

Bimacrocylic NHC transition metal complexes [☆]

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Abstract

The preparation of seven concave NHC metal complexes derived from bimacrocylic imidazolium salt **1** is reported. The silver complex **2**, obtained in 86% yield by reacting **1** with silver(I) oxide, was used to give copper complex **3**, rhodium complex **5** and iridium complex **6** by transmetalation in good yields. Palladium complex **4** was obtained by reaction of the azolium salt **1** with palladium dichloride in 3-chloropyridine. The rhodium and iridium dicarbonyl complexes **7** and **8** were prepared via ligand exchange from the COD complexes **5** and **6**. Silver complex **2**, copper complex **3** and palladium complex **4** were characterized by single-crystal X-ray analysis. Silver complex **2** and copper complex **3** were tested in the cyclopropanation of styrene and indene with EDA (ethyl diazoacetate), where good results were obtained with **3**, while low conversion and catalyst decomposition was observed with **2**.

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Keywords: Carbenes; Bimacrocylics; Transmetalation; *N*-heterocyclic carbenes; Homogeneous catalysis; Cyclopropanation

1. Introduction

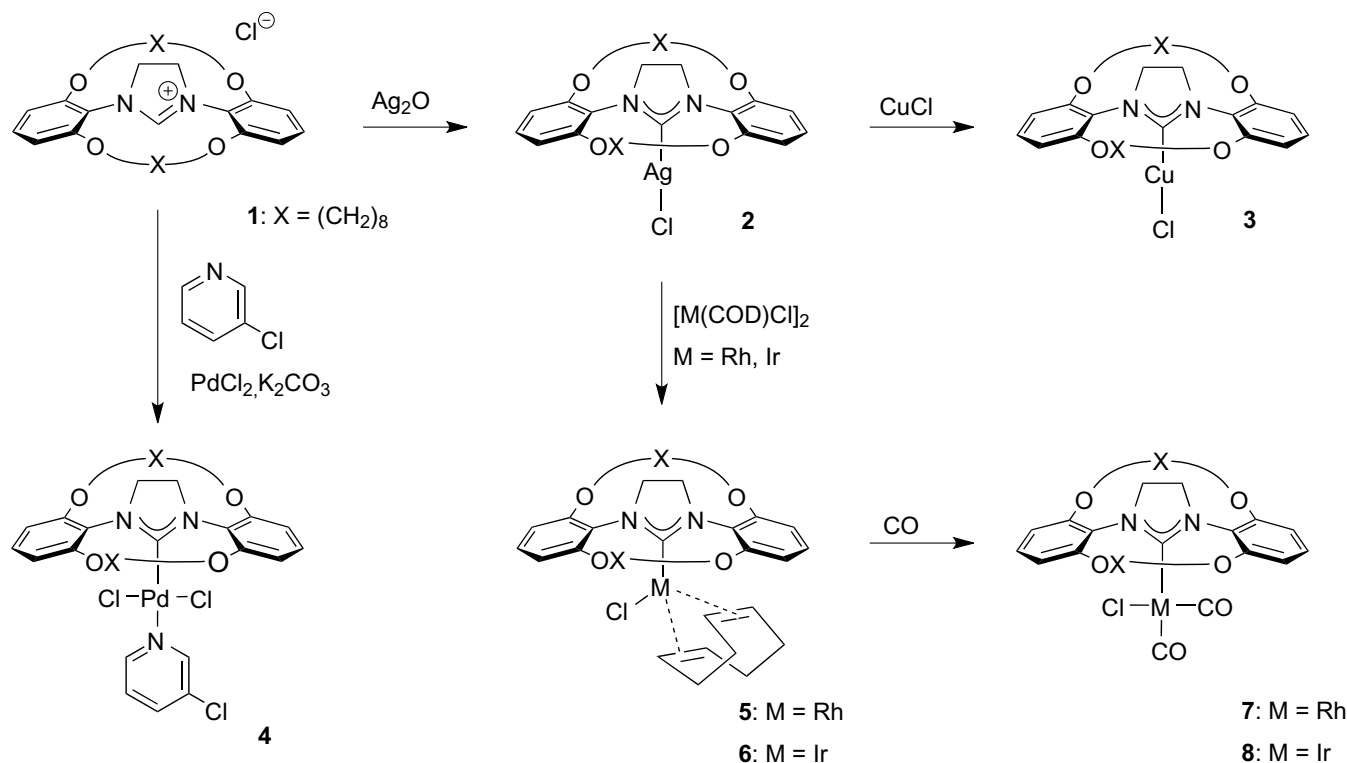
Since the first reports of *N*-heterocyclic carbene (NHC) metal complexes by Wanzlick and Schönherr [1] and Öfele [2] in 1968 and the isolation of a stable crystalline carbene by Arduengo et al. [3] in 1991, NHC and their coordination chemistry are an emerging field of research [4]. Notably, NHC also exhibit excellent catalytic activity in metal-free organocatalysis [5], including umpolung and condensation of carbonyl compounds [6] and transesterification reactions [7]. As ligands, the nucleophilic NHC are strong two-electron σ -donors, displaying similar ligand properties as trialkylphosphines [8]. The extent of their π -accepting ability is under investigation [9]. In comparison to related phosphine complexes, NHC metal complexes have

been shown to possess increased stability and catalytic activity in numerous reactions, the second generation of Grubbs' catalyst for olefin metathesis being a prominent example [10]. Besides their unique electronic properties, the steric demand of the NHC ligands is an important factor in cross-coupling reactions, and bulky NHC have been synthesized for challenging Suzuki-Miyaura [11] or Sonogashira [12] couplings. We have recently reported the synthesis of bimacrocylic imidazolium ions as precursors to respective NHC [13], expecting to effect reactivity and selectivity due to the tailored concave structure of the ligands. In this contribution, we report the synthesis of seven NHC metal complexes derived from the imidazolium salt **1** [13a] and preliminary results on their catalytic activity.

[☆] Concave reagents, Part ##. For part ###, see (current numbers will be inserted in the proofs).

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2. Results and discussion

2.1. Synthesis and reactivity of silver complex 2 and copper complex 3

The reaction of azolium salt **1** with silver(I) oxide in dichloromethane resulted in the formation of complex **2** in 86% yield, with no requirement to exclude oxygen or moisture from the reaction mixture. Ag(I)–NHC complexes are frequently used as carbene transfer reagents to produce NHC metal complexes by transmetalation, avoiding the handling of the sensitive free carbenes [14]. Besides this important application, Ag(I)–NHC have been reported to catalyze the diboration of alkenes [15], carbene transfer from EDA (ethyl diazoacetate) [16] and the hydrosilylation of aldehydes [17]. The thermal decomposition of Ag(I)–NHC was used to generate free carbenes as catalysts for the ring-opening polymerization of lactide and transesterification reactions [18]. The NHC migration in transmetalation reactions is explained by the lability of the Ag–C bond, with the lack of ^{107,109}Ag–¹³C coupling in the ¹³C NMR being a proof of this fluxionality (on the NMR timescale) in solution [19]. The ¹³C resonance for the carbene carbon atom C-2 in **2**, however, was observed with low intensity as a pair of well resolved doublets at 209.7 ppm (¹J_{107AgC} = 234 Hz, ¹J_{109AgC} = 270 Hz), and also the resonance for C-4,5 of the NHC at 50.6 ppm was split into a doublet (³J_{AgC} = 8.6 Hz). To the best of our knowledge, there are eight examples of Ag(I)–NHC with resolved Ag–¹³C couplings reported in the literature [19a,20], and some of these complexes were used in transmetalations. For IMesAgCl (IMes = 1,3-

bis(2,4,6-trimethylphenyl)imidazol-2-ylidene), the ¹³C resonance for C-2 could not be observed at natural abundance of the ¹³C isotope, but for the ¹³C labeled complex it was observed with resolved Ag–¹³C coupling (185 ppm, ¹J_{107AgC} = 234 Hz, ¹J_{109AgC} = 270 Hz) [20d]. In all cases, the ratio of the magnetogyric constants of the silver nuclei is reflected by the observed coupling constants.

Ag(I)–NHC complexes possess a great structural diversity with various ionic and neutral structures in the solid state [14,20e]. The crystal structure analysis of **2** revealed a monomeric structure with an almost linear coordinated silver atom, the angle C1–Ag1–Cl1 being 178.24(7)° (see Figs. 1 and 2). In both ESI and LD-ToF mass spectra, however, a dimeric (NHC)₂Ag⁺ cation was observed with high intensity, while (NHC)Ag⁺ was not observed. The bond lengths C1–Ag1 and Cl1–Ag1 are 2.084(3) Å and 2.3282(7) Å, respectively, the internal ring angle N1–C1–N2 is 108.3(2)°, and these data are comparable to those reported for other Ag(I)–NHC [20a,20d,20e]. In contrast to IMesAgCl and azolium salt **1**, the complex **2** does not possess a crystallographic twofold axis bisecting the heterocycle, with the torsion angles C1–N1–C4–C9 and C1–N2–C23–C18 being 78.66(1)° and 63.16(1)°, respectively, and four different Ag–O distances, which are 3.606(5) Å for Ag1–O1, 3.174(4) Å for Ag1–O2, 4.937(4) Å for Ag1–O3 and 4.621(12) Å for Ag1–O4. This desymmetrization is probably due to packing effects, and the structure is flexible in solution as indicated by both ¹H and ¹³C NMR spectra. The chlorine atom is in vague contact with two of the protons in 4,5-position of the neighbouring heterocycle, with distances of 2.971(7) Å and 2.978(5) Å, respectively.

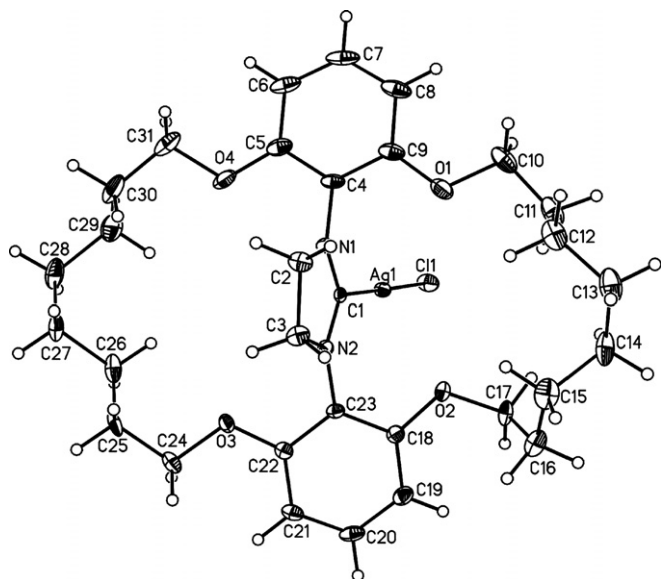


Fig. 1. Crystal structure of silver complex **2** with displacement ellipsoids drawn at the 30% probability level. Five carbon atoms in one octylene chain are disordered in two positions, and only the atoms of higher occupancy are shown for clarity.

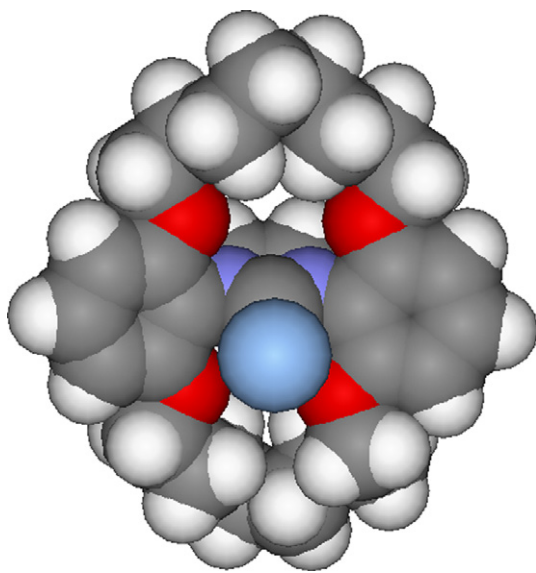


Fig. 2. Space filling representation of the X-ray structure of silver complex **2**, highlighting the concave structure. The chlorine atom is omitted for clarity.

Silver complex **2** was used for transmetalation, and copper complex **3** was obtained in 67% yield by stirring a solution of **2** in dichloromethane with copper(I) chloride. The NMR spectra of the complexes **2** and **3** are very similar (the average $\Delta\delta$ is 0.1 ppm for ^{13}C and 0.01 ppm for ^1H), but the resonance for C-2 was observed as a singlet at 205.3 ppm for **3**. Notably, the reaction of azolium salt **1** with sodium *tert*-butoxide and copper(I) chloride in THF led to a complex mixture of unidentified products, and complex **3** could not be obtained by this general method [21]. In the crystal structure of copper complex **3** (see

Fig. 3), the bond distances Cu1–C1, Cu1–Cl1 are 1.8852(19) Å and 2.1172(6) Å, respectively, in good agreement with the data reported for IPrCuCl [21b] (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) and SIMesCuCl [21c] (SIMes = 1,3-bis(2,4,6-trimethylphenyl)imidazolidin-2-ylidene).

The bond angles C–Cu–Cl reported for these are 178.48(13)° (SIMesCuCl) and 180.00° (IPrCuCl), while C1–Cu1–Cl1 is 173.44(6)° in **3**, respectively. As for **2**, the NHC ligand is not C_2 -symmetric in the solid state, and the heterocycle is twisted out of an idealized geometry inside the bicyclic system, even more expressed in **3** with torsion angles of 60.51(1)° and 61.30(1)° for C1–N1–C4–C9 and C1–N2–C23–C18, respectively. The copper atom is bent out of the plane of the NHC, and the torsion angles C2–N1–C1–Cu1, C3–N2–C1–Cu1 are 169.06(0)° and 164.72(0)°, respectively. This is possibly due to a weak attraction of the copper atom to two of the neighbouring oxygen atoms (bond lengths Cu1–O1, Cu1–O2, Cu1–O3, Cu1–O4 are 2.925(4) Å, 2.868(4) Å, 4.864(10) Å, 4.929(14) Å, respectively). The internal ring angle N1–C1–N2 is 107.09(0)°.

Cu(I)–NHC have been reported to be beneficial catalysts in numerous reactions, including the reduction of α,β -unsaturated carbonyl compounds [21a], hydrosilylation of ketones [21b,21c], [3 + 2] cycloadditions (“click chemistry”) [22] and the methylenation of aldehydes and ketones [23]. As IPrCuCl is known to catalyze the cyclopropanation of styrene [24] and both IPrCuCl and IPrAgCl were reported as catalysts for carbene transfer from EDA into unactivated C–H bonds [16], we investigated the reactivity of the complexes **2** and **3** in the cyclopropanation of styrene and indene with EDA (see Scheme 1 and Table 1).

Very low EDA consumption, along with the formation of unidentified by-products, was observed with silver com-

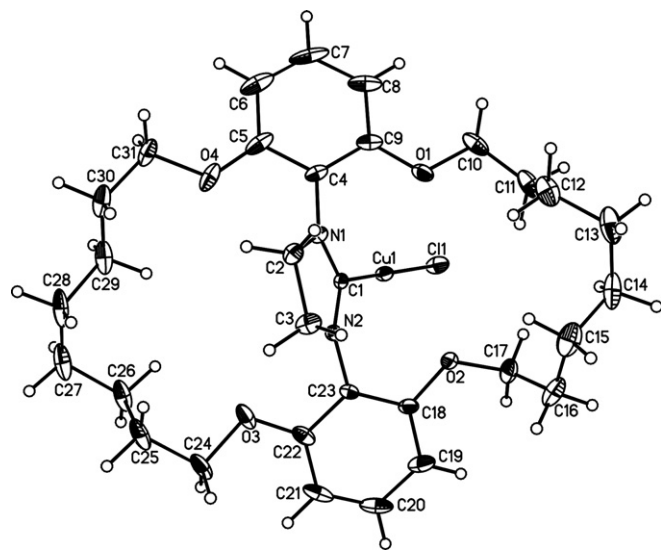
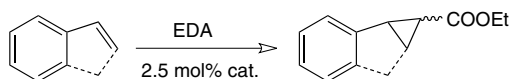


Fig. 3. Crystal structure of copper complex **3** with displacement ellipsoids drawn at the 30% probability level. The chlorine atom and all eight carbon atoms in one octylene chain are disordered in two positions, and only the atoms of higher occupancy are shown for clarity.



Scheme 1. Cyclopropanation of styrene and indene with EDA. The extra methylene group in indene is indicated by the dashed line.

Table 1
Catalytic activity of complexes **2** and **3** in the cyclopropanation^a of styrene and indene

Olefine	Catalyst	Conversion (%) ^{b,c}	d.r. ^c
Styrene	2	<5	42:58 ^d
Indene	2	<5	1:99 ^e
Styrene	3	63 (100) ^f	29:71 ^d (30:70) ^{d,f}
Indene	3	100	22:78 ^e

^a Conditions: 25 μ mol catalyst, 1 mmol EDA, 10 mmol olefine, 16 h at room temperature.

^b Based on EDA.

^c Determined by GC, average of two experiments.

^d Diastereomeric ratio *cis:trans*.

^e Diastereomeric ratio *endo:exo*.

^f 48 hours reaction time.

plex **2**. Product formation could not be raised with higher catalyst loadings or longer reaction time, and a precipitate of silver chloride was observed in the reaction mixtures, indicating catalyst decomposition. In contrast to these unpleasant results, copper complex **3** afforded clean conversion to cyclopropanation products, along with the formation of maleate and fumarate (approx. 20%), known by-products of the reaction. The *cis:trans* ratio (30:70) observed in the cyclopropanation of styrene is comparable to that reported for IPrCuCl (32:68). A higher reactivity and selectivity compared to styrene was observed with indene, due to the more electron-rich double bond and a greater steric hindrance of the substrate.

2.2. Synthesis of palladium complex **4**

In palladium catalyzed C–C and C–N cross coupling reactions, NHC have shown to be valuable ligands, allowing for the oxidative addition of challenging substrates (e.g. hindered aryl-chlorides) due to their electronic properties, while their bulkyness facilitates reductive elimination [4f]. Besides formation of the active catalyst from a palladium source and the azolium precursor in situ, stable Pd–NHC precatalysts are used, which allow to control for the optimum Pd:NHC ratio of 1:1 [25] and are activated upon dissociation of a second, labile ligand. NHC-substituted phosphapalladacycles [26], *N*-palladacycles [27] and palladium-allyl complexes [28] were found to be beneficial in this respect. The heating of azolium salts with palladium dichloride and potassium carbonate in 3-chloropyridine has recently been reported to produce Pd(II)–NHC that were found to be highly active in Suzuki–Miyaura [29], Negishi [30] and Kumada–Tamao–Corriu [31] cross coupling reactions.

Subjecting azolium salt **1** to these reaction conditions gave palladium complex **4** in very poor yield (5%), while

the reaction of silver complex **2** with palladium dichloride in 3-chloropyridine at room temperature afforded none of the desired product. The ¹³C resonance for C-2 was observed at 183.5 ppm for **4**. In the crystal structure of **4** (see Fig. 4), the asymmetric unit contains three crystallographically independent molecules. Selected bond distances and angles are given in Table 2.

Each of the three palladium atoms adopts a slightly distorted square-planar coordination, and these data are comparable to those reported for the respective complex using the IPr NHC ligand [29]. In contrast to the crystal structures of azolium salt **1** and complexes **2** and **3**, the two phenyl substituents of the NHC are oriented almost perpendicular to the heterocycle in **4**, and the torsion angles C1–N1–C4–C5 and C1–N2–C23–C18 are 86.06(2)° and 87.81(2)°, which seems to be due to sterical interactions of the ligands alkyl chains with the two chloride anions. The internal ring angle N1–C1–N2 is 109.39(2)°. Palladium complex **4** has not yet been tested for its catalytic properties in cross coupling reactions because of the insufficient yield.

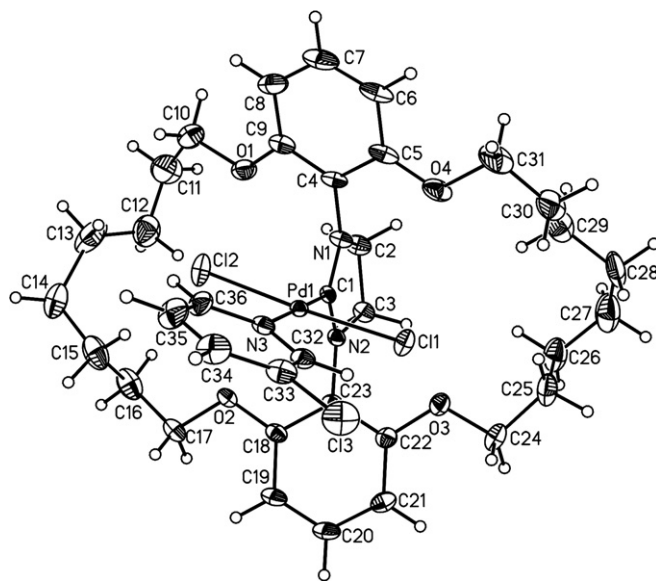


Fig. 4. Crystal structure of palladium complex **4** with displacement ellipsoids drawn at the 30% probability level. Only one of the three crystallographically independent molecules is represented.

Table 2
Selected bond lengths (Å) and bond angles (°) for palladium complex **4**

	Pd1	Pd2	Pd3
<i>Bond lengths</i>			
Pd–C1/C41/C81	1.963(4)	1.949(19)	1.954(2)
Pd–N3/N13/N23	2.178(5)	2.148(11)	2.175(2)
Pd–Cl1/Cl11/Cl21	2.308(12)	2.316(11)	2.308(9)
Pd–Cl2/Cl12/Cl23	2.294(13)	2.294(11)	2.313(8)
<i>Bond angles</i>			
C–Pd–N	179.64(1)	178.19(1)	178.52(1)
Cl–Pd–Cl	175.22(1)	177.40(1)	176.03(1)

Pd1, Pd2, Pd3 belong to the respective crystallographically independent complexes.

The synthesis and reactivity of a related NHC–palladium–allyl complex is currently under investigation in our laboratory.

2.3. Synthesis of rhodium and iridium complexes **5**, **6**, **7**, **8**

We finally prepared the rhodium complex **7** and iridium complex **8** to determine their carbonyl stretching frequencies which are a popular indirect measure of the ligands' electronic properties [32,11]. A low stretching frequency (wavenumber) of CO corresponds to strong σ -donation of the NHC. By using a linear fit procedure [32c], the CO stretching frequencies of respective Ir(I)–NHC can be used to estimate Tolman's electronic parameter (TEP) [33], which is well documented for various phosphines. The CO stretching frequencies and TEP values of respective NHC complexes fall in a narrow range, and the NHC are more electron donating than the most donating phosphines. Compared to standard NHC, our new ligand seems

to be significantly more electron donating. The CO stretching frequencies are listed in Table 3.

The complexes were synthesized by transmetalation from silver complex **2** with the respective chloro(η^4 -1,5-cyclooctadiene = COD)metal dimers to give rhodium complex **5** and iridium complex **6** in good yields (69% and 64%, respectively). Both compounds display restricted rotation about the metal–carbene bond as can be judged from the NMR spectra. A similar behavior of Rh(I)– and Ir(I)–NHC COD complexes has been described before and explained in terms of steric interactions [32c]. The ^{13}C resonance for C-2 was observed as a doublet at 215.2 ppm ($^1J_{\text{RhC}} = 48.4$ Hz) for **5**, while the resonance for C-2 could not be observed for **6**. By bubbling CO through solutions of **5** and **6** in dichloromethane, the complexes **7** and **8** were produced in almost quantitative yields (91% and 93%, respectively). The spectra are consistent with the *cis*-conformation of both carbonyl ligands, showing two strong $\tilde{\nu}_{\text{CO}}$ bands in the IR spectra, and three signals are observed in the ^{13}C NMR spectra between 210 and 165 ppm for both **7** and **8**, corresponding to the two CO carbon atoms and C-2. By using ^{13}C labeled CO in the synthesis of respective Rh(I)–NHC (derived from pyrazolium, imidazolium and benzimidazolium), Herrmann et al. could demonstrate that the two CO carbon atoms resonate at lower field than the carbene carbon atom C-2 [32e]. The C-2 resonance for rhodium complex **7**, however, was undoubtedly identified to appear at 206.6 ppm ($^1J_{\text{RhC}} = 41.3$ Hz) by observing the correlation with 4,5-*H* in the HMBC (heteronuclear multiple bond correlation) spectrum, and so the two resonances at 186.6 ppm ($^1J_{\text{RhC}} = 53.3$ Hz) and 183.2 ppm ($^1J_{\text{RhC}} = 75.6$ Hz) must be assigned to the CO ligands (see Fig. 5). For iridium complex **8**, this correlation could not be observed and the assignment remains uncertain.

Table 3
Carbonyl stretching frequencies $\tilde{\nu}$ (measured in dichloromethane) of complexes **7**, **8** and related complexes known from the literature

Compound	$\tilde{\nu}(\text{CO})$ (cm^{-1})	$\tilde{\nu}(\text{CO})$ (cm^{-1})	TEP ^a (cm^{-1})
7	2069 (2062) ^b	1995 (1984) ^b	–
SIMesRhCl(CO) ₂ ^c	(2081) ^b	(1996) ^b	–
8	2058	1977	2050
SIMesIrCl(CO) ₂ ^c	2068	1981	2055
ICyIrCl(CO) ₂ ^c	2064	1982	2054

^a TEP (Tolman's electronic parameter) = $0.722[\tilde{\nu}_{\text{average}(\text{CO})}] + 593$ cm^{-1} , according to Ref. [32c].

^b Measured in KBr.

^c Literature values [32b,32f,32g]; SIMes = 1,3-bis(2,4,6-trimethylphenyl)imidazolidin-2-ylidene, ICy = 1,3-dicyclohexylimidazol-2-ylidene.

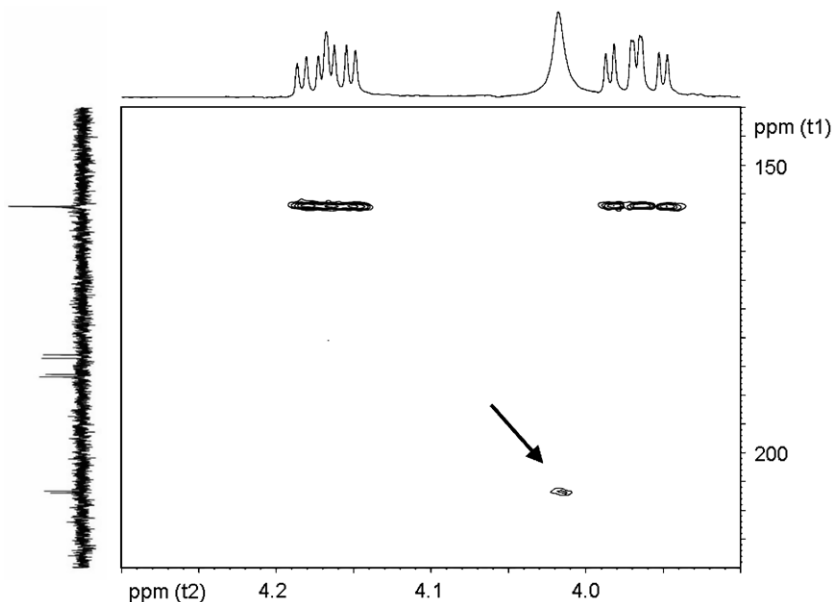


Fig. 5. HMBC spectrum (313 K, parts) of rhodium complex **7** used to assign the carbon atoms of the NHC (C-2, 206.6 ppm) and the carbonyl ligands (186.6 and 183.2 ppm, respectively). The cross-peak between C-2 and H-4,5 is indicated by an arrow.

3. Conclusion

Bimacrocyclic NHC metal complexes can readily be obtained from either azolium salt **1** or via transmetalation from silver complex **2**. All of the synthesized complexes are stable under ambient conditions, and copper complex **3** proved to be active as a catalyst in carbene transfer reactions. Compared to standard NHC, our new concave ligand seems to be more electron donating. The reactivity of the synthesized complexes and the accessibility of other concave NHC metal complexes are under investigation.

4. Experimental

4.1. General

During all reactions and manipulations, no precautions were taken to exclude oxygen or moisture, except for the cyclopropanation reactions. The NHC precursor **1** was prepared according to the method reported earlier [13a]. Melting points were determined with a Büchi 530 melting point apparatus. ^1H and ^{13}C NMR spectra were recorded with Bruker DRX 500 or AV 600 instruments at room temperature and referenced to tetramethylsilane. Assignments are supported by COSY, HSQC and HMBC. The HMBC spectrum of complex **7** was recorded at 313 K, with the first $1/2J$ delay being adjusted for a coupling constant of 5 Hz ($\Delta = 10$ ms). The ^{13}C resonances for the carbene carbon atoms C-2 were observed with low intensities for all compounds. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, $m_{(c)}$ = multiplet (centered), br = broad signal. The following abbreviations are used for assignments: Ar = aromatic, Im = imidazolidin, Py = 3-chloropyridine. Mass spectra were obtained using either an Applied Biosystems Mariner Spectrometry Workstation (ESI), Bruker Biflex III (LD-ToF) or Finnigan MAT 8200 (EI). IR spectra were recorded with a Perkin-Elmer Paragon 1000 spectrometer (a resolution of 4 cm^{-1} was used for routine spectra, while the spectra of **7** and **8** were recorded with a resolution of 1 cm^{-1}). Elemental analyses were carried out with a EuroEA 3000 Elemental Analyzer from Euro Vector. GC analyses were performed on an Agilent 6890 N gas chromatograph.

4.2. Synthesis of chloro(2,11,13,22-tetraoxa-1,12(1,3,2)-dibenzena-23-(1,3)-imidazolidina-bicyclo[10.10.1]-tricosaphane-23²-ylidene)silver(I) (**2**)

A suspension of silver(I) oxide (45 mg, 0.19 mmol) and imidazolinium chloride **1** (210 mg, 387 μmol) in 10 mL of dichloromethane was stirred for 14 h at room temperature excluding light. The reaction mixture was passed through a short pad of silica gel, eluting with dichloromethane. After removal of the solvent *in vacuo*, **2** was obtained as a colorless solid. Yield: 215 mg (331 μmol , 86%).

M.p. 229 °C. ^1H NMR (500 MHz, CDCl_3): δ (ppm) = 7.20 (t, $^3J = 8.5$ Hz, 2H, Ar-*H*-4), 6.57 (d,

$^3J = 8.5$ Hz, 4H, Ar-*H*-3,5), 4.12 ($m_{(c)}$, 4H, OCH_aH_b), 4.01 (s, 4H, Im-4,5-*H*), 3.99 ($m_{(c)}$, 4H, OCH_aH_b), 1.79 ($m_{(c)}$, 4H), 1.70 ($m_{(c)}$, 8H), 1.48 ($m_{(c)}$, 12H). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ (ppm) = 209.7 (dd, $^1J_{107\text{AgC}} = 234$ Hz, $^1J_{109\text{AgC}} = 270$ Hz, Im-C-2), 156.5 (Ar-C-2,6), 129.2 (Ar-C-4), 118.2 (Ar-C-1), 104.7 (Ar-C-3,5), 68.1 (OCH_2), 50.6 (d, $^3J_{\text{AgC}} = 8.6$ Hz, Im-C-4,5), 28.5, 26.4, 23.8. MS (ESI, MeOH): m/z (%) = 1119.54/1121.54 (87/100, $[(\text{C}_{31}\text{H}_{42}\text{N}_2\text{O}_4)_2\text{Ag}]^+$), 507.33 (30, $[\text{C}_{31}\text{H}_{43}\text{N}_2\text{O}_4]^+$). MS (LD-ToF): m/z (%) = 1119/1121 (70/100, $[(\text{C}_{31}\text{H}_{42}\text{N}_2\text{O}_4)_2\text{Ag}]^+$). IR (KBr): $\tilde{\nu}(\text{cm}^{-1}) = 2936, 2854, 1596, 1499, 1463, 1268, 1099, 775, 730$. Anal. Calc. for $\text{C}_{31}\text{H}_{42}\text{AgClN}_2\text{O}_4$ (649.99): C, 57.28; H, 6.51; N, 4.31. Found: C, 57.48; H, 6.61; N, 4.32%.

4.3. Synthesis of chloro(2,11,13,22-tetraoxa-1,12(1,3,2)-dibenzena-23-(1,3)-imidazolidina-bicyclo[10.10.1]-tricosaphane-23²-ylidene)copper(I) (**3**)

A suspension of copper(I) chloride (32 mg, 0.32 mmol) and silver complex **2** (210 mg, 323 μmol) in 15 mL of dichloromethane was stirred for 20 h at room temperature. The reaction mixture was passed through a short pad of silica gel, eluting with dichloromethane. After removal of the solvent *in vacuo*, **3** was obtained as a colorless solid. Yield: 131 mg (216 μmol , 67%).

M.p. 207 °C. ^1H NMR (600 MHz, CDCl_3): δ (ppm) = 7.19 (t, $^3J = 8.4$ Hz, 2H, Ar-*H*-4), 6.57 (d, $^3J = 8.5$ Hz, 4H, Ar-*H*-3,5), 4.12 ($m_{(c)}$, 4H, OCH_aH_b), 4.00 ($m_{(c)}$, 4H, OCH_aH_b), 3.99 (s, 4H, Im-4,5-*H*), 1.81 ($m_{(c)}$, 4H), 1.70 ($m_{(c)}$, 8H), 1.47 ($m_{(c)}$, 12H). $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): δ (ppm) = 205.3 (Im-C-2), 156.3 (Ar-C-2,6), 128.9 (Ar-C-4), 118.2 (Ar-C-1), 104.7 (Ar-C-3,5), 68.1 (OCH_2), 50.4 (Im-C-4,5), 28.5, 26.6, 24.0. MS (LD-ToF): m/z (%) = 569 (13, $[\text{C}_{31}\text{H}_{42}\text{CuN}_2\text{O}_4]^+$), 507 (100, $[\text{C}_{31}\text{H}_{43}\text{N}_2\text{O}_4]^+$). IR (KBr): $\tilde{\nu}(\text{cm}^{-1}) = 2936, 2856, 1593, 1500, 1478, 1459, 1388, 1295, 1258, 1182, 1101, 772, 726$. Anal. Calc. for $\text{C}_{31}\text{H}_{42}\text{ClCuN}_2\text{O}_4$ (605.66): C, 61.47; H, 6.99; N, 4.63. Found: C, 61.72; H, 7.19; N, 4.63%.

4.4. Synthesis of trans-dichloro(3-chloropyridine)-(2,11,13,22-tetraoxa-1,12(1,3,2)-dibenzena-23-(1,3)-imidazolidina-bicyclo[10.10.1]-tricosaphane-23²-ylidene)palladium(II) (**4**)

A suspension of palladium dichloride (89 mg, 0.50 mmol), imidazolinium chloride **1** (299 mg, 550 μmol) and potassium carbonate (346 mg, 2.50 mmol) in 2 mL of 3-chloropyridine was heated for 16 h at 80 °C. After cooling the reaction mixture was diluted with dichloromethane and passed through a short pad of silica gel covered by celite, eluting with dichloromethane. The volatiles were removed *in vacuo* and the crude product was purified by column chromatography on silica gel [dichloromethane/ethyl acetate (3:1), $R_f = 0.12$] to give **4** as a yellow solid. Yield: 18 mg (23 μmol , 5%).

M.p. 233 °C. ^1H NMR (600 MHz, CDCl_3): δ (ppm) = 8.54 (d, $^4J = 2.4$ Hz, 1H, Py-*H*-2), 8.46 (dd, $^3J = 5.5$ Hz, $^4J = 1.3$ Hz, 1H, Py-*H*-6), 7.48 (ddd, $^3J = 8.2$ Hz, $^4J = 2.4$ Hz, $^4J = 1.4$ Hz, 1H, Py-*H*-4), 7.26 (t, $^3J = 8.4$ Hz, 2H, Ar-*H*-4), 6.99 (dd, $^3J = 8.2$ Hz, $^3J = 5.5$ Hz, 1H, Py-*H*-5), 6.60 (d, $^3J = 8.4$ Hz, 4H, Ar-*H*-3,5), 4.20 (m_c, 4H, OCH_aH_b), 4.06 (s, 4H, Im-4,5-*H*), 4.01 (m_c, 4H, OCH_aH_b), 2.09 (m_c, 4H), 1.75 (m_c, 4H), 1.63 (m_c, 4H), 1.51 (m_c, 12H). $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): δ (ppm) = 183.5 (Im-*C*-2), 157.4 (Ar-*C*-2,6), 150.4 (Py-*C*-2), 149.5 (Py-*C*-6), 137.0 (Py-*C*-4), 131.7 (Py-*C*-3), 129.3 (Ar-*C*-4), 124.0 (Py-*C*-5), 117.5 (Ar-*C*-1), 103.7 (Ar-*C*-3,5), 68.1 (OCH_2), 50.5 (Im-*C*-4,5), 28.6, 26.8, 24.1. IR (KBr): $\tilde{\nu}(\text{cm}^{-1}) = 3059, 2923, 2853, 1592, 1506, 1460, 1388, 1298, 1261, 1100, 1024, 802, 726$.

4.5. Synthesis of chloro(η^4 -1,5-cyclooctadiene)-(2,11,13,22-tetraoxa-1,12(1,3,2)-dibenzena-23-(1,3)-imidazolidina-bicyclo[10.10.1]-tricosaphane-23²-ylidene)rhodium(I) (5)

A solution of silver complex **2** (207 mg, 318 μmol) in 5 mL of dichloromethane was added to chloro(η^4 -1,5-cyclooctadiene)rhodium(I) dimer (79 mg, 0.16 mmol). The reaction mixture was stirred for 16 h at room temperature and then passed through a short pad of silica gel, eluting with dichloromethane. The crude product was purified by crystallisation from dichloromethane/diethyl ether. Yellow crystals were obtained. Yield: 165 mg (219 μmol , 69%).

M.p. 228 °C. ^1H NMR (600 MHz, CDCl_3): δ (ppm) = 7.27 (t, $^3J = 8.4$ Hz, 2H, Ar-*H*-4), 6.65 (dd, $^3J = 8.4$ Hz, $^4J = 1.1$ Hz, 2H, Ar-*H*-3), 6.55 (dd, $^3J = 8.4$ Hz, $^4J = 1.1$ Hz, 2H, Ar-*H*-5), 4.39 (br s, 2H, $=\text{CH}_{a\text{COD}}$), 4.30 (m_c, 2H, $\text{OCH}_{a_1}\text{H}_{b_1}$), 4.13 (m_c, 2H, $\text{OCH}_{a_2}\text{H}_{b_2}$), 3.96 (m_c, 2H, $\text{OCH}_{a_1}\text{H}_{b_1}$), 3.91 (m_c, 2H, $\text{OCH}_{a_2}\text{H}_{b_2}$), 3.89 (m_c, 2H, Im-4,5-*H*_a), 3.83 (m_c, 2H, Im-4,5-*H*_b), 3.71 (br s, 2H, $=\text{CH}_{b\text{COD}}$), 2.12 (m_c, 2H), 1.81–1.42 (m, 28H), 1.36 (m_c, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): δ (ppm) = 215.2 (d, $^1J_{\text{RhC}} = 48.4$ Hz, Im-*C*-2), 158.2 (Ar-*C*-6), 156.9 (Ar-*C*-2), 128.9 (Ar-*C*-4), 118.7 (Ar-*C*-1), 104.7 (Ar-*C*-3), 102.7 (Ar-*C*-5), 95.9 (d, $^1J_{\text{RhC}} = 6.7$ Hz, $=\text{C}_a\text{H}_{\text{COD}}$), 68.3 (OCH_2), 67.7 (OCH_2), 67.5 (d, $^1J_{\text{RhC}} = 14.2$ Hz, $=\text{C}_b\text{H}_{\text{COD}}$), 50.7 (Im-*C*-4,5), 32.8, 28.8, 28.4, 28.3, 26.5, 26.1, 23.3, 23.1. MS (ESI, MeOH): m/z (%) = 717.32 (100, $[\text{C}_{39}\text{H}_{54}\text{N}_2\text{O}_4\text{Rh}]^+$). IR (KBr): $\tilde{\nu}(\text{cm}^{-1}) = 2927, 2862, 1591, 1497, 1479, 1466, 1426, 1385, 1296, 1259, 1176, 1101, 770, 722$. Anal. Calc. for $\text{C}_{39}\text{H}_{54}\text{ClN}_2\text{O}_4\text{Rh}$ (753.22): C, 62.19; H, 7.23; N, 3.72. Found: C, 62.24; H, 7.32; N, 3.74%.

4.6. Synthesis of chloro(η^4 -1,5-cyclooctadiene)-(2,11,13,22-tetraoxa-1,12(1,3,2)-dibenzena-23-(1,3)-imidazolidina-bicyclo[10.10.1]-tricosaphane-23²-ylidene)iridium(I) (6)

Dichloromethane (8 mL) was added to a flask containing silver complex **2** (100 mg, 154 μmol) and chloro(η^4 -1,5-cyclooctadiene)iridium(I) dimer (50 mg, 75 μmol). The reaction mixture was stirred for 2 h at 40 °C and then

passed through a short pad of silica gel, eluting with dichloromethane. The crude product was purified by crystallisation from dichloromethane/diethyl ether. Yellow crystals were obtained. Yield: 83 mg (99 μmol , 64%).

M.p. 231 °C. ^1H NMR (600 MHz, CDCl_3): δ (ppm) = 7.23 (t, $^3J = 8.4$ Hz, 2H, Ar-*H*-4), 6.59 (dd, $^3J = 8.4$ Hz, $^4J = 0.9$ Hz, 2H, Ar-*H*-3), 6.51 (dd, $^3J = 8.4$ Hz, $^4J = 1.0$ Hz, 2H, Ar-*H*-5), 4.26 (m_c, 2H, $\text{OCH}_{a_1}\text{H}_{b_1}$), 4.11 (m_c, 2H, $\text{OCH}_{a_2}\text{H}_{b_2}$), 4.01–3.88 (m, 12H, OCH_aH_b , Im-4,5-*H*_a, $=\text{CH}_{a\text{COD}}$), 3.86 (m_c, 2H, Im-4,5-*H*_b), 3.44 (br s, 2H, $=\text{CH}_{b\text{COD}}$), 2.12 (m_c, 2H), 1.80 (m_c, 4H), 1.67 (m_c, 4H), 1.61–1.47 (m, 16H), 1.38 (m_c, 2H), 1.28 (m_c, 4H). $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): δ (ppm) = 158.0 (Ar-*C*-6), 156.8 (Ar-*C*-2), 128.8 (Ar-*C*-4), 118.5 (Ar-*C*-1), 104.5 (Ar-*C*-3), 102.8 (Ar-*C*-5), 81.6 ($=\text{C}_a\text{H}_{\text{COD}}$), 68.3 (OCH_2), 67.6 (OCH_2), 51.4 ($=\text{C}_b\text{H}_{\text{COD}}$), 51.0 (Im-*C*-4,5), 33.4, 29.0, 28.9, 28.3, 26.5, 26.2, 23.3, 23.1; no signal observed for Im-*C*-2. MS (EI): m/z (%) = 840/842 (53/100, $[\text{C}_{39}\text{H}_{54}\text{ClIrN}_2\text{O}_4]^+$). IR (KBr): $\tilde{\nu}(\text{cm}^{-1}) = 2920, 2863, 1593, 1498, 1479, 1459, 1426, 1295, 1259, 1103, 770, 722$. Anal. Calc. for $\text{C}_{39}\text{H}_{54}\text{ClIrN}_2\text{O}_4$ (842.53): C, 55.60; H, 6.46; N, 3.32. Found: C, 55.66; H, 6.64; N, 3.36%.

4.7. Synthesis of cis-dicarbonylchloro(2,11,13,22-tetraoxa-1,12(1,3,2)-dibenzena-23-(1,3)-imidazolidina-bicyclo[10.10.1]-tricosaphane-23²-ylidene)rhodium(I) (7)

CO was bubbled through a solution of **5** (25 mg, 33 μmol) in 2 mL of dichloromethane at 0 °C for 10 min. The solvent was removed *in vacuo*, the residue was washed with cold pentane (3 \times 2 mL) and dried *in vacuo*. A yellow powder was obtained. Yield: 21 mg (30 μmol , 91%).

M.p. >250 °C. ^1H NMR (500 MHz, CDCl_3): δ (ppm) = 7.24 (t, $^3J = 8.4$ Hz, 2H, Ar-*H*-4), 6.57 (d, $^3J = 8.5$ Hz, 4H, Ar-*H*-3,5), 4.17 (m_c, 4H, OCH_aH_b), 4.02 (s, 4H, Im-4,5-*H*), 3.96 (m_c, 4H, OCH_aH_b), 1.94 (br s, 4H), 1.76 (br s, 4H), 1.64 (m_c, 4H), 1.51 (br s, 12H). $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, CDCl_3): δ (ppm) = 206.6 (d, $^1J_{\text{RhC}} = 41.3$ Hz, Im-*C*-2), 186.6 (d, $^1J_{\text{RhC}} = 53.3$ Hz, CO), 183.2 (d, $^1J_{\text{RhC}} = 75.6$ Hz, CO), 157.1 (Ar-*C*-2,6), 129.4 (Ar-*C*-4), 117.6 (Ar-*C*-1), 104.0 (Ar-*C*-3,5), 68.0 (OCH_2), 51.0 (Im-*C*-4,5), 28.4, 26.5, 23.4; the signal for Ar-*C*-2,6 is broad and of low intensity. IR (CH_2Cl_2): $\tilde{\nu}_{\text{CO}}(\text{cm}^{-1}) = 2069, 1995$; IR (KBr): $\tilde{\nu}(\text{cm}^{-1}) = 2928, 2858, 2062, 1984, 1596, 1508, 1478, 1459, 1383, 1297, 1260, 1183, 1103, 774, 726$. Anal. Calc. for $\text{C}_{33}\text{H}_{42}\text{ClN}_2\text{O}_6\text{Rh}$ (701.06): C, 56.54; H, 6.04; N, 4.00. Found: C, 56.48; H, 6.18; N, 4.05%.

4.8. Synthesis of cis-dicarbonylchloro(2,11,13,22-tetraoxa-1,12(1,3,2)-dibenzena-23-(1,3)-imidazolidina-bicyclo[10.10.1]-tricosaphane-23²-ylidene)iridium(I) (8)

CO was bubbled through a solution of **6** (34 mg, 40 μmol) in 2 mL of dichloromethane at 0 °C for 10 min. The solvent was removed *in vacuo*, the residue was washed

with cold pentane (3 × 2 mL) and dried *in vacuo*. A yellow powder was obtained. Yield: 29 mg (37 μmol, 93%).

M.p. 234 °C. ¹H NMR (600 MHz, CDCl₃): δ (ppm) = 7.24 (t, ³J = 8.4 Hz, 2H, Ar-*H*-4), 6.55 (d, ³J = 8.4 Hz, 4H, Ar-*H*-3,5), 4.17 (br s, 4H, OCH_aH_b), 4.07–3.90 (m, 8H, 4,5-*H*, OCH_aH_b), 1.95 (br s, 4H), 1.77 (br s, 4H), 1.64 (m_c, 4H), 1.52 (br s, 12H). ¹³C{¹H} NMR (150 MHz, CDCl₃): δ (ppm) = 203.0(*), 182.2(*), 169.0(*), 157.1 (Ar-*C*-2,6), 129.5 (Ar-*C*-4), 117.2 (Ar-*C*-1), 103.9 (Ar-*C*-3,5), 68.0 (OCH₂), 51.2 (Im-*C*-4,5), 28.4, 26.4, 23.4; *: Im-*C*-2 and CO, assignment uncertain; the signal for Ar-*C*-2,6 is broad and of low intensity. IR (CH₂Cl₂): $\tilde{\nu}_{\text{CO}}(\text{cm}^{-1}) = 2058, 1977$; IR (KBr): $\tilde{\nu}(\text{cm}^{-1}) = 2928, 2857, 2050, 1968, 1595, 1508, 1478, 1459, 1383, 1296, 1183, 1101, 773, 726$. Anal. Calc. for C₃₃H₄₂ClIrN₂O₆ (790.37): C, 50.15; H, 5.36; N, 3.54. Found: C, 50.57; H, 5.52; N, 3.54%.

4.9. Cyclopropanation experiments

A flask was charged with the respective catalyst (25 μmol), EDA (114 mg, 1 mmol) and 1,2-dichloroethane (2 mL). The flask was flushed with nitrogen, sealed with a rubber septum and the mixture was stirred for 5 min. The respective olefine (10 mmol) was injected via syringe and the mixture was stirred at room temperature. After 16 h, the mixture was passed through a short pad of silica gel

and the silica gel was rinsed with diethylether (20 mL). The filtrate was then filled up to 25 mL with diethylether and analyzed by GC, following an established procedure [34]; conditions: split ratio 11:1, injector temp. 250 °C, detector temp. 300 °C; column: HP-5/30 m; temperature: 80 °C for 5 min, 10 °C/min until 140 °C, 1 min 140 °C, 2 °C/min until 160 °C, 1 min 160 °C, 20 °C/min until 240 °C, 20 min 240 °C.

4.10. Single-crystal X-ray structure determination of compounds 2–4

General: Crystal data and details of the structure determination are given in Table 4. Suitable single crystals were grown by slow diffusion of either diethyl ether (**2**, **3**) or *n*-pentane (**4**) into solutions of the respective complexes in dichloromethane. Data collection was performed using an STOE Imaging Plate Diffraction System (IPDS-1) with graphite-monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). Structure solutions were performed with direct methods using SHELXS-97. Structure refinements were performed against F² with SHELXL-97 [35]. Some of the carbon atoms in the alkyl chains of compounds **2**, **3** and **4** and the chlorine atom in **3** are disordered in two positions and were refined using a split model. All non-hydrogen atoms except the disordered carbon atoms of lower occupancy were refined anisotropic. The hydrogen atoms were placed in

Table 4
Crystallographic data for 2–4

Compound	2	3	4
Formula	C ₃₁ H ₄₂ AgClN ₂ O ₄	C ₃₁ H ₄₂ ClCuN ₂ O ₄	C ₃₆ H ₄₆ Cl ₃ N ₃ O ₄ Pd
Formula weight	649.99	605.66	797.51
Color/habit	Colorless/block	Colorless/block	Yellow/block
Crystal size (mm)	0.2 × 0.14 × 0.08	0.3 × 0.1 × 0.2	0.5 × 0.4 × 0.3
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>c</i> (no. 14)	<i>P</i> 2 ₁ / <i>c</i> (no. 14)	<i>P</i> $\bar{1}$ (no. 2)
<i>a</i> (Å)	9.8314(6)	9.5044(6)	15.7630(11)
<i>b</i> (Å)	32.2408(15)	17.1456(10)	20.0189(14)
<i>c</i> (Å)	9.7324(6)	18.3443(14)	21.1372(14)
α (°)	90	90	108.412(8)
β (°)	93.374(8)	92.551(8)	90.506(8)
γ (°)	90	90	100.428(8)
<i>V</i> (Å ³)	3079.6(3)	2986.4(3)	6208.5(7)
<i>Z</i>	4	4	6
<i>T</i> (K)	170(2)	170(2)	200(2)
μ (mm ⁻¹)	0.778	0.859	0.679
θ Range (°)	2.17–22.38	2.52–28.03	2.28–26.02
Index ranges (<i>h</i> , <i>k</i> , <i>l</i>)	±10, ±34, ±10	±11, ±22, ±19	±19, ±24, ±24
Measured reflections	18 554	21 940	48 286
Independent reflections	3964	6991	23979
<i>R</i> _{int}	0.0434	0.0404	0.0387
Reflections with [<i>I</i> > 2σ(<i>I</i>)]	3257	5567	17870
Parameters	370	388	1306
<i>R</i> ₁ / <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)] ^a	0.0254/0.0661	0.0387/0.0972	0.0416/0.1047
<i>R</i> ₁ / <i>wR</i> ₂ (all data) ^a	0.0330/0.0685	0.0516/0.1033	0.0592/0.1113
GOF (on <i>F</i> ²) ^a	0.982	1.031	0.960
Largest difference in peak and hole (e Å ⁻³)	+0.356 and -0.357	+0.547 and -0.591	+0.897 and -0.681

^a $R_1 = \sum(|F_o| - |F_c|) / \sum |F_o|$; $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2] / \sum w(F_o^2)^2\}^{1/2}$; GOF = $\{\sum[w(F_o^2 - F_c^2)^2] / (n - p)\}^{1/2}$.

ideal positions and refined using a riding model. The asymmetric unit of **4** contains three crystallographically independent molecules.

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Appendix A. Supplementary material

CCDC 664014, 664015 and 664016 contain the supplementary crystallographic data for **2**, **3** and **4**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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