2$. Here, the equilibrium is shifted by extraction of copper chloride into the aqueous phase. To the best of our knowledge, these are the first examples of rhodium(I) NHC complexes prepared by transmetalation from copper(I) NHC complexes.

Experimental Section

General Comments: Reactions involving metal complexes were carried out under an argon atmosphere in dried solvents using Schlenk techniques. All products could be handled in air as solids. Solvents were dried using standard procedures. All other reagents were used as received from commercial sources. Most compounds were prepared in both enantiomeric forms.

1-Ethoxycarbonylmethyl-3-(1-phenylethyl)phenanthro[9,10-*d*]imidazolium Chloride (2c): 1-(1-Phenylethyl)-phenanthro[9,10-*d*]imidazole (1.92 g, 5.96 mmol) was mixed with ethyl 2-bromoacetate (10 mL, 90 mmol) and *N*-methyl-2-pyrrolidone (5 mL) and stirred for 3 d at 70 °C. After cooling, diethyl ether (20 mL) was added to the suspension, the white precipitate was filtered off and washed with another aliquot diethyl ether (5 mL). The raw product was dissolved in dichloromethane (10 mL) and precipitated with diethyl ether (10 mL). For further purification, this procedure was repeated twice. After filtration and drying under reduced pressure 2.4 g (82%) of imidazolium bromide were obtained as a hygroscopic white powder. 500 mg of the imidazolium bromide were dissolved in methanol and passed through a column charged with the anion exchange resin (Amberlyst A21 charged with HCl). The solvent was removed under reduced pressure to give 450 mg of **2c** as a hygroscopic white powder. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 10.25 (s, 1 H, NC*H*N), 9.02–9.07 (m, 1 H, Ar*H*), 9.01 (d, ^3J = 8.0 Hz, 1 H, Ar*H*), 8.49 (d, ^3J = 8.3 Hz, 1 H, Ar*H*), 8.29–8.34 (m, 1 H, Ar*H*), 7.85–7.90 (m, 2 H, Ar*H*), 7.78 (t, ^3J = 7.2 Hz, 1 H, Ar*H*), 7.69 (t, ^3J = 8.1 Hz, 1 H, Ar*H*), 7.27–7.40 (m, 5 H, Ar*H*), 6.94 (q, ^3J = 6.6 Hz, 1 H, NC*H*), 6.22 (d, ^2J = 18.5 Hz, 1 H, NCH_2), 6.17 (d, ^2J = 18.5 Hz, 1 H, NCH_2), 4.23–4.35 (m, 2 H, OCH_2), 2.14 (d, ^3J = 6.6 Hz, 3 H, NCCH_3), 1.23 (t, ^3J = 7.1 Hz, 3 H, OCH$_2$CH_3) ppm. ^{13}C{^{1}H} NMR (101 MHz, [D$_6$]DMSO): δ = 166.5 [*C*(O)O], 141.8 (N*C*HN), 139.5, 129.4, 129.3, 129.2, 128.5, 128.5, 128.4, 128.2, 128.1, 126.8, 125.8, 125.7, 124.7, 124.6, 123.1, 121.9, 120.2, 119.9 (Ar*C*), 62.3 (O*C*H$_2$), 60.0 (N*C*H), 51.5 (N*C*H$_2$), 23.8 (NC*C*H$_3$), 14.0 (OCH$_2$*C*H$_3$) ppm. HRMS (ESI$^+$ in MeCN) of $C_{27}H_{25}N_2O_2Cl$: calcd. for cation ($C_{27}H_{25}N_2O_2^+$) 409.191054, found 409.190734.

Chloro-[1-butyl-3-(1-phenylethyl)phenanthro[9,10-*d*]imidazolin-2-ylidene]copper(I) (3a): 1-Butyl-3-(1-phenylethyl)phenanthro[9,10-*d*]imidazolium chloride (**2a**) (920 mg, 2.22 mmol) were mixed with Cu_2O (320 mg, 2.24 mmol), suspended in dry 1,4-dioxane (20 mL) and stirred for 16 h at reflux. After cooling, the solvent was evaporated, the residue suspended in dichloromethane (20 mL) and filtered via cannula. The solution was concentrated to a quarter of its volume by evaporation and the product precipitated as a white powder by addition of diethyl ether (10 mL). After filtration the product was dried under reduced pressure to obtain a white powder, yield 900 mg (85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.77–8.86 (m, 2 H, Ar*H*), 8.38 (d, ^3J = 7.8 Hz, 1 H, Ar*H*), 8.20 (br. s, 1 H, Ar*H*), 7.71–7.81 (m, 2 H, Ar*H*), 7.65 (br. t, 1 H, Ar*H*), 7.55 (br. s, 1 H, Ar*H*), 7.30–7.44 (m, 5 H, Ar*H*), 6.71 (br. s, 1 H, NC*H*), 5.07 (t, ^3J = 7.4 Hz, 2 H, NCH_2), 2.35 (br. s, 3 H, $NCHCH_3$), 2.01–2.11 (m, 2 H, NCH_2CH_2), 1.52–1.64 (m, 2 H, CH_2CH_3), 1.02 (t, ^3J = 7.3 Hz, 3 H, CH_2CH_3) ppm. ^{13}C NMR spectra showed only a few broadened signals. Some could be assigned with HSQC and HMBC spectroscopy. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 182.9 (N*C*N), 139.7, 129.3, 127.9, 126.8, 124.3, 121.6 (Ar*C*), 53.2 (NCH_2), 32.7 (NCH_2CH_2), 19.8 (CH_2CH_3), 13.6 (CH_2CH_3) ppm. $C_{27}H_{26}ClCuN_2$ (477.51): calcd. C 67.91, H 5.49, N 5.87; found C 67.72, H 5.28, N 5.82.

Chloro[1-benzyl-3-(1-phenylethyl)phenanthro[9,10-*d*]imidazolin-2-ylidene]copper(I) (3b): 1-Benzyl-3-(1-phenylethyl)phenanthro[9,10-*d*]imidazolium chloride (**2b**) (740 mg, 1.65 mmol) was mixed with Cu_2O (236 mg, 1.65 mmol), suspended in dry 1,4-dioxane (20 mL) and stirred for 16 h at reflux. After cooling, the solvent was evaporated, the residue suspended in dichloromethane (20 mL) and filtered via cannula. The solution was concentrated to a quarter of its volume by evaporation and the product precipitated as a white powder by addition of diethyl ether (10 mL). After filtration the product was dried under reduced pressure to obtain **3b** with 0.4 equiv. CH_2Cl_2, yield 670 mg (75%). The product was used without further purification and a small amount was washed with dichloromethane for elemental analysis and NMR measurements. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.78 (d, ^3J = 8.3 Hz, 1 H, Ar*H*), 8.75 (d, ^3J = 8.3 Hz, 1 H, Ar*H*), 8.24 (br. s, 1 H, Ar*H*), 7.47–7.70 (m, 4 H, Ar*H*), 7.23–7.46 (m, 8 H, Ar*H*), 7.13 (d, ^3J = 7.1 Hz, 2 H, Ar*H*), 6.81 (br. s, 1 H, NC*H*), 6.32 (s, 2 H, NCH_2), 2.42 (br. s, 3 H, $NCHCH_3$) ppm. ^{13}C NMR spectra showed only a few broadened signals. Some could be assigned with HSQC and HMBC spectroscopy at 50 °C. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 184.4 (N*C*N), 139.8, 135.3, 129.5, 128.4, 127.8, 126.8, 125.8, 123.7, 122.1, 121.3 (Ar*C*), 59.7 (N*C*H), 56.8 (NCH_2) ppm. $C_{30}H_{24}ClCuN_2{\cdot}0.4CH_2Cl_2$ (545.50): calcd. C 66.93, H 4.58, N 5.14; found C 66.73, H 4.31, N 5.18.

Chloro[1-ethoxycarbonylmethyl-3-(1-phenylethyl)phenanthro[9,10-*d*]imidazolin-2-ylidene]copper(I) (3c): Compound **2c** (450 mg, 1.01 mmol) was mixed with Cu_2O (145 mg, 1.01 mmol), suspended in dry 1,4-dioxane (15 mL) and stirred for 18 h at reflux. After cooling, the solvent was evaporated, the residue suspended in dichloromethane (20 mL) and filtered via cannula. The solvent was evaporated and the residue washed with petroleum ether (10 mL). After filtration the product was dried under reduced pressure to obtain **3c** as an off-white powder, yield 380 mg (74%). The product was used without further purification. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.78–8.85 (m, 2 H, Ar*H*), 8.27 (br. s, 1 H, Ar*H*), 8.08–8.14 (m, 1 H, Ar*H*), 7.52–7.76 (m, 4 H, Ar*H*), 7.32–7.46 (m, 5 H, Ar*H*), 6.72 (br. s, 1 H, NC*H*), 5.84 (s, 2 H, NCH_2), 4.29 (q, ^3J = 7.1 Hz, 2 H, OCH_2), 2.38 (br., 3 H, $NCHCH_3$), 1.28 (t, ^3J = 7.1 Hz, 3 H, OCH_2CH_3) ppm. ^{13}C NMR spectra showed only a few broadened signals. Some could be assigned with HSQC and HMBC spectroscopy. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 184.8 (N*C*N), 167.1 (C=O), 129.6, 127.9, 126.8, 126.6, 124.4, 120.7 (Ar*C*), 62.5 (OCH_2), 14.0 (CH_2CH_3) ppm. $C_{27}H_{24}ClCuN_2O_2$ (507.49): calcd. C 63.90, H 4.77, N 5.52; found C 64.34, H 5.01, N 5.36.

Chloro(η^4-1,5-cod)[1-butyl-3-(1-phenylethyl)phenanthro[9,10-*d*]-imidazolin-2-ylidene]rhodium(I) ($\mathbf{4_{Cl}}$): $[RhCl(cod)]_2$ (43 mg, 87 µmol) and copper complex **3a** (83 mg, 174 µmol) were dissolved in acetonitrile (2 mL) and stirred for approximately 1 h till the product precipitated as a yellow solid. The mixture was filtered via cannula and the product washed twice with 1 mL of acetonitrile each. After drying under reduced pressure 74 mg (68%) of $\mathbf{4_{Cl}}$ were obtained. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.78 (d, ^3J = 8.0 Hz, 1 H, Ar*H*), 8.70 (d, ^3J = 8.4 Hz, 1 H, Ar*H*), 8.51 (q, ^3J = 7.1 Hz, 1 H, NC*H*), 8.42 (d, ^3J = 7.8 Hz, 1 H, Ar*H*), 7.72–7.77 (m, 1 H, Ar*H*), 7.64–7.70 (m, 2 H, Ar*H*), 7.44–7.49 (m, 1 H, Ar*H*), 7.26–7.36 (m, 5 H, Ar*H*), 7.19–7.25 (m, 1 H, Ar*H*), 5.91 (ddd, ^2J = 13.8, ^3J = 12.6, 5.1 Hz, 1 H, NCH_2CH_2), 5.38 (ddd, ^2J = 13.9, ^3J = 12.4, 4.3 Hz, 1 H, NCH_2CH_2), 5.17–5.25 (m, 1 H, CH_{cod}), 5.03–5.10 (m, 1 H, CH_{cod}), 3.47–3.56 (m, 2 H, CH_{cod}), 2.35–2.59 (m, 3 H), 2.25 (d, ^3J = 7.2 Hz, 3 H, $NCHCH_3$), 2.15–2.26 (m, 1 H), 1.69–2.12 (m, 8 H), 1.21 (t, ^3J = 7.4 Hz, 3 H, CH_2CH_3) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 193.0 (d, $^1J_{RhC}$ = 51.6 Hz, N*C*N), 141.7, 129.0, 128.7, 128.7, 128.4, 128.2, 127.3, 127.0, 126.2, 125.8, 125.5, 125.3, 125.2, 124.0, 123.4, 121.7, 121.5, 120.7 (Ar*C*), 99.1 (d, ^1J = 6.8 Hz, CH_{cod}), 98.5 (d, ^1J = 6.9 Hz, CH_{cod}), 69.5 (d, ^1J = 14.2 Hz, CH_{cod}), 68.5 (d, J = 14.5 Hz, CH_{cod}), 62.3 (N*C*H), 52.0 (NCH_2), 33.2, 32.3, 31.6, 29.6, 28.1, 20.4, 18.9 ($CHCH_3$), 13.8 (CH_2CH_3) ppm. $C_{35}H_{38}ClN_2Rh$ (625.05): calcd. C 67.25, H 6.13, N 4.48; found C 67.25, H 6.00, N 4.66.

Chloro(η^4-1,5-cod)[1-benzyl-3-(1-phenylethyl)phenanthro[9,10-*d*]-imidazolin-2-ylidene]rhodium(I) ($\mathbf{5_{Cl}}$): $[RhCl(cod)]_2$ (23 mg, 47 µmol) and copper complex **3b** (52 mg, 95 µmol) were dissolved in acetonitrile (1 mL) and stirred until the product precipitated as a yellow solid. The mixture was filtered via cannula and the product washed with acetonitrile (0.5 mL). After drying under reduced pressure 51 mg (80%) of $\mathbf{5_{Cl}}$ were obtained. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.67–8.75 (m, 2 H, Ar*H*), 8.61 (q, ^3J = 7.2 Hz, 1 H, NC*H*), 8.13 (d, ^3J = 8.4 Hz, 1 H, Ar*H*), 7.74 (d, ^3J = 8.2 Hz, 1 H, Ar*H*), 7.70 (d, ^2J = 17.1 Hz, 1 H, NCH_2), 7.22–7.59 (m, 14 H, Ar*H*), 6.40 (d, ^2J = 17.7 Hz, 1 H, NCH_2), 5.11–5.21 (m, 1 H, CH_{cod}), 5.00–5.08 (m, 1 H, CH_{cod}), 3.47–3.55 (m, 1 H, CH_{cod}), 3.24–3.33 (m, 1 H, CH_{cod}), 2.27–2.40 [m, 1 H, $(CH_2)_{cod}$], 2.30 (d, ^3J = 7.2 Hz, 3 H, CH_3), 2.12–2.24 [m, 1 H, $(CH_2)_{cod}$], 1.52–1.95 [m, 6 H, $(CH_2)_{cod}$] ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 194.6 (d, $^1J_{RhC}$ = 51.9 Hz, N*C*N), 141.6, 137.4, 129.9, 129.1, 129.1, 128.7, 128.6, 128.1, 127.5, 127.2, 127.1, 126.3, 125.9, 125.7, 125.4, 125.1, 123.6, 123.4, 122.1, 121.2, 120.7 (Ar*C*), 99.4 (d, ^3J = 6.8 Hz, CH_{cod}), 98.5 (d, ^3J = 6.9 Hz, CH_{cod}), 69.5 (d, ^3J = 14.1 Hz, CH_{cod}), 69.4 (d, ^3J = 14.3 Hz, CH_{cod}), 62.4 (N*C*H), 55.5 (NCH_2), 32.9 [$(CH_2)_{cod}$], 32.0 [$(CH_2)_{cod}$], 29.1 [$(CH_2)_{cod}$], 28.2 [$(CH_2)_{cod}$], 18.7 (CH_3) ppm. $C_{38}H_{36}ClN_2Rh{\cdot}0.33MeCN$ (672.61): calcd. C 69.03, H 5.54, N 4.85; found C 69.01, H 5.81, N 4.79.

Chloro(η^4-1,5-cod)[1-ethoxycarbonylmethyl-3-(1-phenylethyl)-phenanthro[9,10-*d*]imidazolin-2-ylidene]rhodium(I) ($\mathbf{6_{Cl}}$): $[RhCl(cod)]_2$ (23 mg, 47 µmol) and copper complex **3c** (50 mg, 99 µmol) were dissolved in chloroform (2 mL), whereby a precipitation of copper(I)chloride occurred. A saturated aqueous $CaCl_2$ solution (2 mL) were added and the mixture stirred vigorously for a few minutes. The organic layer was separated and the aqueous phase extracted with $CHCl_3$ (1 mL). The organic phases were combined and again washed with the saturated $CaCl_2$ solution (2 mL). The organic phase was dried with $MgSO_4$ and passed through a

small column containing silica gel and kieselguhr. The column was washed with approximately chloroform (3 mL). The solvent was evaporated and the residue washed with acetonitrile (1 mL). After filtration the product was dried under reduced pressure to give 37 mg (61%) of $\mathbf{6}_{Cl}$ as a yellow powder. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.75–8.80 (m, 1 H, Ar*H*), 8.70 (d, ^3J = 8.4 Hz, 1 H, Ar*H*), 8.45 (q, ^3J = 7.2 Hz, 1 H, NC*H*), 8.06–8.11 (m, 1 H, Ar*H*), 7.63–7.70 (m, 3 H, ArH), 7.50–7.70 (br. m, 1 H, NCH_2), 7.45–7.51 (m, 1 H, Ar*H*), 7.28–7.41 (m, 5 H, Ar*H*), 7.20–7.26 (m, 1 H, Ar*H*), 5.48–5.96 (br. m, 1 H, NCH_2), 5.17–5.26 (m, 1 H, CH_{cod}), 5.03–5.12 (m, 1 H, CH_{cod}), 4.42 (q, ^3J = 7.0 Hz, 2 H, OCH_2), 3.63–3.72 (m, 1 H, CH_{cod}), 3.48–3.56 (m, 1 H, CH_{cod}), 2.21–2.50 [m, 3 H, (CH_2)$_{cod}$], 2.24 (d, ^3J = 7.2 Hz, 3 H, NCHCH_3), 1.83–2.04 [m, 4 H, (CH_2)$_{cod}$], 1.65–1.77 [m, 1 H, (CH_2)$_{cod}$], 1.38 (t, ^3J = 7.0 Hz, 3 H, CH_2CH_3) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 194.8 (d, $^1J_{RhC}$ = 51.3 Hz, N*C*N), 169.3 (*C*=O), 141.3, 129.7, 129.1, 128.9, 128.6, 128.0, 127.4, 127.2, 126.3, 126.0, 125.5, 125.4, 125.3, 124.1, 123.5, 121.5, 120.7, 120.6 (Ar*C*), 100.1 (d, ^1J = 6.2 Hz, *C*H$_{cod}$), 99.4 (d, ^1J = 6.2 Hz, *C*H$_{cod}$), 69.9 (d, ^1J = 14.0 Hz, *C*H$_{cod}$), 69.0 (d, ^1J = 14.0 Hz, *C*H$_{cod}$), 62.4 (N*C*H), 62.2 (O*C*H$_2$), 54.2 (N*C*H$_2$), 32.9, 32.5, 28.9, 28.6 [(*C*H$_2$)$_{cod}$], 18.8 (NCH*C*H$_3$), 14.3 (CH_2*C*H$_3$) ppm. $C_{35}H_{36}ClN_2O_2Rh$ (655.03): calcd. C 64.18, H 5.54, N 4.28; found C 64.06, H 5.33, N 4.46.

CCDC-974757 (for $\mathbf{5}_{Cl/Br}$), CCDC-974758 (for $\mathbf{4}_{Br}$), CCDC-974759 (for $\mathbf{4}_{I}$) and CCDC-974760 (for $\mathbf{6}_{Cl}$) 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.

Supporting Information (see footnote on the first page of this article): A complete description of the X-ray crystallographic determinations on $\mathbf{4}_{Br}$, $\mathbf{4}_{I}$, $\mathbf{5}_{Cl/Br}$ and $\mathbf{6}_{Cl}$. ^{1}H NMR spectra of all compounds, ^{13}C NMR spectra of the rhodium complexes.

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