

PAPER

View Article Online
View Journal | View Issue

Cite this: *Dalton Trans.*, 2022, **51**, 2464

Received 13th November 2021,
Accepted 6th January 2022

DOI: 10.1039/d1dt03857e

rsc.li/dalton

Bi- and trimetallic complexes with macrocyclic xanthene-4,5-diNHC ligands†

Alexander Kaps, Sabine Foro and Herbert Plenio *

Three different types of bimetallic NHC-metal complexes were synthesized, whose NHC units are attached at the 4,5-positions of xanthene. The NHC units are in close proximity and are designed such that each carbene coordinates one ML unit, while the chelation of one metal by two NHC is not possible. Several xanthene-((NHC)ML)₂ complexes with ML = RhCl(cod), IrCl(cod), RhCl(CO)₂, IrCl(CO)₂, AuCl, AgCl, CuCl and Pd(allyl)Cl were synthesized and investigated.

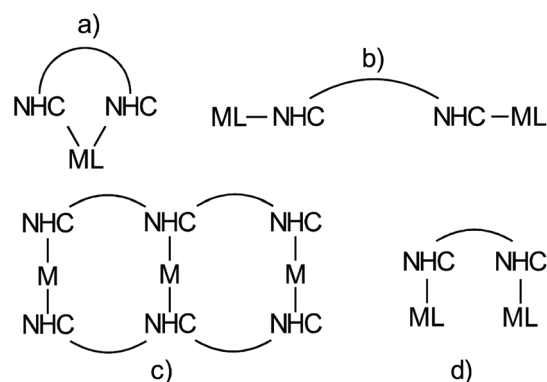
Introduction

The chemistry of N-heterocyclic carbenes has experienced an enormous development in the last decades following the seminal work of Arduengo *et al.*¹ and Herrmann.² Monographies provide a comprehensive overview of NHC chemistry,^{3,4} while succinct reviews, such as for example the one by Glorius *et al.* provide an inspiring, excellent introduction to the field.⁵ NHC-metal complexes involving transition metals play an essential role in homogeneous catalysis, and are real game changers in ruthenium based olefin metathesis catalysts of the Grubbs type^{6–8} and in several gold-catalyzed transformations.⁹ Other highlighted applications of NHC-metal complexes are Pd- and Ni-catalyzed cross coupling reactions^{10,11} or olefin polymerizations,¹² and catalytic reactions involving other M(NHC) complexes with M = Mo and W,¹³ Fe,¹⁴ Pt,¹⁵ Co,¹⁶ Rh,¹⁷ Ir,^{18–20} coinage metals,²¹ Zn²² or main group elements.²³

These applications rely on a correspondingly large variety of different NHC ligands.^{24–31} Most such ligands contain only a single NHC unit and obviously ligands containing several NHC ligands are less common. Four different motifs involving metal complexes with ligands containing more than a single NHC unit can be distinguished (Scheme 1).

Structure (a), in which two NHC ligands bind a single metal in a chelating fashion, represents a common theme, which has also been used in numerous catalytic transformations.³² Motif (b) in which two NHC bind different metals individually, which cannot directly interact with each other was established

by Bielawski *et al.*^{33,34} and used to generate polymeric materials.³⁵ This approach was foremost extended by Peris *et al.* in numerous Janus type NHC metal complexes.³⁶ Approach (c) leading to complex supramolecular motifs is actively pursued by E. Hahn and Ying-Feng Han³⁷ and the Peris group.³⁸ Typically, diverse arrays of coinage metal complexes of the type M(NHC)₂⁺ are formed in which the coordination sphere of the metal is saturated by the two NHC ligands. The basic concept in motif (d) (Scheme 1) is to synthesize ligands containing two NHC ligands, which are able to bind two metals in close proximity and which in addition also possess ligands other than NHC. The ligands also need to be designed in such a way that the two NHC ligands cannot bind a single metal atom in a chelating fashion like in (a). Accordingly, one metal is bonded to each of the two NHC ligands. Consequently, the two metal centers are in close proximity and are potentially able to interact and to cooperate. To the best of our knowledge such complexes have not been reported before.



Scheme 1 Different structural motifs in metal complexes with bidentate or polydentate NHC ligands.

Organometallic Chemistry, Technical University of Darmstadt, Alarich-Weiss-Str. 12, 64287 Darmstadt, Germany. E-mail: herbert.plenio@tu-darmstadt.de

† Electronic supplementary information (ESI) available: NMR spectra (¹H and ¹³C), infrared spectra, high mass specs, cyclic voltammetry, and X-ray crystal structures. CCDC 2120202 2120204 2120205. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d1dt03857e



Experimental

General experimental

All chemicals were purchased as reagent grade from commercial suppliers and used without further purification, unless otherwise noted. Tetrahydrofuran and toluene were dried with sodium, MeOH/CH₃CN/CH₂Cl₂/DMF and DMSO were dried over CaH₂, and distilled under nitrogen or argon. All dried solvents were stored over molecular sieves (4 Å). Cy/EA stands for "cyclohexane/ethyl acetate". ¹H and ¹³C NMR spectra were recorded with a Bruker AC300 or DRX500 spectrometer. The chemical shifts are given in parts per million (ppm) on the δ scale and are referenced to the residual peak of CDCl₃ (δ_H = 7.26 ppm, δ_C = 77.16 ppm), DMSO-d₆ (δ_H = 2.50 ppm, δ_C = 39.52 ppm), CDCl₂ (δ_H = 5.32 ppm, δ_C = 53.84 ppm) or MeOD (δ_H = 3.31 ppm, δ_C = 49.00 ppm). Abbreviations for NMR: s = singlet, bs = broad singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sept = septet, m = multiplet. TLC was performed by using silica 60 F 254 (0.2 mm) on alumina plates. Preparative chromatography was carried out on Merck silica 60 (0.063–0.2 mm). Cyclic voltammograms were recorded in dry CH₂Cl₂ under nitrogen at ambient temperature. A three-electrode configuration was employed: the working electrode was a Pt disk (diameter 1 mm) sealed in soft glass with a Pt wire as counter electrode, and the pseudo-reference electrode was an Ag wire. Potentials were calibrated internally against the formal potential of octamethylferrocene [*E*_{1/2} = −0.01 V (CH₂Cl₂)]. Bu₄NPF₆ (0.1 mol L^{−1}) was used as supporting electrolyte.

2,3,6,7,9,9-Hexamethylxanthene (2)

2,3,6,7,9,9-Hexamethylxanthene was prepared according to a modified literature procedure.³⁹ A mixture of 3,4-dimethylphenol (210 g, 1.74 mol, 10 eq.), acetone (12.8 mL, 174 mmol, 1.0 eq.) and methanesulfonic acid (1.1 mL, 17.4 mmol, 0.1 eq.) was heated at 110 °C for 5 d and then at 150 °C for 6 h. The product mixture was diluted with 200 mL toluene, washed 3 times with 10% NaOH aq. (300 mL) and water, dried over MgSO₄, and concentrated under reduced pressure to give a dark waxy solid. The residue was slurried in boiling methanol and filtered over a fritted funnel. The filtrate was then concentrated under reduced pressure to give an off-white solid. ¹H NMR (300 MHz, CDCl₃): δ 7.13 (s, 2H), 6.82 (s, 2H), 2.25 (s, 6H), 2.24 (s, 6H), 1.61 (s, 6H). ¹³C NMR (126 MHz, CDCl₃): δ 148.4, 135.8, 130.8, 127.2, 117.2, 33.4, 33.0, 19.5, 19.4. Yield: 32% (14.8 g, 55.6 mmol).

4,5-Dibromo-2,3,6,7,9,9-hexamethylxanthene (3)

4,5-Dibromo-2,3,6,7,9,9-hexamethylxanthene was prepared according to a modified literature procedure.⁴⁰ To a Schlenk flask containing 2,3,6,7,9,9-hexamethylxanthene (13.9 g, 52.2 mmol) and 350 mL DCM was added Br₂ (6.15 mL, 120 mmol, 2.3 eq.) dropwise at −78 °C. The reaction mixture was stirred at rt overnight. Na₂S₂O₃ (aq.) was added to quench excess of bromine. The layers were separated and aqueous phase was extracted with DCM. The combined organic phase

was washed with water and brine, and was dried over MgSO₄. The volatiles were evaporated to afford 4,5-dibromo-2,3,6,7,9,9-hexamethylxanthene as a white solid. ¹H NMR (300 MHz, CDCl₃): δ 7.10 (s, 2H), 2.40 (s, 6H), 2.33 (s, 6H), 1.59 (s, 6H). Yield: 92% (20.4 g, 48.1 mmol).

2,3,6,7,9,9-Hexamethylxanthene-4,5-dicarboxylic acid (4)

2,3,6,7,9,9-Hexamethylxanthene-4,5-dicarboxylic acid was prepared according to the literature procedure for 2,7-di-*tert*-butyl-9,9-dimethyl-9*H*-xanthene-4,5-dicarboxylic acid.⁴¹ In a three-necked round flask, 4,5-dibromo-2,3,6,7,9,9-hexamethylxanthene (18.7 g, 44.1 mmol) was dissolved in 500 mL dry THF and cooled with an acetone/dry ice bath to −78 °C. A solution of *n*-butyllithium (1.6 M in *n*-hexane, 82.7 mL, 132.3 mmol) was slowly added and the mixture stirred for further 30 min at −78 °C. CO₂ was produced by evaporating dry ice (excess) in a round flask, bubbled through a drying tube filled with silica desiccant and passed into the solution for approx. 2 h. The reaction was quenched with ice and conc. HCl. The layers were separated and the aqueous phase was extracted with diethyl ether. The organic phases were combined, washed with brine, dried over MgSO₄, filtered and the solvent evaporated. The residue was suspended in pentane, stirred and filtered and the solid was washed again with pentane, affording the product as a white solid. ¹H NMR (300 MHz, DMSO-d₆): δ 12.94 (bs, 2H), 7.35 (s, 2H), 2.23 (s, 6H), 2.12 (s, 6H), 1.56 (s, 6H). ¹³C NMR (75 MHz, DMSO-d₆): δ 168.0, 143.2, 131.2, 127.5, 126.6, 124.4, 33.1, 32.4, 19.2, 15.9. HRMS (ESI): calcd for C₂₁H₂₃O₅ (M + H)⁺ 355.15400. Found 355.15364 (Δ = 0.36 mmu). Yield: 60% (9.4 g, 26.5 mmol).

Dibenzyl (2,3,6,7,9,9-hexamethylxanthene-4,5-diyl)dicarbamate (5)

Dibenzyl (2,3,6,7,9,9-hexamethylxanthene-4,5-diyl)dicarbamate was prepared according to a modified literature procedure for dibenzyl (2,7-di-*tert*-butyl-9,9-dimethyl-9*H*-xanthene-4,5-diyl)dicarbamate.⁴¹ 2,3,6,7,9,9-Hexamethylxanthene-4,5-dicarboxylic (6.0 g, 16.9 mmol, 1.0 eq.) was suspended in 120 mL dry toluene under molecular sieve. Then diphenylphosphoryl azide (9.01 mL, 47.4 mmol, 2.8 eq.) was slowly added and the solution stirred for 5 min at rt. Triethylamine (6.61 mL, 47.4 mmol, 2.8 eq.) was added and the mixture was refluxed for 2 h. After this time benzyl alcohol (3.70 mL, 54.2 mmol, 3.2 eq.) was added and refluxed overnight. The solvent was evaporated and the residue purified by column chromatography (Cy/EA 10:1→3:1) affording the pure product as a white solid. ¹H NMR (300 MHz, CDCl₃): δ 7.49–7.25 (m, 10H), 7.09 (s, 2H), 6.52 (s, 2H), 5.15 (s, 4H), 2.27 (s, 6H), 2.16 (s, 6H), 1.57 (s, 6H). ¹³C NMR (75 MHz, CDCl₃): δ 144.0, 136.7, 131.4, 128.6, 128.3, 128.2, 125.0, 67.3, 34.2, 31.8, 20.4, 14.7. R_f = 0.21 (Cy/EA = 10:1). HRMS (ESI): calcd for C₃₅H₃₇N₂O₅ (M + H)⁺ 565.26970. Found 565.26979 (Δ = 0.09 mmu). Yield: 62% (3.1 g, 5.49 mmol).

4,5-Diamino-2,3,6,7,9,9-hexamethylxanthene (6)

4,5-Diamino-2,3,6,7,9,9-hexamethylxanthene was prepared according to the literature procedure for 2,7-di-*tert*-butyl-9,9-



dimethyl-9*H*-xanthene-4,5-diamine.⁴¹ A solution of potassium hydroxide (3.43 g, 61.1 mmol, 15.0 eq.) in water (30 mL) was added to a solution of dibenzyl (2,3,6,7,9,9-hexamethyl-xanthene-4,5-diyl)dicarbamate (2.3 g, 4.07 mmol, 1.0 eq.) in ethanol (80 mL). The mixture was refluxed for 24 h. Ethanol was removed under reduced pressure and the aqueous residue was diluted with water and extracted with diethyl ether. The organic phases were combined, dried with magnesium sulfate, filtered and the solvent evaporated. The residue was purified by column chromatography (Cy/EA 10:1→1:1) affording the pure product as a light brown solid. ¹H NMR (300 MHz, CDCl₃): δ 6.68 (s, 2H), 3.83 (s, 4H), 2.27 (s, 6H), 2.11 (s, 6H), 1.59 (s, 6H). ¹³C NMR (75 MHz, CDCl₃): δ 136.8, 132.4, 130.6, 127.2, 119.4, 116.5, 33.8, 32.4, 20.5, 13.0. *R*_f = 0.43 (Cy/EA = 1:1). Yield: 83% (1.0 g, 3.37 mmol).

Cu-catalyzed from 4,5-dibromo-2,3,6,7,9,9-hexamethyl-xanthene. 4,5-Diamino-2,3,6,7,9,9-hexamethylxanthene was prepared in a modified way according to the literature procedure.⁴⁰ To a 50 mL Schlenk flask containing 4,5-dibromo-2,3,6,7,9,9-hexamethyl-xanthene (4.0 g, 9.4 mmol, 1.0 eq.), CuI (3.50 g, 18.9 mmol, 2.0 eq.), NaN₃ (1.84 g, 28.3 mmol, 3.0 eq.), Na₂CO₃ (1.0 g, 9.4 mmol, 1.0 eq.) and dry DMSO (25 mL) under nitrogen was added DMEDA (2.1 mL, 19.8 mmol, 2.1 eq.) and stirred at 100 °C for 24 h. The reaction mixture was cooled to rt and sat. NH₄Cl aq. (5 mL) and ethyl acetate (5 mL) was added and stirred for 1 h. The reaction mixture was filtered through Celite, and organic phase was extracted with ethyl acetate, washed with brine, and dried over MgSO₄. The organic solvent was evaporated to afford a mixture of 4,5-diamino-2,3,6,7,9,9-hexamethylxanthene, 4-amino-2,3,6,7,9,9-hexamethylxanthene and 2,3,6,7,9,9-hexamethylxanthene which was separated by column chromatography (Cy/EA 20:1→4:1→1:1). Yield: 16% (0.22 g). (4.7 mmol scale)→no Na₂CO₃; yield: 40% (0.13 g). (1.2 mmol scale)→with 2 eq. Na₂CO₃; yield: 36% (0.25 g). (2.4 mmol scale)→with 2 eq. Na₂CO₃; yield: 43% (0.60 g). (4.7 mmol scale)→with 2 eq. Na₂CO₃; yield: 38% (1.06 g). (9.4 mmol scale)→with 1 eq. Na₂CO₃.

4-Amino-2,3,6,7,9,9-hexamethylxanthene (7)

4-Amino-2,3,6,7,9,9-hexamethylxanthene was obtained as side product from the Cu-catalyzed synthesis of 4,5-diamino-2,3,6,7,9,9-hexamethylxanthene. The mixture was purified by column chromatography (Cy/EA 20:1→4:1→1:1) affording the pure product as a light brown solid. ¹H NMR (300 MHz, CDCl₃): δ 7.15 (s, 1H), 6.89 (s, 1H), 6.66 (s, 1H), 3.90 (s, 2H), 2.27 (s, 3H), 2.26 (s, 3H), 2.25 (s, 3H), 2.11 (s, 3H), 1.61 (s, 6H). ¹³C NMR (75 MHz, CDCl₃): δ 148.3, 136.7, 135.6, 132.5, 130.9, 130.4, 127.4, 127.2, 126.9, 119.2, 117.2, 116.2, 33.6, 32.7, 20.5, 19.5, 19.4, 13.0. *R*_f = 0.39 (Cy/EA = 10:1). Yield: 40%.

Xanthene diimine (8)

A suspension of 4,5-diamino-2,3,6,7,9,9-hexamethylxanthene (350 mg, 1.18 mmol, 2.0 eq.), glyoxal (40% aq., 135 μL, 1.18 mmol, 2.0 eq.), and 2 mg of *p*-toluenesulfonic acid monohydrate in *n*-BuOH (8 mL) was stirred under nitrogen in a Schlenk tube at 50 °C for 24 h. The cooled reaction mixture

was filtered and residual solid was washed with cold methanol and pentane to give xanthene diimine **8** as a yellow solid. ¹H NMR (500 MHz, CD₂Cl₂): δ 8.28 (s, 4H), 7.09 (s, 4H), 2.30 (s, 12H), 2.14 (s, 12H), 1.64 (s, 12H). ¹³C NMR (126 MHz, CD₂Cl₂): δ 166.7, 138.6, 138.3, 131.8, 128.9, 128.9, 123.9, 34.7, 32.0, 20.2, 14.3. HRMS (ESI): calcd for C₄₂H₄₅N₄O₂ (M + H)⁺ 637.35370. Found 637.35397 (Δ = 0.27 mmu). Yield: 85% (0.32 g, 0.50 mmol).

General procedure for the synthesis of imidazolium chloride

To a flame dried Schlenk tube containing a solution of the corresponding diimine (1.0 eq.) and paraformaldehyde (1.1–2.4 eq.) in EA was added Me₃SiCl (1.5–2.5 eq.). After being stirred at 70 °C overnight, the resulting suspension was cooled to –20 °C, filtered and washed with cold EA, diethyl ether gave the title compound.

Xanthene diimidazolium salt (9-2HCl)

According to the general procedure starting materials used were xanthene diimine (**8**) (150 mg, 0.235 mmol, 1.0 eq.), paraformaldehyde (17 mg, 0.565 mmol, 2.4 eq.), Me₃SiCl (74.7 μL, 0.589 mmol, 2.5 eq.) in 2 mL EA. The title compound was obtained as an off-white solid. ¹H NMR (300 MHz, DMSO-*d*₆): δ 9.70 (s, 2H), 8.16 (s, 4H), 7.80 (s, 4H), 2.38 (s, 12H), 2.02 (s, 12H), 1.80 (s, 6H), 1.64 (s, 6H). ¹H NMR (300 MHz, CDCl₃): δ 9.78 (s, 2H), 8.26 (s, 4H), 7.39 (s, 4H), 2.35 (s, 12H), 2.05 (s, 12H), 1.74 (s, 6H), 1.65 (s, 6H). ¹³C NMR (75 MHz, CDCl₃): δ 141.9, 138.8, 133.4, 132.8, 130.5, 128.0, 127.2, 121.3, 33.9, 33.6, 33.0, 20.2, 14.2. HRMS (ESI): calcd for C₄₄H₄₆ClN₄O₂ [M – Cl]⁺ 697.33038. Found 697.33064 (Δ = 0.26 mmu). Yield: 85% (146 mg, 0.199 mmol).

General procedure for the synthesis of imidazolium tetrafluoroborate

The halide salt (50 mg) was dissolved in acetonitrile, and a water solution with an excess of NaBF₄ added. After stirring the solution for 15 min the solvent was removed under reduced pressure. Then water was added and extracted several times with dichloromethane. The organic solution was subsequently collected and dried over MgSO₄, filtrated, concentrated under reduced pressure and then diethyl ether was added to precipitate the product as a white crystalline powder.

Xanthene diimidazolium salt (9-2HBF₄)

According to the general procedure 9-2HCl (50 mg) was used. ¹H NMR (500 MHz, CD₂Cl₂): δ 8.57 (t, *J* = 1.6 Hz, 2H), 7.75 (d, *J* = 1.1 Hz, 4H), 7.51 (s, 4H), 2.38 (s, 12H), 2.00 (s, 12H), 1.79 (s, 6H), 1.69 (s, 6H). ¹³C NMR (126 MHz, CD₂Cl₂): δ 142.7, 139.0, 133.7, 133.3, 131.1, 128.6, 126.6, 121.6, 34.4, 33.9, 32.8, 20.4, 14.3. Yield: 99% (56 mg, 0.067 mmol).

General procedure for the synthesis of (NHC)metal complexes

Method A: A vial was charged with the corresponding NHC salt (1.0 eq.), metal precursor (0.5–1.0 eq.) (M = Ir, Rh, Au) and K₂CO₃ (3.0 eq.). The resulting mixture was suspended in acetone or acetone/DCM (3:1 v/v) and stirred for 24 h at 50 °C.



After this time the solvent was removed *in vacuo* and dichloromethane was added. The mixture was filtered through a pad of silica. The pad of silica was washed with dichloromethane until filtrate becomes colorless and the solvent was removed *in vacuo*.

Method B: To a Schlenk tube containing a solution of NHC salt (1.0 eq.) in dry THF was added sodium amylate (2.5 M, 2.0 eq.) at $-78\text{ }^{\circ}\text{C}$. After stirring for 10 min, the cooling bath was removed and the solution stirred for 30 min at rt. After cooling again to $-78\text{ }^{\circ}\text{C}$, $[\text{MCl}(\text{cod})]_2$ (1.0 eq.) ($\text{M} = \text{Rh}, \text{Ir}$) was added and the mixture stirred overnight. The mixture was filtered through a pad of Celite then the Celite was washed with DCM until the filtrate becomes colorless and the solvent was removed *in vacuo*.

Method C: A vial was charged with the corresponding NHC salt (1.0 eq.) and silver(i) oxide (1.0–1.5 eq.) were dissolved in dry MeOH and stirred at rt in the absence of light for 24 h. After this time metal precursor (1.0–2.0 eq.) ($\text{M} = \text{Au}, \text{Rh}$) was added, and in the absence of light the mixture was stirred at $50\text{ }^{\circ}\text{C}$ for 2 h, then 12 h at rt. The mixture was filtered through Celite and the solvent was removed under reduced pressure. The residue was then dissolved in a minimum amount of DCM and diethyl ether was added. The precipitate was filtered and dried under reduce pressure.

Method D: A vial was charged with the corresponding NHC salt (1.0 eq.), metal precursor (1.0–2.0 eq.) ($\text{M} = \text{Ir}, \text{Rh}$), NaOAc (2.0 eq.), K_2CO_3 (2.0 eq.) and KBr (excess) were dissolved in dry MeCN and stirred at $80\text{ }^{\circ}\text{C}$ for 12 h. After this time the mixture was filtered through Celite and the solvent was removed under reduced pressure.

Method E $[\text{MX}(\text{CO})_2(\text{NHC})]$ complexes ($\text{X} = \text{Cl}, \text{Br}$) via substitution of cod by CO: The respective $[\text{IrX}(\text{cod})(\text{NHC})]$, $[\text{RhX}(\text{cod})(\text{NHC})]$ complex was dissolved in CH_2Cl_2 and cooled to $0\text{ }^{\circ}\text{C}$. Then CO was bubbled through this solution for 30 min. The solvent was evaporated and the residue washed with pentane to obtain the products as yellow powders. The conversions for all reactions are quantitative, the lower isolated yields result from small losses (several mg) of material during workup.

$[(\text{IrCl}(\text{cod}))_2(9)]$. Method B. Starting materials **9-2HCl** (100 mg, 0.136 mmol, 1.0 eq.), sodium amylate (2.5 M in toluene, 0.11 mL, 0.273 mmol, 2.0 eq.), $[\text{IrCl}(\text{cod})]_2$ (91.5 mg, 0.136 mmol, 1.0 eq.) in 20 mL dry THF. The complex was purified *via* column chromatography (Cy/EA 8 : 1, v/v) to obtain the desired complex as yellow solid. (Product partial decomposed upon attempted chromatographic purification.) Single crystals of $[(\text{IrCl}(\text{cod}))_2(9)]$ were obtained from of a MeCN/DCM solution of the Ir-complex at $-20\text{ }^{\circ}\text{C}$. ^1H NMR (500 MHz, CDCl_3): δ 7.40 (s, 4H), 6.78 (s, 4H), 4.14–4.02 (m, 4H), 3.36–3.20 (m, 4H), 2.37 (s, 12H), 2.24 (s, 12H), 1.95 (s, 6H), 1.56 (s, 6H), 1.53–1.45 (m, 6H), 1.30–1.25 (m, 6H), 1.17–1.08 (m, 4H). ^{13}C NMR (126 MHz, CDCl_3): δ 183.8 (C_{NHC}), 146.2, 135.7, 133.0, 129.4, 127.4, 126.2, 124.6, 82.7, 51.9, 34.6, 34.1, 33.7, 29.1, 25.4, 20.5, 17.4. HRMS (ESI): calcd for $\text{C}_{44}\text{H}_{46}\text{N}_4\text{O}_2\text{Ir}_2\text{Cl}$ $[\text{M} - \text{Cl}]^+$ 1297.42838. Found 1297.42960 ($\Delta = 1.75$ mmu). Yield: 27% (50 mg, 37.3 μmol).

$[(\text{IrCl}(\text{CO})_2)_2(9)]$. Method E. Complex $[(\text{IrCl}(\text{cod}))_2(9)]$ (15.0 mg, 11.2 μmol) was used. ^1H NMR (500 MHz, CDCl_3): δ 7.38 (s, 4H), 6.90 (s, 4H), 2.35 (s, 12H), 2.10 (s, 12H), 1.90 (s, 6H), 1.46 (s, 6H). ^{13}C NMR (126 MHz, CDCl_3): δ 180.0 (C_{CO}), 178.8 (C_{NHC}), 167.2 (C_{CO}), 145.8, 135.0, 132.2, 129.7, 128.8, 127.2, 126.2, 123.9, 34.8, 34.3, 29.9, 28.2, 25.3, 20.5, 16.2. HRMS (ESI): calcd for $\text{C}_{48}\text{H}_{45}\text{Ir}_2\text{N}_4\text{O}_7$ $[\text{M} - 2\text{Cl} + \text{OH}]^+$ 1175.25363. Found 1175.25413 ($\Delta = 1.12$ mmu). IR ($\nu(\text{CO})$; $[\text{cm}^{-1}]$): 2066/1981. Yield: 99% (14 mg, 11.2 μmol).

$[(\text{RhCl}(\text{cod}))_2(9)]$. Method B. Starting materials **9-2HCl** (30 mg, 40.88 μmol), sodium amylate (2.5 M in toluene, 32.7 μL , 81.77 μmol , 2.0 eq.), $[\text{RhCl}(\text{cod})]_2$ (20.2 mg, 40.88 μmol , 1.0 eq.) in 10 mL dry THF. The complex was obtained as crude yellow/brown solid. (Product decomposed upon attempted chromatographic purification.) ^1H NMR (300 MHz, CDCl_3): δ 7.44 (s, 4H), 6.75 (s, 4H), 4.49 (s, 4H), 3.50 (s, 4H), 2.41 (s, 12H), 2.27 (s, 12H), 1.99 (s, 6H), 1.60 (s, 6H). HRMS (ESI): calcd for $\text{C}_{60}\text{H}_{68}\text{N}_4\text{O}_2\text{Rh}_2\text{Cl}$ $[\text{M} - \text{Cl}]^+$ 1117.31415. Found 1117.31354 ($\Delta = 0.61$ mmu). Yield: 55% (25 mg, 22.4 μmol , crude product).

$[(\text{AuCl})_2(9)]$. Method C. Starting materials **9-2HBF₄** (20 mg, 23.9 μmol , 1.0 eq.), silver(i) oxide (6.1 mg, 26.3 μmol , 1.1 eq.), $[\text{AuCl}(\text{SMe}_2)]$ (14.8 mg, 47.8 μmol , 2.0 eq.) 3 mL dry MeOH. The title complex was obtained as a white solid. ^1H NMR (500 MHz, CD_2Cl_2): δ 7.34 (s, 4H), 6.93 (s, 4H), 2.38 (s, 12H), 1.92 (s, 6H), 1.70 (s, 12H), 1.27 (s, 6H). ^{13}C NMR (126 MHz, CD_2Cl_2): δ 144.6, 133.4, 132.3, 129.6, 128.2, 126.3, 125.2, 125.1, 36.5, 34.8, 24.5, 20.9, 14.2. Au–C could not be observed. HRMS (APCI): calcd for $\text{C}_{44}\text{H}_{44}\text{Au}_2\text{ClN}_4\text{O}_2$ $[\text{M} - \text{Cl}]^+$ 1089.24787. Found 1089.24795 ($\Delta = 0.08$ mmu). Yield: 48% (13 mg, 11.6 μmol).

Xanthene diimine (10)

A suspension of 4-amino-2,3,6,7,9,9-hexamethylxanthene (250 mg, 0.89 mmol, 2.0 eq.), glyoxal (40% aq., 51 μL , 0.44 mmol, 1.0 eq.), and 2 mg of *p*-toluenesulfonic acid monohydrate in EtOH (4 mL) was stirred under nitrogen in a Schlenk tube at $50\text{ }^{\circ}\text{C}$ for 24 h. The cooled reaction mixture was filtered and residual solid was washed with cold methanol and pentane to give xanthene diimine **2** as a yellow solid. ^1H NMR (300 MHz, CDCl_3): δ 8.53 (s, 2H), 7.15 (s, 2H), 7.07 (s, 2H), 6.85 (s, 2H), 2.33 (s, 6H), 2.25 (s, 12H), 2.21 (s, 6H), 1.64 (s, 12H). ^{13}C NMR (75 MHz, CDCl_3): δ 165.9, 148.5, 138.4, 137.8, 135.8, 131.1, 130.9, 128.2, 128.1, 127.3, 126.8, 124.0, 117.5, 34.0, 32.5, 20.2, 19.5, 19.4, 14.4. HRMS (ESI): calcd for $\text{C}_{40}\text{H}_{45}\text{N}_2\text{O}_2$ ($\text{M} + \text{H}$)⁺ 585.34756. Found 585.34718 ($\Delta = 0.37$ mmu). Yield: 67% (0.35 g, 0.599 mmol).

Xanthene imidazolium salt (11·HCl)

Method B. Starting materials: xanthene diimine (**10**) (160 mg, 0.274 mmol, 1.0 eq.), paraformaldehyde (9 mg, 0.301 mmol, 1.1 eq.), Me_3SiCl (52 μL , 0.410 mmol, 1.5 eq.) in 2 mL EA. The title compound was obtained as a white solid. ^1H NMR (300 MHz, CDCl_3): δ 10.11 (bs, 1H), 7.96 (s, 2H), 7.39 (s, 2H), 7.14 (s, 2H), 6.56 (s, 2H), 2.38 (s, 6H), 2.31 (s, 6H), 2.23 (s, 6H), 2.12 (s, 6H), 1.65 (s, 12H). ^{13}C NMR (75 MHz, CDCl_3): δ 146.9,



143.3, 136.3, 132.6, 132.4, 132.2, 130.1, 128.9, 127.3, 126.4, 125.7, 121.3, 117.0, 33.8, 32.8, 20.2, 19.4, 14.9. HRMS (ESI): calcd for $C_{41}H_{45}N_2O_2 [M - Cl]^+$ 597.34756. Found 597.34806 ($\Delta = 0.51$ mmu). Yield: 63% (110 mg, 0.173 mmol).

[(AuCl)(11)]. Method A. Starting materials: 11-HCl (40 mg, 63 μ mol), $[AuCl(SMe_2)]$ (21 mg, 69 μ mol, 1.1 eq.), K_2CO_3 (34.9 mg, 0.253 mmol, 4.0 eq.) in 2 mL acetone. The complex was purified *via* column chromatography (Cy/EA 2:1, v/v) to obtain xanthene-gold complex as a white solid. 1H NMR (500 MHz, $CDCl_3$): δ 7.33 (s, 2H), 7.18 (s, 2H), 7.14 (s, 2H), 6.50 (s, 2H), 2.36 (s, 6H), 2.24 (s, 6H), 2.20 (s, 6H), 2.19 (s, 6H), 1.66 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 175.3 (C_{NHC}), 147.6, 144.4, 136.0, 133.1, 131.7, 131.3, 128.7, 128.4, 127.2, 126.8, 125.7, 122.9, 117.0, 33.8, 32.9, 32.7, 20.2, 19.6, 19.4, 14.7. HRMS (ESI): calcd for $C_{43}H_{47}AuN_3O_2 [M - Cl + CH_3CN]^+$ 834.33285. Found 834.33251 ($\Delta = 0.34$ mmu). Yield: 31% (16 mg, 19.3 μ mol).

[(IrCl(cod))(11)]. Method A. Starting materials: 11-HCl (100 mg, 0.158 mmol, 1.0 eq.), $[IrCl(cod)]_2$ (53.0 mg, 79 μ mol, 0.50 eq.), K_2CO_3 (87.3 mg, 0.632 mmol, 4.0 eq.) in 2 mL acetone. The title complex (*syn/anti* isomer) was obtained as a yellow solid. 1H NMR (500 MHz, $CDCl_3$): δ 7.33 (s, 2H), 7.18 (s, 2H), 7.06 (s, 2H), 6.70 (s, 2H), 4.04 (d, $J = 5.8$, 2H), 3.35 (d, $J = 5.4$, 2H), 2.36 (s, 6H), 2.26 (s, 6H), 2.25 (s, 6H), 2.19 (s, 6H), 1.76 (s, 6H), 1.64 (s, 6H), 1.55–1.47 (m, 2H), 1.35–1.16 (m, 4H), 1.18–0.98 (m, 2H). (Signals shown for main isomer only.) ^{13}C NMR (126 MHz, $CDCl_3$): δ 184.0 (C_{NHC}), 147.6, 144.2, 135.9, 135.5, 131.5, 131.4, 127.6, 127.3, 127.3, 127.0, 123.6, 117.2, 81.9, 52.3, 34.5, 33.7, 33.5, 31.8, 29.2, 20.4, 19.7, 19.5, 16.7. (Signals shown for main isomer only.) HRMS (ESI): calcd for $C_{49}H_{56}IrN_2O [M - Cl]^+$ 897.39776. Found 897.39656 ($\Delta = 0.86$ mmu). Yield: 74% (109 mg, 0.12 mmol, mixture of *syn/anti* isomers).

[(IrCl(CO)₂)(11)]. Method E. Starting materials: $[(IrCl(cod))(11)]$ (26.6 mg, 28.5 μ mol). 1H NMR (500 MHz, $CDCl_3$): δ 7.35 (s, 3H), 7.21 (s, 1H), 7.19 (s, 2H), 7.17 (s, 2H), 7.12 (s, 1H), 6.79 (s, 2H), 6.60 (s, 1H), 2.37 (s, 9H), 2.35 (s, 6H), 2.25 (s, 9H), 2.23 (s, 6H), 2.23 (s, 6H), 2.19 (s, 3H), 2.17 (s, 6H), 2.08 (s, 6H), 1.74 (s, 6H), 1.70 (s, 3H), 1.63 (s, 6H), 1.61 (s, 6H) (isomer mixture, assignment unclear). ^{13}C NMR (126 MHz, $CDCl_3$): δ 181.5 (C_{CO}), 181.1 (C_{CO}), 179.3 (C_{NHC}), 168.3 (C_{CO}), 167.7 (C_{CO}), 147.7, 147.6, 144.3, 135.8, 135.7, 134.0, 133.5, 131.5, 131.1, 130.9, 128.8, 128.5, 128.3, 128.1, 127.8, 127.1, 126.9, 126.8, 125.9, 125.8, 124.0, 123.8, 117.8, 117.6, 34.3, 33.8, 33.7, 31.7, 31.7, 29.9, 28.2, 20.3, 19.6, 19.4, 19.4, 19.4, 15.8, 15.4. (Isomer mixture, assignment unclear.) HRMS (ESI): calcd for $C_{43}H_{44}IrN_2O_4 [M - Cl]^+$ 845.29276. Found 845.29256 ($\Delta = 0.20$ mmu). IR ($\nu(CO)$; $[cm^{-1}]$): 2064/1984. Yield: 99% (25 mg, 28.4 μ mol, isomer mixture 70:30), isomers could not be separated.

Xanthene tetraamide (12)

A solution of 4,5-diamino-2,3,6,7,9,9-hexamethylxanthene (0.60 g, 2.0 mmol, 1.0 eq.) and triethylamine (0.56 mL, 4.0 mmol) in 15 mL of DCM was added dropwise to the solution of the acid chloride (0.91 g, 4.0 mmol, 2.0 eq.) in 10 mL of

DCM at 0 °C. The resulting mixture was stirred at 0 °C for 1 h then at rt overnight. The reaction was filtered, and the collected solid was washed with diethyl ether to give the desired product. The filtrate was then washed with water several times. The organic phase was dried over $MgSO_4$, and concentrated to give a residue, which was washed with 10% of DCM/diethyl ether. The combined solids were dried under reduced pressure to give xanthene tetraamide as a white solid. 1H NMR (500 MHz, $DMSO-d_6$): δ 10.08 (s, 2H), 9.98 (s, 2H), 7.32 (s, 2H), 6.78 (s, 4H), 2.28 (s, 6H), 2.24 (s, 6H), 2.03 (s, 6H), 1.98 (s, 12H), 1.57 (s, 6H). ^{13}C NMR (126 MHz, $DMSO-d_6$): δ 159.2, 158.2, 143.7, 135.6, 134.8, 132.2, 131.5, 131.1, 128.2, 128.1, 124.8, 122.7, 45.6, 33.8, 31.0, 20.6, 19.9, 18.0, 14.8. HRMS (ESI): calcd for $C_{41}H_{47}N_4O_5 [M + H]^+$ 675.35410. Found 675.35474 ($\Delta = 0.64$ mmu). Yield: 73% (1.00 g, 1.48 mmol).

Xanthene tetramine (13)

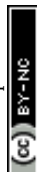
Under nitrogen, xanthene tetraamide (12) (0.8 g, 1.19 mmol, 1.0 eq.) was dissolved in $BH_3 \cdot THF$ (1 M, 15 mL, 15 mmol, 13 eq.) and heated at reflux for 3 d. After cooling to room temp., the solution was poured into a mixture of ice, water, and aq. HCl (1 M). The precipitate was filtered off and dissolved in THF/water (1:2). The solution was basified with sodium hydroxide. The product was extracted with diethyl ether, the combined fractions were washed with brine, dried with $MgSO_4$, and concentrated under reduced pressure. The crude product was then purified by column chromatography (Cy/EA 10:1) to give the diamine as a white solid. 1H NMR (500 MHz, $CDCl_3$): δ 6.87 (s, 2H), 6.75 (s, 4H), 3.79 (s, 4H), 3.22 (t, $J = 5.6$ Hz, 4H), 3.00 (t, $J = 5.6$ Hz, 4H), 2.26 (s, 6H), 2.21 (s, 6H), 2.20 (s, 6H), 2.13 (s, 12H), 1.61 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 143.5, 141.3, 135.1, 131.5, 130.2, 129.5, 127.4, 127.3, 120.3, 49.5, 48.9, 34.1, 32.6, 20.7, 20.6, 18.4, 14.7. HRMS (ESI): calcd for $C_{41}H_{55}N_4O [M + H]^+$ 619.43704. Found 619.43711 ($\Delta = 0.07$ mmu). Yield: 26% (190 mg, 0.307 mmol).

Imidazolinium chloride

The corresponding diamine (1.0 eq.) and NH_4Cl (1.0 eq.) were suspended in $HC(OEt)_3$ and 2 drops of formic acid were added. The reaction mixture was stirred at 110 °C for 12–24 h. After this time the mixture was cooled to rt and poured into water. The aqueous phase was washed with diethyl ether and extracted with DCM. The combined organic layers were dried over $MgSO_4$. After drying under reduced pressure, the imidazolinium chloride was obtained as a white solid.

Xanthene diimidazolinium salt (14·2HCl)

Starting materials: xanthene tetramine (13) (100 mg, 0.162 mmol, 1.0 eq.), NH_4Cl (17.3 mg, 0.323 mmol, 2.0 eq.) in 4 mL triethyl orthoformate. The title compound was obtained as a white solid. 1H NMR (500 MHz, MeOD): δ 7.63 (s, 2H), 7.15 (s, 4H), 5.22–4.88 (m, 4H), 4.79–4.63 (m, 4H), 2.66–2.21 (m, 30H), 1.73 (s, 6H). ^{13}C NMR (126 MHz, MeOD): δ 144.9, 142.3, 136.4, 135.1, 134.9, 131.7, 131.2, 131.2, 129.5, 122.9, 53.1, 52.7, 34.7, 33.8, 21.0, 20.2, 18.2, 15.3. HRMS (ESI): calcd



for $\text{C}_{43}\text{H}_{52}\text{ClIrN}_4\text{O} [\text{M} - \text{Cl}]^+$ 675.38242. Found 675.38155 ($\Delta = 0.86$ mmu). Yield: 63% (73 mg, 0.103 mmol).

[[IrCl(cod)]₂(14)]. Method A. Starting materials: **14**·2HCl (24.6 mg, 34.6 μmol), [IrCl(cod)]₂ (23.2 mg, 34.6 μmol), K₂CO₃ (19.1 mg, 0.138 mmol, 4.0 eq.) in acetone/DCM (3 mL/1 mL). The complex was then purified by column chromatography (Cy/EA 8 : 1, v/v) to obtain the desired complex as yellow solid. ¹H NMR (500 MHz, CD₂Cl₂): δ 7.40–7.24 (m, 2H), 7.00–6.89 (m, 4H), 5.31–5.12 (m, 1H), 4.43–4.31 (m, 1H), 4.18–3.87 (m, 8H), 3.85–3.55 (m, 2H), 3.25–3.07 (m, 1H), 3.07–2.99 (m, 2H), 2.97–2.88 (m, 1H), 2.55 (s, 3H), 2.45–2.38 (m, 6H), 2.38–2.27 (m, 18H), 2.24 (s, 3), 1.80 (s, 3H), 1.75 (s, 3H), 1.66 (s, 1H), 1.60 (s, 2H), 1.51–1.21 (m, 10H), 1.21–1.13 (m, 1H), 1.08–0.95 (m, 2H). ¹³C NMR (126 MHz, CD₂Cl₂): δ 210.0 (C_{NHC}), 209.3 (C_{NHC}), 146.9, 144.7, 139.0, 138.9, 138.8, 138.4, 138.2, 137.6, 136.9, 136.5, 136.4, 135.9, 135.2, 135.1, 134.6, 133.1, 132.3, 131.2, 130.3, 130.2, 130.1, 129.3, 129.2, 129.1, 128.1, 128.0, 127.8, 127.7, 127.5, 127.3, 127.1, 127.0, 86.9, 85.9, 85.5, 85.3, 84.7, 82.9, 80.8, 79.8, 54.8, 53.7, 53.3, 53.1, 52.9, 52.3, 52.2, 51.9, 51.6, 48.3, 36.8, 36.7, 34.6, 34.4, 34.2, 34.1, 34.0, 33.6, 33.2, 32.5, 31.5, 31.4, 31.3, 30.3, 30.2, 29.9, 29.7, 29.2, 29.0, 28.6, 26.7, 26.5, 23.3, 21.3, 20.7, 20.6, 20.5, 20.3, 19.8, 19.1, 18.9, 18.7, 17.7, 17.5, 16.7, 14.5. HRMS (ESI): calcd for $\text{C}_{59}\text{H}_{74}\text{ClIr}_2\text{N}_4\text{O} [\text{M} - \text{Cl}]^+$ 1275.4804. Found 1275.4791 ($\Delta = 1.3$ mmu). Yield: 53% (24 mg, 18.3 μmol).

[[IrCl(CO)₂](14)]. Method E. [[IrCl(cod)]₂(14)] (10 mg, 10.4 μmol , 1.0 eq.) was used. ¹H NMR (300 MHz, CD₂Cl₂): δ 7.32 (s, 2H), 7.01 (s, 2H), 6.94 (s, 2H), 5.05 (s, 2H), 4.33–4.14 (m, 2H), 4.10–3.91 (m, 4H), 2.44 (s, 6H), 2.34 (s, 12H), 2.31 (s, 12H), 1.65 (s, 6H). ¹³C NMR (75 MHz, CD₂Cl₂): δ 203.5 (C_{NHC}), 181.3 (C_{CO}), 169.1 (C_{CO}), 145.6, 139.5, 136.1, 135.5, 134.8, 132.3, 130.2, 130.0, 128.4, 127.9, 126.4, 52.7, 34.0, 33.7, 30.3, 28.6, 21.4, 20.6, 19.5, 18.8, 16.6. HRMS (ESI): calcd for $\text{C}_{47}\text{H}_{50}\text{ClIr}_2\text{N}_4\text{O}_5 [\text{M} - \text{Cl}]^+$ 1171.27228. Found 1171.26929 ($\Delta = 2.15$ mmu). IR ($\nu(\text{CO})$; [cm^{−1}]): 2070/1982. Yield: 99% (9 mg, 7.5 μmol).

[[AuCl]₂(14)]. Method A. Starting materials: **14**·2HCl (20.5 mg, 28.80 μmol , 1.0 eq.), [AuCl(SMe₂)] (17.0 mg, 57.6 μmol , 2.0 eq.), K₂CO₃ (15.9 mg, 0.115 mmol, 4.0 eq.) in acetone/DCM (3 mL/1 mL). The title complex was obtained as a white solid. Single crystals of [[AuCl]₂(14)] were obtained by slow diffusion of diethyl ether into a DCM/MeOH solution of the gold complex at 2–8 °C. ¹H NMR (500 MHz, CD₂Cl₂): δ 7.37 (s, 2H), 7.05 (s, 2H), 6.99 (s, 2H), 4.67–4.57 (m, 2H), 4.27–4.13 (m, 2H), 4.10–3.97 (m, 4H), 2.40 (s, 6H), 2.35 (s, 6H), 2.32 (s, 12H), 2.30 (s, 6H), 1.69 (s, 6H). ¹³C NMR (126 MHz, CD₂Cl₂): δ 197.7 (C_{NHC}), 145.0, 140.0, 136.2, 135.3, 135.2, 134.9, 133.3, 130.8, 130.2, 129.1, 128.3, 126.3, 52.2, 51.7, 34.1, 33.9, 21.4, 20.7, 18.9, 18.7, 16.6. HRMS (ESI): calcd for $\text{C}_{45}\text{H}_{53}\text{Au}_2\text{ClN}_5\text{O} [\text{M} - \text{Cl} + \text{MeCN}]^+$ 1108.3265. Found 1108.3269 ($\Delta = 0.6$ mmu). Yield: 62% (20 mg, 18.1 μmol).

1,1'-(2,3,6,7,9,9-Hexamethyl-9H-xanthene-4,5-diyl)bis(1H-imidazole) (15)

Cu-Catalyzed from 4,5-dibromo-2,3,6,7,9,9-hexamethyl-xanthene (3). A mixture of 4,5-dibromo-2,3,6,7,9,9-hexamethyl-

xanthene (1.0 g, 2.36 mmol, 1.0 eq.), imidazole (803 mg, 11.8 mmol, 5.0 eq.), K₂CO₃ (1.63 g, 11.8 mmol, 5.0 eq.) and copper(i) iodide (449 mg, 2.36 mmol, 1.0 eq.) in DMF (80 mL) was heated to 180 °C for 48 h. The mixture was filtered through Celite. DCM (100 mL) was added to the filtrate and stirred in a solution of ammonia (28%, 30 mL) and water (50 mL). The organic layer was separated washed with water, dried over MgSO₄ filtered and the solvent removed *in vacuo* yielding an oily residue. Purification by column chromatography (DCM/MeOH 20 : 1) affording the pure product as a off white solid. ¹H NMR (300 MHz, CD₂Cl₂): δ 7.30 (s, 2H), 7.23 (s, 2H), 7.01 (s, 2H), 6.69 (s, 2H), 2.30 (s, 6H), 1.87 (s, 6H), 1.66 (s, 6H). ¹³C NMR (75 MHz, CD₂Cl₂): δ 144.0, 138.0, 134.1, 132.6, 129.6, 128.1, 127.8, 125.0, 120.9, 34.4, 32.9, 20.4, 14.4. HRMS (ESI): calcd for $\text{C}_{25}\text{H}_{27}\text{N}_4\text{O} (\text{M} + \text{H})^+$ 399.21794. Found 399.21831 ($\Delta = 0.37$ mmu). Yield: 46% (432 mg, 1.08 mmol).

Alternative synthesis from 4,5-diamino-2,3,6,7,9,9-hexamethylxanthene (6). A mixture of glacial acetic acid (5 mL), paraformaldehyde (127 mg, 4.22 mmol, 2.5 eq.) and 39% aqueous glyoxal (0.48 mL, 4.22 mol, 2.5 eq.) was heated to 70 °C. Then a solution of 4,5-diamino-2,3,6,7,9,9-hexamethylxanthene (6) (500 mg, 1.69 mmol, 1.0 eq.), ammonium acetate (273 mg, 3.54 mmol, 2.1 eq.) in 1 mL water and glacial acetic acid (2 mL) was added after which the reaction mixture was heated at 70 °C for 24 h. After cooling to rt the resulting brown solution was added very slowly to a stirred solution of a sat. NaHCO₃, the precipitate was filtered and washed with water. The crude product was then purified by column chromatography (DCM/MeOH 20 : 1) to give a off white solid. Yield: 28% (190 mg, 0.477 mmol).

Xanthene diimidazolium salt (16-2HBr)

1,1'-(2,3,6,7,9,9-Hexamethyl-9H-xanthene-4,5-diyl)bis(1H-imidazole) (443 mg, 1.11 mmol, 1.0 eq.) and 1,5-dibromopentane (256 mg, 151.4 μL , 1.11 mmol, 1.0 eq.) were added to 60 mL acetonitrile in a Schlenk flask. The mixture was stirred under reflux for 5 d while a precipitate formed. The mixture was allowed to cool before diethyl ether was added. The precipitate was filtrated, washed with pentane and dried under reduce pressure to obtain the title compound as a white powder. ¹H NMR (500 MHz, MeOD): δ 9.31 (s, 2H), 8.03 (d, *J* = 1.6 Hz, 2H), 7.80 (d, *J* = 1.6 Hz, 2H), 7.72 (s, 2H), 4.64–4.54 (m, 2H), 4.51–4.43 (m, 2H), 2.44 (s, 6H), 2.24–2.09 (m, 4H), 2.02 (s, 6H), 1.86 (s, 3H), 1.73 (s, 3H), 1.63–1.50 (m, 1H), 0.55–0.42 (m, 1H). ¹³C NMR (126 MHz, MeOD): δ 143.6, 139.1, 134.9, 134.8, 131.6, 129.5, 126.7, 124.9, 122.6, 50.1, 35.0, 34.5, 32.1, 27.4, 20.7, 19.9, 14.1. HRMS (ESI): calcd for $\text{C}_{30}\text{H}_{35}\text{Br}_2\text{N}_4\text{O} [\text{M} - \text{H}]^+$ 625.11825. Found 625.11831 ($\Delta = 0.21$ mmu). Yield: 84% (590 mg, 0.939 mmol).

Xanthene diimidazolium salt (16-2HBF₄)

According to the general procedure **16-2HBr** (50 mg) was used. ¹H NMR (500 MHz, CD₂Cl₂): δ 8.55 (s, 2H), 7.81 (s, 2H), 7.47 (s, 2H), 7.33 (s, 2H), 4.45–4.27 (m, 4H), 2.33 (s, 6H), 2.17–2.01 (m, 4H), 1.83 (s, 6H), 1.75 (s, 3H), 1.68 (s, 3H), 1.56–1.41 (m, 1H), 0.72–0.62 (m, 1H). ¹³C NMR (126 MHz, CD₂Cl₂): δ 142.7, 137.6,



134.0, 133.8, 131.1, 128.6, 125.8, 124.2, 121.4, 50.1, 34.2, 32.8, 26.9, 20.3, 20.2, 14.4. Yield: 99% (51 mg, 79.4 μmol).

[[AgBr]₂(16)]. Method C. Starting materials: **16-2HBr** (100 mg, 159 μmol , 1.0 eq.) and silver(i) oxide (40.6 mg, 175 μmol , 1.1 eq.) in 3 mL dry MeOH. The title complex was obtained as a white solid. ¹H NMR (500 MHz, CD₂Cl₂): δ 7.69 (s, 2H), 7.44 (s, 2H), 6.90 (s, 2H), 4.17–4.05 (m, 2H), 3.31–3.21 (m, 2H), 2.33 (s, 6H), 1.91 (s, 3H), 1.77 (s, 6H), 1.64–1.56 (m, 2H), 1.55 (s, 3H), 1.35–1.26 (m, 3H), 0.70–0.60 (m, 1H), 0.22–0.12 (m, 1H). ¹³C NMR (126 MHz, CD₂Cl₂): δ 181.4 and 181.5 (dd, $J_{\text{Ag-C}} = 195.6$ Hz, $J_{\text{Ag-C}} = 195.0$ Hz) 143.8, 135.0, 133.3, 128.9, 128.2, 127.1, 123.9, 123.7, 50.3, 37.1, 34.5, 29.5, 27.7, 20.5, 20.4, 15.1. HRMS (APCI): calcd for C₃₀H₃₄Ag₂BrN₄O [M – Br]⁺ 759.00124. Found 759.00121 ($\Delta = 0.04$ mmu). Yield: 63% (85 mg, 101 μmol).

[[AuCl]₂(16)]. Method C. Starting materials: **16-2HBr** (40 mg, 63.7 μmol , 1.0 eq.), silver(i) oxide (16.2 mg, 70.0 μmol , 1.1 eq.), [AuCl(SMe₂)] (37.5 mg, 127 μmol , 2.0 eq.) in 3 mL dry MeOH. The title complex was obtained as a white solid. ¹H NMR (500 MHz, CD₂Cl₂): δ 7.49 (s, 2H), 7.40 (s, 2H), 6.96 (s, 2H), 3.92–3.84 (m, 2H), 3.47–3.38 (m, 2H), 2.35 (s, 6H), 1.94 (s, 3H), 1.74 (s, 6H), 1.60–1.56 (m, 2H), 1.54 (s, 3H), 1.48–1.39 (m, 2H), 0.80–0.69 (m, 1H), 0.41–0.28 (m, 1H). ¹³C NMR (126 MHz, CD₂Cl₂): δ 185.5 (C_{NHC}), 143.8, 135.4, 133.3, 129.1, 128.4, 126.2, 124.3, 122.6, 50.1, 37.3, 34.6, 29.3, 28.4, 21.0, 20.5, 15.1. HRMS (APCI): calcd for C₃₀H₃₄Au₂ClN₄O [M – Cl]⁺ 895.17470. Found 895.17477 ($\Delta = 0.06$ mmu). Yield: 46% (27 mg, 29 μmol).

[[CuI]₂(16)]. **[[AgBr]₂(16)]** (20 mg, 23.8 μmol , 1.0 eq.) and CuI (9.1 mg, 47.5 μmol , 2.0 eq.) were dissolved in 3 mL dry DCM and stirred at rt in the absence of light for 24 h. The mixture was filtered through Celite and the solvent was removed under reduced pressure to obtain the desired complex as a white solid. ¹H NMR (500 MHz, CD₂Cl₂): δ 7.49–7.46 (m, 4H), 6.89 (d, $J = 1.8$ Hz, 2H), 4.00–3.93 (m, 2H), 3.16–3.06 (m, 2H), 2.35 (s, 6H), 1.96 (s, 2H), 1.79 (s, 6H), 1.58 (s, 6H), 1.35–1.27 (m, 2H), 0.57–0.46 (m, 1H), 0.23–0.15 (m, 1H). ¹³C NMR (126 MHz, CD₂Cl₂): δ 177.6 (C_{NHC}), 144.1, 135.3, 133.5, 128.7, 128.6, 126.8, 124.1, 122.5, 50.0, 37.2, 34.7, 28.6, 28.3, 20.5, 20.5, 15.2. HRMS (APCI): calcd for C₃₀H₃₄CuN₄O₂ [M – CuI₂ + O]⁺ 545.19723. Found 545.19762 ($\Delta = 0.40$ mmu). Yield: 35% (7 mg, 8.3 μmol).

[[RhCl(cod)]₂(16)]. Method C. Starting materials: **16-2HBr** (50.0 mg, 79.6 μmol , 1.0 eq.), silver(i) oxide (20.3 mg, 87.5 μmol , 1.1 eq.), [RhCl(cod)]₂ (39.2 mg, 79.6 μmol , 1.0 eq.) in 5 mL dry MeOH. The crude product was purified by short column chromatography (pure DCM then switched to pure EA) to obtain the desired complex as yellow solid. Single crystals of **[[RhCl(cod)]₂(16)]** were obtained by slow diffusion of diethyl ether into a DCM solution of the Rh-complex at 2–8 °C. ¹H NMR (500 MHz, CD₂Cl₂): δ 7.43 (s, 2H), 6.83 (d, $J = 2.0$ Hz, 2H), 6.73 (d, $J = 2.0$ Hz, 2H), 5.25–5.17 (m, 2H), 4.77–4.70 (m, 2H), 4.62–4.54 (m, 2H), 4.03–3.96 (m, 2H), 3.48–3.38 (m, 2H), 2.75–2.66 (m, 2H), 2.50–2.42 (m, 2H), 2.42 (s, 6H), 2.34–2.28 (m, 2H), 2.21 (s, 6H), 2.14–2.06 (m, 2H), 1.89 (s, 3H), 1.87–1.75 (m, 6H), 1.75–1.66 (m, 2H), 1.62–1.55 (m, 2H), 1.49 (s, 3H),

1.38–1.26 (m, 5H), 0.62–0.47 (m, 1H). ¹³C NMR (126 MHz, CD₂Cl₂): δ 182.35 (d, $J = 51.8$ Hz, C_{NHC}), 144.3, 136.3, 132.9, 127.7, 127.5, 127.4, 124.8, 121.3, 97.0, 96.9, 96.0, 95.9, 69.8, 69.7, 67.5, 67.4, 51.0, 35.9, 34.6, 34.0, 31.5, 30.0, 29.1, 29.0, 27.8, 21.3, 20.4, 17.3. HRMS (APCI): calcd for C₄₆H₅₈ClN₄ORh₂ [M – Cl]⁺ 923.24012. Found 923.24037 ($\Delta = 0.26$ mmu). Yield: 26% (20 mg, 20.8 μmol).

[[RhBr(cod)]₂(16)]. Method D. Starting materials: **16-2HBr** (30.0 mg, 47.74 μmol , 1.0 eq.), [RhCl(cod)]₂ (23.54 mg, 47.7 μmol , 1.0 eq.), NaOAc (7.8 mg, 95.5 μmol , 2.0 eq.), K₂CO₃ (13.2 mg, 95.5 μmol , 2.0 eq.) and KBr (excess) in 6 mL dry MeCN. The crude product was purified by short column chromatography (pure DCM then switched to pure EA) to obtain the desired complex as yellow solid. ¹H NMR (500 MHz, CD₂Cl₂): δ 7.43 (s, 2H), 6.84 (d, $J = 1.9$ Hz, 2H), 6.74 (d, $J = 1.8$ Hz, 2H), 5.26–5.16 (m, 2H), 4.86–4.78 (m, 2H), 4.73–4.66 (m, 2H), 4.05–3.96 (m, 2H), 3.56–3.47 (m, 2H), 2.85–2.78 (m, 2H), 2.41 (s, 6H), 2.33–2.27 (m, 2H), 2.22 (s, 6H), 2.11–2.05 (m, 2H), 1.89 (s, 3H), 1.85–1.77 (m, 5H), 1.74–1.68 (m, 4H), 1.61–1.54 (m, 2H), 1.54–1.52 (m, 2H), 1.49 (s, 3H), 1.39–1.29 (m, 4H), 0.59–0.46 (m, 1H). ¹³C NMR (126 MHz, CD₂Cl₂): δ 182.3 (d, $J = 51.8$ Hz, C_{NHC}), 144.6, 136.5, 133.2, 127.8, 127.6, 125.4, 121.2, 96.8, 96.7, 95.8, 95.8, 70.7, 70.6, 68.7, 68.5, 51.8, 36.0, 34.7, 34.3, 31.4, 30.5, 29.2, 28.9, 28.1, 21.5, 20.5, 18.4. HRMS (APCI): calcd for C₄₆H₅₈BrN₄ORh₂ [M – Br]⁺ 967.18986. Found 967.18920 ($\Delta = 0.65$ mmu). Yield: 38% (19 mg, 18.1 μmol).

[[IrBr(cod)]₂(16)]. Method D. Starting materials: **16-2HBr** (100 mg, 0.16 mmol, 1.0 eq.), [IrCl(cod)]₂ (106.9 mg, 0.16 mmol, 1.0 eq.), NaOAc (26.1 mg, 0.32 mmol, 2.0 eq.), K₂CO₃ (43.9 mg, 0.32 mmol, 2.0 eq.) and KBr (excess) in 10 mL dry MeCN. The crude product was purified by short column chromatography (pure DCM then switched to pure EA) to obtain the desired complex as yellow/orange solid. Single crystals of **[[IrBr(cod)]₂(16)]** were obtained by slow diffusion of diethyl ether into a DCM solution of the Ir-complex at 2–8 °C. ¹H NMR (300 MHz, CD₂Cl₂): δ 7.41 (s, 2H), 6.89 (d, $J = 1.9$ Hz, 2H), 6.75 (d, $J = 1.9$ Hz, 2H), 5.09–4.97 (m, 2H), 4.53–4.43 (m, 2H), 4.26–4.14 (m, 2H), 3.95–3.83 (m, 2H), 3.28–3.15 (m, 2H), 2.60–2.47 (m, 2H), 2.35 (s, 6H), 2.29–2.20 (m, 2H), 2.10 (s, 6H), 2.07–2.01 (m, 2H), 1.98–1.92 (m, 2H), 1.88 (s, 3H), 1.83–1.67 (m, 4H), 1.64–1.57 (m, 2H), 1.54–1.51 (m, 2H), 1.48 (s, 3H), 1.37–1.33 (m, 2H), 1.20–1.03 (m, 3H), 1.01–0.89 (m, 2H), 0.68–0.56 (m, 1H). ¹³C NMR (75 MHz, CD₂Cl₂): δ 180.3 (C_{NHC}), 144.7, 136.2, 133.1, 127.8, 127.7, 127.4, 125.1, 121.3, 83.3, 81.4, 52.2, 51.3, 35.9, 35.4, 34.3, 32.3, 31.1, 29.0, 28.7, 28.6, 21.7, 20.5, 18.3. HRMS (APCI): calcd for C₄₆H₅₈BrN₄OIr₂ [M – Br]⁺ 1147.3047. Found 1147.3019 ($\Delta = 1.0$ mmu). Yield: 44% (86 mg, 70 μmol).

[[RhCl(CO)₂]₂(16)]. Method E. **[[RhCl(cod)]₂(16)]** (10 mg, 10.4 μmol , 1.0 eq.) was used. ¹H NMR (500 MHz, CD₂Cl₂): δ 7.42 (s, 2H), 7.00 (d, $J = 1.8$ Hz, 2H), 6.90 (d, $J = 1.8$ Hz, 2H), 5.10–5.02 (m, 2H), 4.00–3.93 (m, 2H), 2.43–2.38 (m, 2H), 2.36 (s, 6H), 2.06 (s, 6H), 1.85 (s, 3H), 1.82–1.76 (m, 2H), 1.41 (s, 3H), 1.32–1.27 (m, 1H), 0.51–0.37 (m, 1H). ¹³C NMR (126 MHz, CD₂Cl₂): δ 186.4 (d, $J_{\text{Rh-C}} = 54.3$ Hz, C_{CO}), 181.9 (d, $J_{\text{Rh-C}} = 74.2$ Hz, C_{NHC}), 177.4 (d, $J_{\text{Rh-C}} = 44.8$ Hz, C_{CO}), 144.3, 135.6, 133.2,



128.8, 128.6, 126.9, 124.6, 123.8, 50.4, 35.7, 34.4, 29.2, 29.1, 21.0, 20.5, 16.6. HRMS (ESI): calcd for $C_{34}H_{34}ClN_4O_5Rh_2 [M - Cl]^+$ 819.03223. Found 819.03115 ($\Delta = 1.09$ mmu). IR ($\nu(CO)$; $[cm^{-1}]$): 2076/1994. Yield: 90% (8 mg, 9.4 μ mol).

[[IrBr(CO)₂]₂(16)]. Method E. **[[IrBr(cod)]₂(16)]** (10 mg, 8.2 μ mol, 1.0 eq.) was used. 1H NMR (500 MHz, CD_2Cl_2): δ 7.43 (s, 2H), 7.04 (d, $J = 1.9$ Hz, 2H), 6.91 (d, $J = 1.9$ Hz, 2H), 5.11–5.00 (m, 2H), 3.99–3.89 (m, 2H), 2.41–2.35 (m, 2H), 2.34 (s, 6H), 2.00 (s, 6H), 1.86 (s, 4H), 1.81–1.68 (m, 3H), 1.41 (s, 3H), 0.48–0.33 (m, 1H). ^{13}C NMR (126 MHz, CD_2Cl_2): δ 181.6 (C_{CO}), 176.2 (C_{NHC}), 166.7 (C_{CO}), 144.7, 135.3, 133.2, 129.1, 128.6, 126.6, 124.9, 123.7, 50.9, 35.4, 34.6, 28.8, 28.3, 20.9, 20.5, 17.2. HRMS (APCI): calcd for $C_{34}H_{34}BrN_4O_5Ir_2 [M - Br]^+$ 1043.09656. Found 1043.0936 ($\Delta = 0.83$ mmu). IR ($\nu(CO)$; $[cm^{-1}]$): 2072/1982. Yield: 98% (9 mg, 8.0 μ mol).

[[PdCl(allyl)]₂(16)]. **[[AgBr]₂(16)]** (25 mg, 29.7 μ mol, 1.0 eq.) and **[[PdCl(allyl)]₂** (11.5 mg, 31.2 μ mol, 1.05 eq.) were dissolved in 6 mL dry DCM and stirred at rt in the absence of light for 24 h. The mixture was filtered through Celite and the solvent was removed under reduced pressure. The crude product was purified by short column chromatography (pure DCM then switched to pure EA) to obtain the desired complex as a pale, yellow solid. 1H NMR (500 MHz, CD_2Cl_2): 7.34 (s, 2H), 6.98 (s, 2H), 6.87 (s, 2H), 5.15 (s, 1H), 4.96 (s, 2H), 4.60 (s, 1H), 3.90 (s, 4H), 3.13 (s, 1H), 3.08–2.88 (m, 2H), 2.83 (s, 2H), 2.31 (s, 6H), 2.13 (s, 3H), 2.03–1.91 (m, 3H), 1.82 (s, 3H), 1.79–1.58 (m, 4H), 1.52 (s, 3H), 1.20–0.99 (m, 1H), 0.66–0.35 (m, 1H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 181.6 (C_{NHC}), 144.1, 143.7, 136.0, 133.0, 128.4, 128.2, 128.0, 127.8, 123.7, 123.4, 123.0, 114.8, 114.4, 111.7, 71.4, 63.2, 49.9, 36.1, 34.1, 30.1, 29.2, 20.9, 20.5, 15.9. HRMS (ESI): calcd for $C_{36}H_{44}ClN_4OPd [M - Cl]^+$ 795.12679. Found 795.12789 ($\Delta = 0.41$ mmu). Yield: 52% (13 mg, 15.5 μ mol).

[[Au(AuCl)₂(Cl)](16)₂]. 16-2HBr (20 mg, 31.8 μ mol, 1.0 eq.) and silver(i) oxide (11.1 mg, 47.7 μ mol, 1.5 eq.) were dissolved in 3 mL dry MeOH and stirred at rt in the absence of light for 24 h. After this time **[AuCl(SMe₂)]** (13.8 mg, 46.7 μ mol, 1.5 eq.) was added, the mixture was stirred at 50 °C for 2 h then for 12 h at rt. in the absence of light. The mixture was filtered through Celite and the solvent was removed under reduced pressure. The residue was dissolved in a minimum amount of DCM and diethyl ether was added. The precipitate was filtered and dried under reduce pressure to obtain the title compound as a white solid. Single crystals of **[[Au(AuCl)₂(Cl)](16)₂]** were obtained by slow diffusion of diethyl ether into a DCM solution of the gold complex at 2–8 °C. 1H NMR (500 MHz, CD_2Cl_2): δ 7.40 (s, 1H), 7.36 (s, 1H), 7.33 (d, $J = 1.9$ Hz, 1H), 7.27 (d, $J = 1.8$ Hz, 1H), 6.84 (d, $J = 2.0$ Hz, 1H), 6.79 (d, $J = 1.9$ Hz, 1H), 4.63–4.52 (m, 1H), 4.45–4.34 (m, 1H), 4.14–4.07 (m, 1H), 4.07–3.99 (m, 1H), 2.32 (s, 3H), 2.23 (s, 3H), 2.03–1.94 (m, 2H), 1.85 (s, 3H), 1.83–1.77 (m, 1H), 1.73 (s, 3H), 1.64 (s, 3H), 1.43 (s, 3H), 1.37–1.25 (m, 2H), 1.11–0.98 (m, 1H). ^{13}C NMR (126 MHz, CD_2Cl_2): δ 185.6 (C_{NHC}), 172.8 (C_{NHC}), 143.8, 143.8, 134.8, 134.7, 133.1, 132.3, 129.1, 129.0, 128.2, 128.2, 126.3, 126.0, 123.8, 123.6, 122.5, 122.0, 51.2, 50.6, 34.4, 34.4, 32.1, 28.8, 28.5, 21.4, 20.6, 20.5, 15.1, 14.5. HRMS (APCI): calcd for $C_{30}H_{34}Au_2ClN_4O [M - Cl]$

– $C_{30}H_{34}AuClN_4O]^+$ 895.17470. Found 895.17496 ($\Delta = 0.26$ mmu). Yield: 58% (15 mg, 9.2 μ mol).

Results and discussion

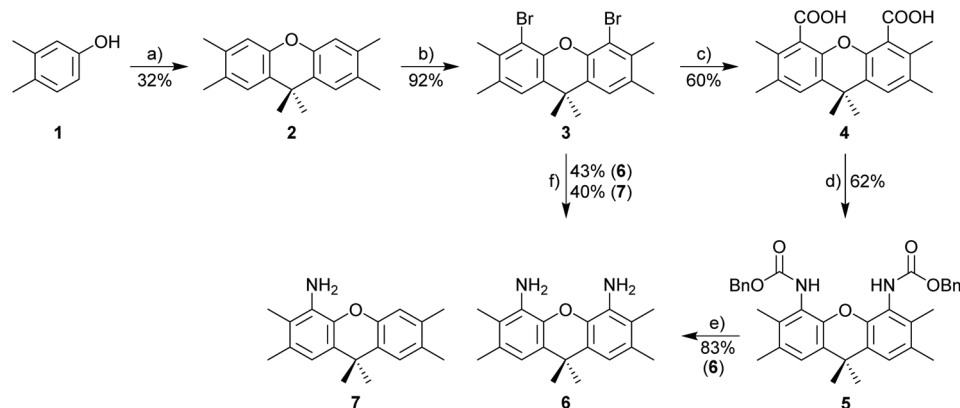
In order to realize binuclear structures (Scheme 1d), the 4,5-positions at the xanthene scaffold appear to be ideal anchoring points for the N-heterocyclic carbenes. The two 4,5-nitrogen atoms belonging to an imidazolylidene or imidazolidinylidene unit are positioned at a distance of almost 500 pm and since the tilt angle between the two heterocyclic rings allows for some variability, the distances of metals bound the carbene carbon can range between approx. 300–700 pm. The coordination of a single metal in a chelating fashion appears to be unfavorable. In order to retain the orthogonality of the planes of the respective NHC units relative to the xanthene plane, additional methyl group next to the 4,5-NHC site at the 3,6-positions of the xanthene are needed. The advantage of the xanthene unit (as opposed to a naphthalene scaffold) is the absence of atoms between the two NHC units, which for naphthalene would host a CH-unit prone to CH-activation reactions. Based on these considerations 3,6,9,9-tetramethyl-9H-xanthene-4,5-diamine appears to be the ideal building block for the construction of the bisNHC ligands. Similar ligands, but without the crucial 3,6-dimethyl units were reported previously by Messerle *et al.*⁴² and the Saito group.⁴³

Synthesis

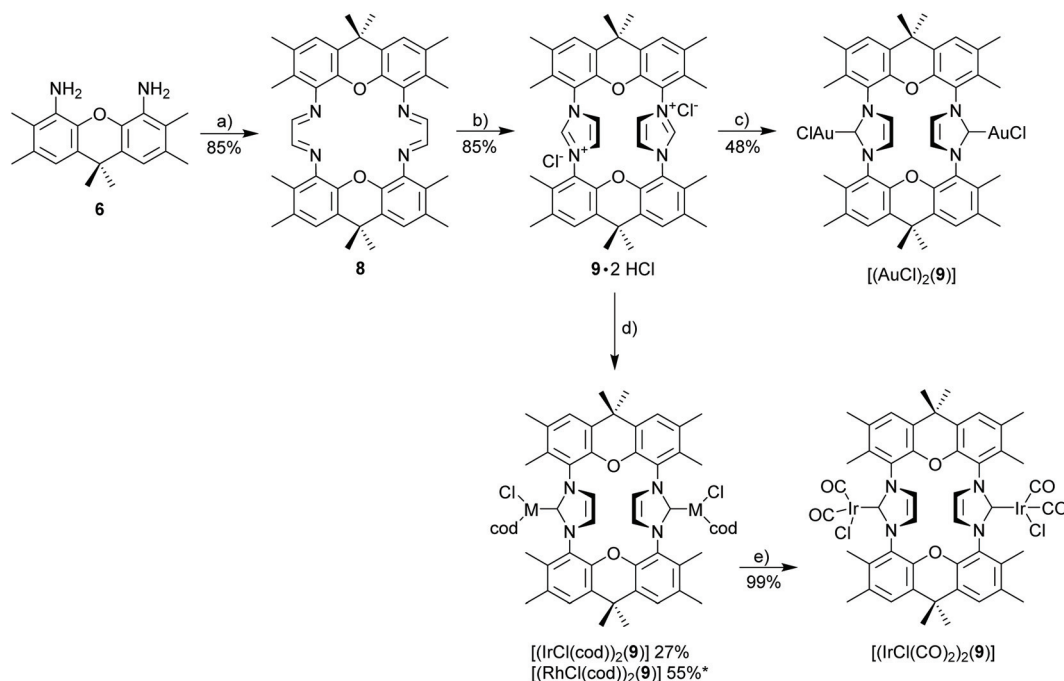
The synthesis of 3,6,9,9-tetramethyl-9H-xanthene-4,5-diamine **6** as the key component for macrocyclic NHC ligands is shown in Scheme 2. Hexamethylxanthene was synthesized according to a modified procedure by Caruso and Lee.³⁹ The Takeuchi *et al.* synthesis of 1,8-diamino-xanthene⁴⁰ was significantly improved by adding Na_2CO_3 to the reaction mixture. Nonetheless, a significant amount of monoamine **7** (yield 40%) is still formed. The hazardous azide chemistry and the tedious purification of the diamino-xanthene (chromatographic separation from monoamino-xanthene, which is produced in approx. equimolar amounts) prompted us to develop an alternative approach *via* carboxylic acid and carbamate and Hofmann rearrangement, since attempts to directly introduce the amino group *via* Pd- or Cu-catalyzed cross coupling reactions utilizing 1,8-dibromo-xanthene were not successful. In contrast to the azide route, the sequence of reactions to **6** *via* **4** and **5** provides exclusively diamine **6**.

Diamine **6** is converted into diimine **8** according to the general Hintermann procedure⁴⁴ and then into the respective diimidazolium salt **9-2HCl** (Scheme 3)²⁸ in 85% yield (Scheme 3). Initial attempts to synthesize dinuclear NHC metal complexes employing the weak base approach^{45,46} turned out to be unsuccessful. In the case of the gold complex the transmetalation employing the *in situ* generated **[[AgCl]₂(9)]** provides a reasonable yield (48%) of **[[AuCl]₂(9)]**. The transfer of the NHC to **[MCl(cod)]₂** ($M = Rh, Ir$) using AgNHC, normally is a very reliable method,⁴⁷ but also fails





Scheme 2 Synthesis of 4,5-diaminoxanthene **6**. Reagents and conditions: (a) $\text{CH}_3\text{SO}_3\text{H}$, 110 °C for 5 d, then 150 °C for 6 h; (b) Br_2 , CH_2Cl_2 , –78 °C to rt, 12 h; (c) $n\text{BuLi}$, CO_2 , THF, –78 °C, 2 h; (d) DPPA, BnOH , NEt_3 , toluene, 80 °C, 12 h; (e) KOH , EtOH , 90 °C, 24 h; (f) NaN_3 , CuI , DMEDA, Na_2CO_3 , DMSO, 100 °C, 24 h.



Scheme 3 Synthesis of azolium salt **9·2HCl** and derived metal complexes. Reagents and conditions: (a) glyoxal, $p\text{TsOH}$, $n\text{BuOH}$, 50 °C; (b) paraformaldehyde, Me_3SiCl , EtOAc , 70 °C, 24 h; (c) Ag_2O , MeOH , rt, 24 h then $[\text{AuCl}(\text{SMe}_2)]$, 50 °C, 2 h; (d) $[\text{MCl}(\text{cod})]_2$ ($\text{M} = \text{Ir}, \text{Rh}$), sodium amylate, THF, –78 °C; (e) CO , 0 °C, CH_2Cl_2 30 min; (* yield of crude complex).

with the diimidazolium salt **9·HCl**. Finally, the complexes $[\text{MCl}(\text{cod})]_2(\mathbf{9})$ ($\text{M} = \text{Rh}, \text{Ir}$) were obtained from the reaction of the free carbene (generated with sodium amylate and diimidazolium salt **9·2HCl**) with $[\text{MCl}(\text{cod})]_2$ ($\text{M} = \text{Rh}, \text{Ir}$). Normally, $[\text{MCl}(\text{cod})(\text{NHC})]$ complexes are very stable,^{29,48–50} however, $[\text{RhCl}(\text{cod})(\mathbf{9})]$ turned out to be labile and purification was difficult since the complex suffers from very significant decomposition during chromatographic purification. The closely related iridium complex $[\text{IrCl}(\text{cod})]_2(\mathbf{9})$ is slightly more stable and chromatographic purification affords pure complex, albeit in moderate yield since again a significant amount of the complex decom-

poses during chromatographic purification. The substitution of the cyclooctadiene by CO proceeds cleanly to provide $[\text{IrCl}(\text{CO})_2]_2(\mathbf{9})$ in virtually quantitative yield, while the analogous reaction of the Rh-based relative was not successful.

X-Ray crystal structure of $[(\text{IrCl}(\text{cod}))_2(\mathbf{9})]^{51}$

The bisNHC ligand **9** binds two $\text{IrCl}(\text{cod})$ units in a slightly distorted square-planar geometry (Fig. 1). The distance between the two iridium (702.4 pm) is sufficiently large to accommodate the two bulky 1,5-cyclooctadiene ligands between the two metals, while the two smaller chloro ligands are located in the periphery



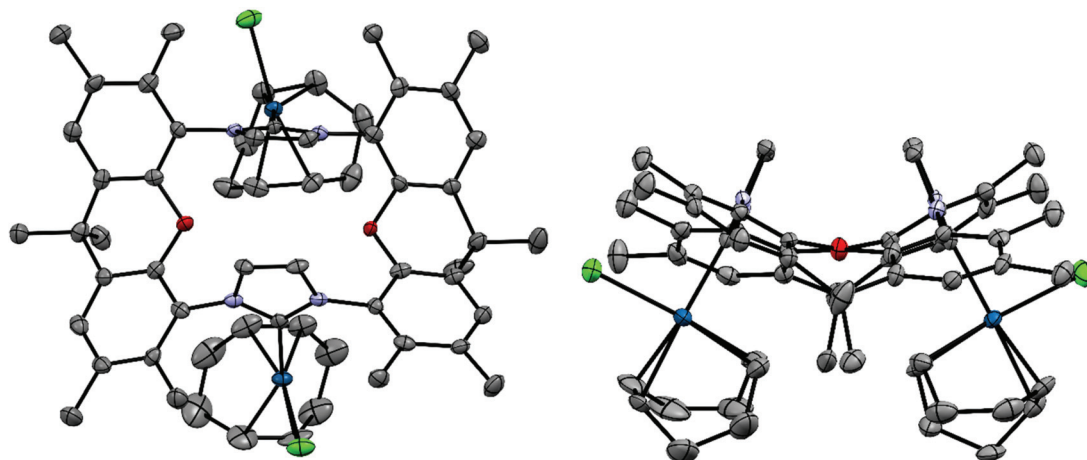


Fig. 1 X-ray crystal structure (thermal ellipsoids 80%) of $[(\text{IrCl}(\text{cod}))_2(\mathbf{9})]$ (colour code: Ir blue, Cl green, O red, N blue, H not displayed) plots: perpendicular to xanthene plane and along the oxygen–oxygen axis. Important distances (pm), bond lengths (pm) and angles ($^\circ$): Ir...Ir 702.4, Ir–C (NHC) 205.0(6), 206.1(6), Ir–Cl 238.0(2), 238.1(2), Ir–C(cod) 210.7(6), 214.2(7), 215.0(6), 219.7(7) (av. 214.9), 209.6(6), 211.4(7), 215.7(8), 220.3(8) (av. 214.3), Cl–Ir–C(NHC) 91.8(2), 92.3(2), C(NHC)–Ir–C(cod) 173.6(3), 173.1(3) and 149.9(2), 149.1(2).

of the molecule. With a view to the structure of $[(\text{Au})(\text{AuCl})_2\text{Cl}](\mathbf{16})_2$ (Fig. 4) the central placement of the two bulky cod-units in the Ir complex and in $[(\text{RhCl}(\text{cod}))_2(\mathbf{16})]$ (Fig. 3) is unexpected (see also discussion of $[(\text{Au})(\text{AuCl})_2\text{Cl}](\mathbf{16})_2$) but eventually the attractive contribution of dispersion forces between the two cod units are underestimated.

The bonds lengths in the coordination sphere of the two distinct iridium atoms are similar to those observed in related complexes.^{52–55} Typically, the Ir–C(cod) bond lengths of a *trans*-olefin is 10 pm longer than for the respective *cis*-olefin due to the *trans*-effect of the NHC ligand, which is also observed for $[(\text{IrCl}(\text{cod}))_2(\mathbf{9})]$.

The limited stability of metal complexes (Scheme 3) prompted us to attempt the synthesis of the related “open” complexes to better understand the properties of the macrocyclic ligand (Scheme 4). This is convenient since monoamine **7** is formed in significant amounts as a by-product of diamine **6** via the azide route. In order to better understand, why the metal complexes with NHC **9** show untypical behavior, the closely related azolium salt **11**·HCl (Scheme 4) was synthesized from amino-xanthene **7**. NHC **11** contains only a single NHC ligand and the weak base approach provides good yields (75%) of the respective $[\text{IrCl}(\text{cod})(\mathbf{11})]$. The stability of the complex is comparable to that of the established $[(\text{IrCl}(\text{cod}))(\text{IMes})]$ complexes.⁴⁷ Both complexes are stable during chromatographic purification and solutions remain unchanged over several days. Bulky metal complexes with NHC **11** occur as a mixture of *syn/anti*-isomers, since the bulky *ortho*-substituents prevent N–C-rotation along which the two isomers (for $[\text{IrCl}(\text{cod})(\mathbf{11})]$ ratio 70 : 30) could interconvert. Temperature-variable NMR-experiments (up to 370 K in toluene- d_8) with $[\text{IrCl}(\text{cod})(\mathbf{11})]$ did not provide evidence for isomer interconversion.

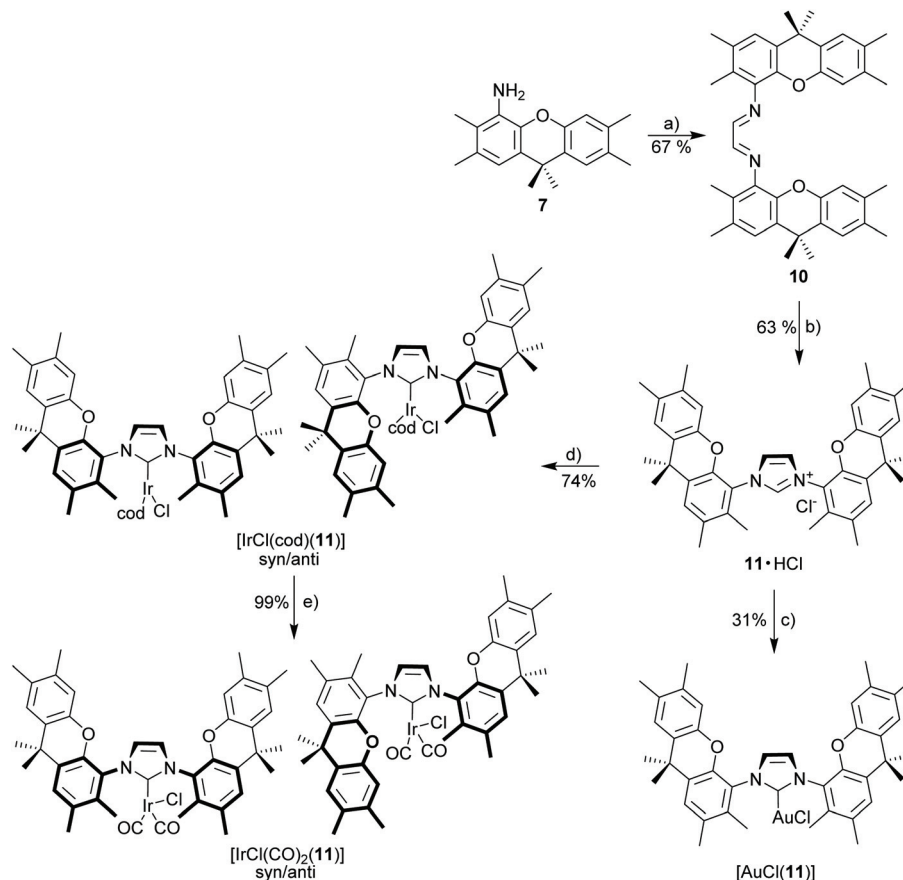
In order to better evaluate the properties of binuclear open complexes compared to binuclear, closed (macrocyclic) com-

plexes with NHC **9** (Scheme 3) complexes with the open NHC ligand **14** were synthesized. Azolium salt **14**·2HCl containing two NHC units in an open structure was synthesized according to Scheme 5. NHC **14** is similar to NHC **9** concerning the groups directly bonded to the NHC ligands. However, the two NHC units in **8** are part of a macrocyclic structure with an enforced *syn*-orientation of the two NHC units, while NHC **14** has a flexible structure and the NHC units also have the chance to be in an *anti*-orientation. NHC metal complexes with NHC **9** were synthesized following established synthetic methodology. Both complexes $[(\text{AuCl})_2(\mathbf{14})]$ and $[(\text{IrCl}(\text{cod}))(\mathbf{14})]$ are stable with properties very similar to those of the monometallic $[\text{IrCl}(\text{cod})(\text{IMes})]$ complex. $[(\text{IrCl}(\text{cod}))_2(\mathbf{14})]$ is closely related to complexes reported by Messerle *et al.*⁴² The important difference to previously synthesized xanthene-bisNHC complexes are the four *ortho*-methyl groups, which enforce an approximately orthogonal orientation of the imidazolium ring relative to the xanthene unit. Based on this, a chelate type complex involving both NHC ligands in **11** and a single metal appears not to be possible, which is intended to enforce the close proximity of two metal centers. In the absence of those methyl groups the xanthene-based NHC ligands were reported to act as tweezer type ligands, with both NHC ligands coordinating the same metal.^{43,56,57} The derived metal complexes (Scheme 5) are stable and consist of a single isomer.

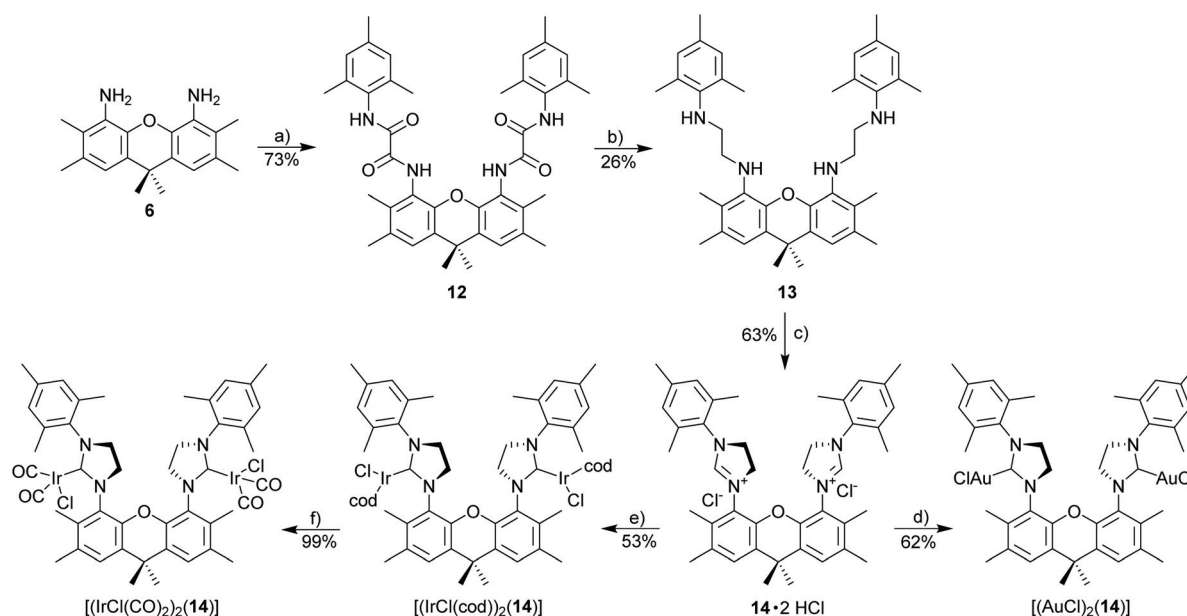
Due to potentially unfavorable steric interactions of the mesityl groups in the *syn*-isomer the *anti*-isomer is expected to be the favored isomer, which is confirmed by the X-ray crystal structure of $[(\text{AuCl})_2(\mathbf{14})]$ (Fig. 2).⁵⁸ The most obvious feature of the crystal structure is the *anti*-orientation of the two (NHC) AuCl – units resulting in Au...Au distance of 904 pm, with gold displaying the typical linear coordination.

So far, our attempts to obtain stable binuclear metal complexes were not entirely satisfactory. Based on this, a different approach was chosen by linking the two imidazoles with an





Scheme 4 Synthesis of imidazolium salt **11·HCl** and derived metal complexes. Reagents and conditions: (a) glyoxal, *p*TsOH, EtOH, 50 °C; (b) paraformaldehyde, Me₃SiCl, EtOAc, 70 °C, 24 h; (c) [AuCl(SMe₂)], K₂CO₃, acetone, 50 °C; (d) [IrCl(cod)]₂, K₂CO₃, acetone, 50 °C; (e) CO, 0 °C, 30 min, CH₂Cl₂.



Scheme 5 Synthesis of imidazolium salt **14·2HCl** and derived metal complexes. Reagents and conditions: (a) MesNHC(O)COCl, NEt₃, 0 °C to rt, 1 h; (b) BH₃·THF, reflux, 3 d; (c) triethyl orthoformate, NH₄Cl, 110 °C, 24 h; (d) [AuCl(SMe₂)], K₂CO₃, acetone/CH₂Cl₂, 50 °C; (e) [IrCl(cod)]₂, K₂CO₃, acetone/CH₂Cl₂, 50 °C; (f) CO, 0 °C, 30 min, CH₂Cl₂.



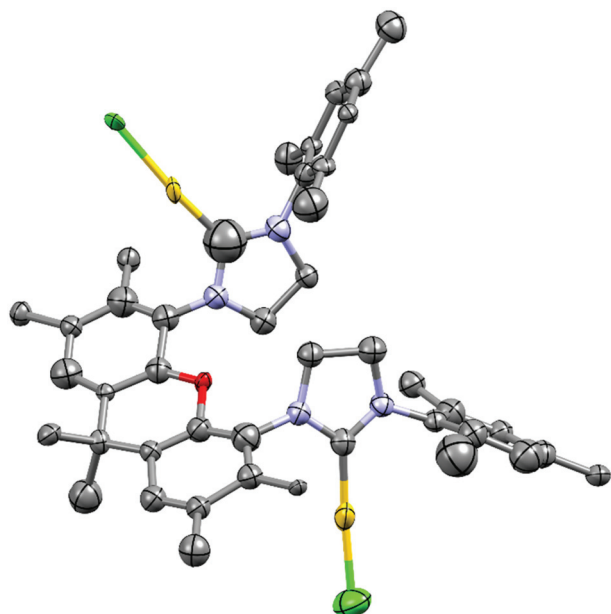


Fig. 2 X-ray crystal structure (thermal ellipsoids 80%) of $[(\text{AuCl})_2(\mathbf{14})]$ (colour code: Au yellow, Cl green, O red, N blue, H not displayed). Important distances (pm), bond lengths (pm) and angles ($^\circ$): Au...Au 904, Au–C(NHC) 195(2), 196(5), Au–Cl 221(2), 233(3).

alkyl chain (Scheme 6) to provide macrocyclic diimidazolium salt **16**·2HBr. A C_5 -chain was chosen, since this corresponds to the number of atoms of the xanthene unit linking the two imidazoles and based on this it can be expected to be a strain-free linker.

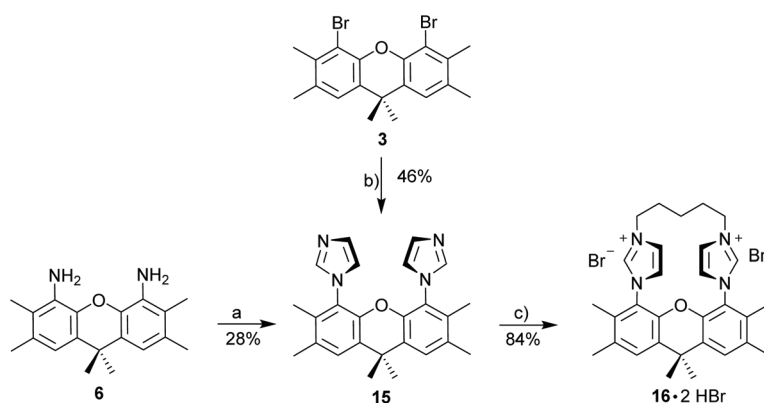
The synthesis of **15** is possible starting from 4,5-dibromo-xanthene **3** or from 4,5-diamino-xanthene **6**. Both reactions are simple, but since **6** needs to be prepared from **3**, the copper-catalyzed reaction is more convenient. However, even though the synthesis of **15** from **3** was successfully carried out more than five times with yields in excess of 40%, it is important to note, that this yield is not always reproducible and in a few instances the reaction fails entirely. We have carefully studied

the reaction conditions, but have not been able to identify the factors which sometimes preclude product formation. Utilizing diimidazolium salt **16**·2HBr a number of metal complexes with Ag, Au, Cu, Ir, Pd and Rh could be synthesized (Scheme 7). Most complexes were synthesized *via* $[(\text{AgBr})_2(\mathbf{16})]$ – either using the isolated silver complex for the preparation of $[(\text{CuI})_2(\mathbf{16})]$ and $[(\text{Pd}(\text{allyl})\text{Cl})_2(\mathbf{16})]$ or the *in situ* generated silver complex for the synthesis of $[(\text{AuCl})_2(\mathbf{16})]$, $[(\text{Au}(\text{AuCl})_2(\text{Cl}))(\mathbf{16})_2]$ and $[(\text{RhCl}(\text{cod}))_2(\mathbf{16})]$. However, for the Ir and Rh complexes the direct synthesis using the weak base approach provides better yields than utilizing the silver salt.

Depending on the stoichiometric ratio of NHC **16** and the gold precursor $[\text{AuCl}(\text{SMe}_2)]$ different complexes are formed. A 2 : 1-ratio Au/NHC provides $[(\text{AuCl})_2(\mathbf{16})]$ as the only isolable product in 46% yield, while a 3 : 2-ratio gives $[(\text{Au})(\text{AuCl})_2(\text{Cl})(\mathbf{16})_2]$. The latter complex contains two (NHC)AuCl and one (NHC) $_2\text{Au}^+$ units – both are common motifs in this chemistry, but we are not aware, that both units have been observed in a single complex.

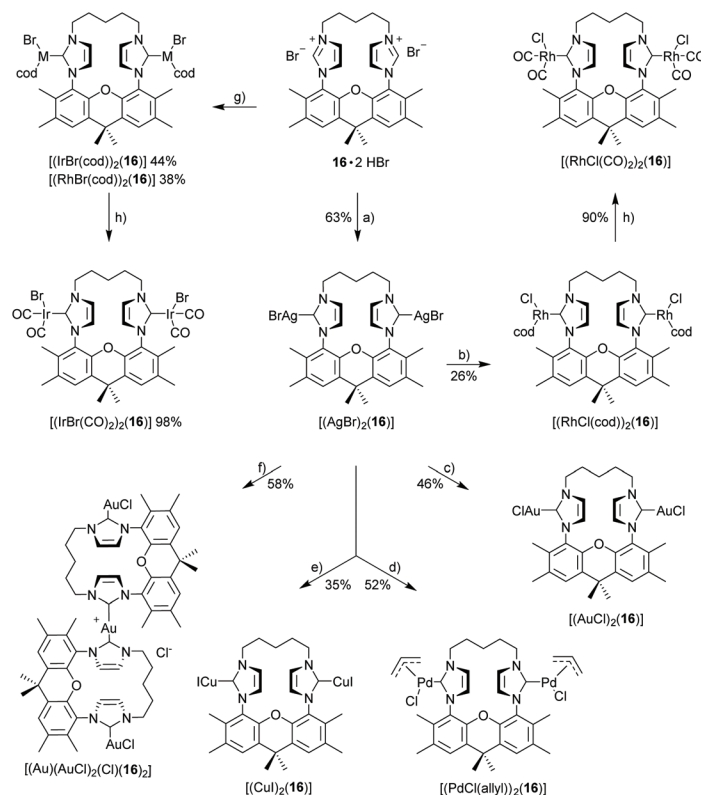
The metal complexes with NHC **16** occur as single isomers – both in the solid state and in solution. The ^1H NMR spectra of the respective metal complexes display two different signals for the two bridgehead methyl groups, which is incompatible with the *anti*-isomer. The *syn*-orientation is confirmed in the X-ray crystal structures of $[(\text{RhCl}(\text{cod}))_2(\mathbf{16})]$ (Fig. 3) and of $[(\text{Au})(\text{AuCl})_2(\text{Cl})(\mathbf{16})_2]$ (Fig. 4).⁵¹ In the solid state structure of $[(\text{RhCl}(\text{cod}))_2(\mathbf{16})]$ the molecule is bisected by a mirror plane and the two *syn*-Rh units are symmetry equivalents. The Rh...Rh distance of 703.2 pm is very similar to the Ir...Ir distance in $[(\text{IrCl}(\text{cod}))_2(\mathbf{9})]$ (702.4 pm).

The crystal structure of $[(\text{Au})(\text{AuCl})_2(\text{Cl})(\mathbf{16})_2]$ contains two (NHC)AuCl and a single (NHC) $_2\text{Au}^+$ unit. The chloride counterion is located in a spherical void without any significant contact to the cation. The two peripheral gold atoms are located at distances of 586 pm and 573 pm to the central NHC_2Au^+ -unit, respectively, which is more than 100 pm shorter than the Ir...Ir or Rh...Rh distances in the other bi-metallic complexes $[(\text{IrCl}(\text{cod}))_2(\mathbf{9})]$ and $[(\text{RhCl}(\text{cod}))_2(\mathbf{16})]$. It seems, that in the absence of steric hindrance, the intermetal-



Scheme 6 Synthesis of diimidazolium salt **16**·2HBr. Reagents and conditions: (a) imidazole, K_2CO_3 , CuI, DMF, 180 $^\circ\text{C}$, 48 h; (b) paraformaldehyde, glyoxal, NH_4OAc , AcOH, 80 $^\circ\text{C}$, 12 h; (c) 1,5-dibromopentane, MeCN, reflux; 5 d; (d) MeI, MeCN, 50 $^\circ\text{C}$, 24 h.





Scheme 7 Synthesis of metal complexes with NHC 16. Reagents and conditions: (a) Ag₂O, MeOH, rt, 24 h; (b) [RhCl(cod)]₂, 50 °C, 2 h; (c) [AuCl(SMe₂)] (2.0 eq.), 50 °C, 2 h; (d) [PdCl(allyl)]₂, DCM, rt, 24 h; (e) CuI, DCM, rt, 24 h; (f) [AuCl(SMe₂)] (1.5 eq.), 50 °C, 2 h; (g) [MCl(cod)]₂ (M = Ir, Rh), K₂CO₃, NaOAc, KBr, MeCN, 80 °C, 12 h; (h) CO, 0 °C, CH₂Cl₂, 30 min.

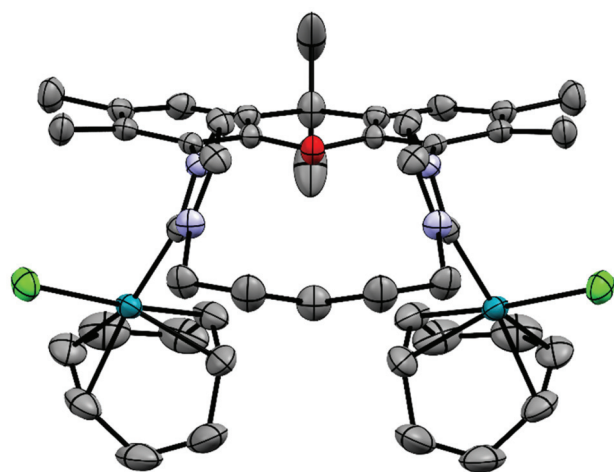


Fig. 3 X-ray crystal structure (thermal ellipsoids 80%) of [RhCl(cod)]₂(16) (colour code: Rh turquoise, Cl green, O red, N blue, H not displayed). Important distances (pm), bond lengths (pm) and angles (°): Rh...Rh 703.19(5), Rh–Cl 238.4(1), Rh–C(NHC) 203.9(4), Rh–C(cod) 211.7(5), 208.2(5), 218.4(5), 222.4(5); Cl–Rh–C(cod) 168.9(1), 152.2(1), C(NHC)–Rh–C(cod) 169.4(2), 154.7(2).

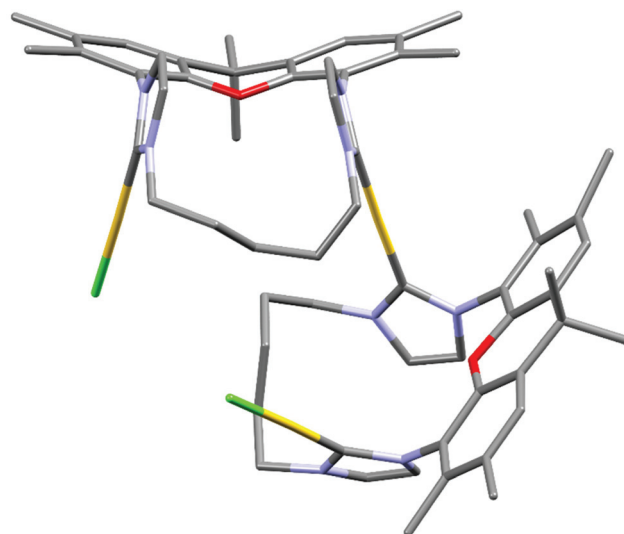


Fig. 4 X-ray crystal structure (sticks representation for improved clarity) of [Au(AuCl)₂(Cl)]₂(16) (colour code: Au yellow, Cl green, O red, N blue, H not displayed). Important bond lengths (pm) and angles (°): Au...Au 586.2(1), 572.8(1), 660.6(1), Au–C(NHC) 197(2), 198(2), 199(2), Au–Cl 28.4(4), 226.1(5); Cl–Au–C(NHC) 177.2(6), 178.2(6), C(NHC)–Au–C(NHC) 177.3(7).

lic distances tend to be much shorter than in the Ir and the Rh complexes. Again, the question arises, why the cod ligands of the Ir and the Rh complexes are located in the center of the



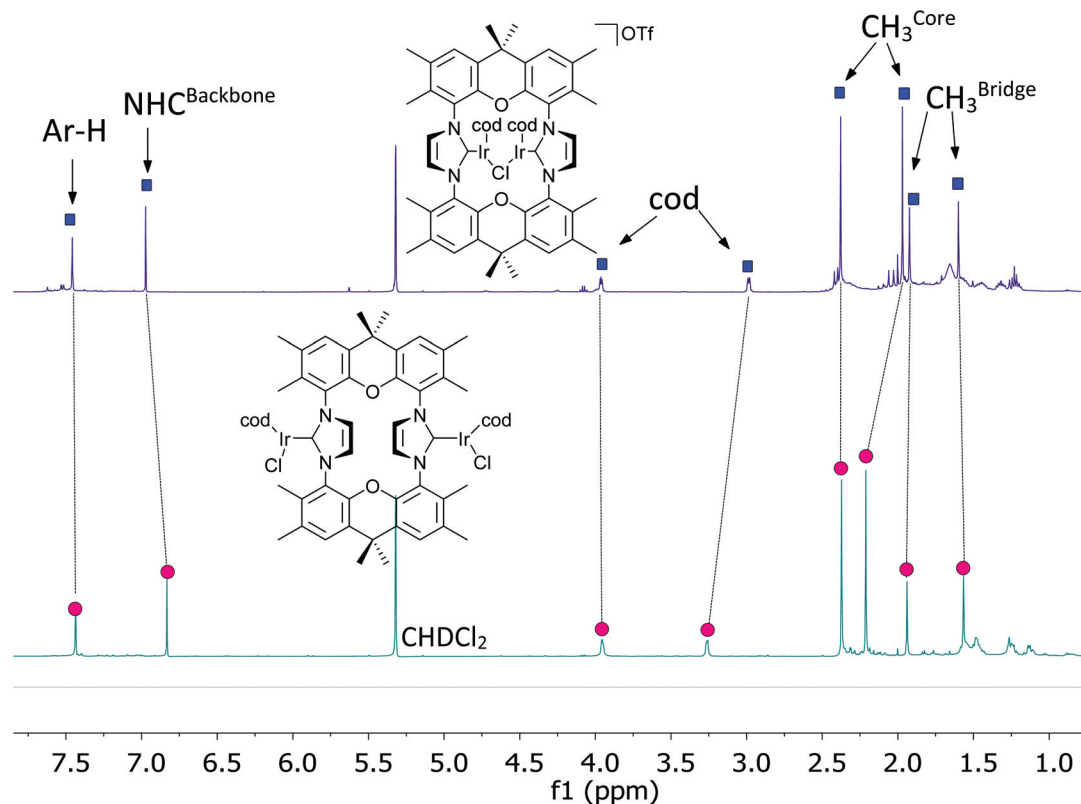


Fig. 5 ^1H spectra of $[(\text{IrCl}(\text{cod}))_2(\mathbf{9})]$ and $[(\text{IrCl}(\text{cod}))_2(\mathbf{9})] + \text{AgOTf}$ @24 h in CD_2Cl_2 .

complexes even though the two bulky groups push the metal centers apart. Probably the energy cost of this is relatively small. Alternatively, one could ask, why the two chlorides are not located in the center with the bulkier cod on the periphery. Probably, the square-planar geometry at the d^8 -metals and the orthogonal orientation of the plane of the imidazolylidene unit relative to the square-planar coordination sphere of Ir and Rh would place the two chlorides too close to each other and lead to even more unfavorable steric repulsion.

The structural flexibility of the xanthene allows a planar xanthene, while the other one displays the butterfly structure tilted at the oxygen and the $\text{sp}^3\text{-CMe}_2$ unit. All gold atoms display an almost linear coordination geometry. The Au–C (NHC) distances in the monoNHC and the bisNHC unit are virtually identical and these and other structural parameters are within expectations for such complexes.^{59,60}

Monocationic complexes

The behavior of the binuclear $[(\text{MX}(\text{cod}))_2(\text{NHC})]$ ($\text{X} = \text{halide}$; $\text{M} = \text{Rh}, \text{Ir}$) in the chromatography purification is unusual, since the observed $R_f(\text{CH}_2\text{Cl}_2)$ is approx. 0.1 for such complexes. In contrast, for mononuclear complexes like $[\text{MCl}(\text{cod})(\text{IMes})]$ ($\text{M} = \text{Rh}, \text{Ir}$) chromatographic $R_f(\text{CH}_2\text{Cl}_2) > 0.9$ are normally observed, which is in accord with the covalent, non-polar nature of the complexes. Based on this, the dinuclear complexes may be able to release one chloride forming cationic complexes stabilized by M-X-M ($\text{M} = \text{Rh}, \text{Ir}$; $\text{X} = \text{halide}$)

units. This would also lessen steric pressure and allow the demanding cod units to move to the periphery of the complex, previously occupied by the two chloride ions. Such tendency to release anions has also been observed for the related monometallic complexes.⁶¹ Based on preliminary DFT calculations the structural flexibility of the complex is sufficient to enable a symmetric structure with a halide bridging the two metal centers. To provide further evidence, a CD_2Cl_2 solution of complex $[(\text{IrCl}(\text{cod}))_2(\mathbf{9})]$ was treated with one equivalent of AgOTf leading to the precipitation of AgCl and the formation of a cationic complex $[(\text{Ir}(\text{cod}))_2\text{Cl}(\mathbf{9})](\text{OTf})$. This complex displays a simple NMR spectrum (Fig. 5), which would be in accord with a symmetric halide bridged complex. It is unlikely, that such complexes are highly dynamic with the structural interconversion being very fast on the NMR time scale. Further evidence for the bridged structure comes from the NMR spectrum, since the ^1H NMR resonance of the cod ligands experience significant shifts, which are expected when relocating cod ligands from the interior of the complexes to the periphery. We were not able to obtain the complex in pure state or single crystals, since such complexes tend to decompose upon attempted isolation and purification.

Infrared spectroscopy

The averaged CO-stretch frequencies of the complexes $[(\text{MCl}(\text{CO}))_2(\text{NHC})]$ ($\text{M} = \text{Ir}, \text{Rh}$) provide information on the donor capacity of the respective NHC ligands.^{47,62} The IR data for the



Table 1 IR-spectroscopic $\nu(\text{CO})$ (*sym./asym.*) and $\nu_{\text{av}}(\text{CO})$ data for $[(\text{MX}(\text{CO})_2)_n(\text{NHC})]$ ($\text{M} = \text{Ir}, \text{Rh}$; $n = 1$ or 2 , $\text{X} = \text{Br}, \text{Cl}$) complexes in CH_2Cl_2 solution

Complex	$\nu(\text{CO})/\text{cm}^{-1}$	$\nu_{\text{av}}(\text{CO})/\text{cm}^{-1}$
$[\text{IrCl}(\text{CO})_2(\text{IMes})]$	2067/1980	2023.5
$[(\text{IrCl}(\text{CO})_2)_2(\mathbf{9})]$	2066/1981	2023.5
$[(\text{IrCl}(\text{CO})_2)_2(\mathbf{11})]$	2064/1984	2024
$[(\text{IrCl}(\text{CO})_2)_2(\mathbf{14})]$	2070/1982	2026
$[(\text{IrBr}(\text{CO})_2)_2(\mathbf{16})]$	2072/1982	2027
$[\text{RhCl}(\text{CO})_2(\text{IMes})]$	2082/1997	2039.5
$[(\text{RhCl}(\text{CO})_2)_2(\mathbf{16})]$	2077/2001	2039

related complexes with the new NHC ligands reported here were determined (Table 1). Despite the constrained geometry of the macrocyclic NHC ligands **9** and **16** the donation of those ligands appears to be nearly the same as that of the reference complexes with IMes ligands. The influence of the anions (chloride, bromide) on the $\nu(\text{CO})$ is almost identical. Ligand **14** appears to be slightly less donating than the other NHC ligands studied.

Electrochemistry

The electrochemistry of the mono- and the binuclear complexes were determined to obtain information on the donor properties of the NHC ligands and to learn, whether the metal centers in the binuclear complexes interact with each other. The electrochemistry of the mononuclear metal complexes $[(\text{IrCl}(\text{cod}))(\mathbf{11})]$ is reversible ($E_{1/2} = 0.689$, $\Delta E = 69$ mV), which is typical for such complexes.⁶³ However, the electrochemistry of all binuclear complexes tested $[(\text{MCl}(\text{CO})_2)_2(\text{NHC})]$ ($\text{M} = \text{Ir}, \text{Rh}$ and $\text{NHC} = \mathbf{9}$ or **16**) turns out to be irreversible, and do not provide information about potential metal–metal interactions.

Conclusions

BisNHC metal complexes containing two distinct (NHC)ML units in close proximity based on a 4,5-substituted xanthene backbone have been synthesized. Four metal complexes were structurally characterized displaying M–M distance as short as 573 pm. Based on the remaining structural flexibility even shorter M–M distance appear to be possible in binuclear complexes. Several of the binuclear metal complexes reported here are significantly less stable than the respective mononuclear complexes, when the coordination sphere contains bulky ligands, like in $\text{MX}(\text{cod})$ ($\text{M} = \text{Ir}, \text{Rh}$) complexes. Binuclear complexes with stability comparable to that of the related mononuclear complexes are those with Cu, Ag and Au metals. Further studies will be directed towards establishing metal–metal cooperativity in catalytic transformations.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the TU Darmstadt.

References

- 1 A. J. Arduengo, H. V. R. Dias, R. L. Harlow and M. Kline, *J. Am. Chem. Soc.*, 1992, **114**, 5530.
- 2 W. A. Herrmann, *Angew. Chem., Int. Ed.*, 2002, **41**, 1290–1309.
- 3 *N-heterocyclic Carbenes*, ed. S. P. Nolan, Wiley-VCH, Weinheim, 2014.
- 4 E. Peris, *Chem. Rev.*, 2018, **118**, 9988–10031.
- 5 M. N. Hopkinson, C. Richter, M. Schedler and F. Glorius, *Nature*, 2014, **510**, 485–496.
- 6 R. H. Grubbs, *Angew. Chem., Int. Ed.*, 2006, **45**, 3760–3765.
- 7 T. P. Montgomery, T. S. Ahmed and R. H. Grubbs, *Angew. Chem., Int. Ed.*, 2017, **56**, 11024–11036.
- 8 J. Morvan, M. Mauduit, G. Bertrand and R. Jazzar, *ACS Catal.*, 2021, **11**, 1714–1748.
- 9 A. S. K. Hashmi, *Chem. Rev.*, 2021, **121**, 8309–8310.
- 10 R. D. J. Froese, C. Lombardi, M. Pompeo, R. P. Rucker and M. G. Organ, *Acc. Chem. Res.*, 2017, **50**, 2244–2253.
- 11 A. J. Nett, S. Cañellas, Y. Higuchi, M. T. Robo, J. M. Kochkodan, M. T. Haynes, J. W. Kampf and J. Montgomery, *ACS Catal.*, 2018, **8**, 6606–6611.
- 12 D.-A. Park, S. Byun, J. Y. Ryu, J. Lee, J. Lee and S. Hong, *ACS Catal.*, 2020, **10**, 5443–5453.
- 13 M. R. Buchmeiser, *Chem. – Eur. J.*, 2018, **24**, 14295–14301.
- 14 Q. Liang and D. Song, *Chem. Soc. Rev.*, 2020, **49**, 1209–1232.
- 15 L. M. Martínez-Prieto, L. Rakers, A. M. López-Vinasco, I. Cano, Y. Coppel, K. Philippot, F. Glorius, B. Chaudret and P. W. N. M. van Leeuwen, *Chem. – Eur. J.*, 2017, **23**, 12779–12786.
- 16 Y. Gao, L. Wang and L. Deng, *ACS Catal.*, 2018, **8**, 9637–9646.
- 17 J. Lee, H. Hahm, J. Kwak and M. Kim, *Adv. Synth. Catal.*, 2019, **361**, 1479–1499.
- 18 G. Sipos and R. Dorta, *Coord. Chem. Rev.*, 2017, **375**, 13–68.
- 19 J. Atzrodt, V. Derdau, W. J. Kerr and M. Reid, *Angew. Chem., Int. Ed.*, 2018, **57**, 3022–3047.
- 20 M. Iglesias and L. A. Oro, *Chem. Soc. Rev.*, 2018, **47**, 2772–2808.
- 21 R. Jazzar, M. Soleilhavoup and G. Bertrand, *Chem. Rev.*, 2020, **120**, 4141–4168.
- 22 S. Dagorne, *Synthesis*, 2018, **50**, 3662–3670.
- 23 V. Nesterov, D. Reiter, P. Bag, P. Frisch, R. Holzner, A. Porzelt and S. Inoue, *Chem. Rev.*, 2018, **118**, 9678–9842.
- 24 G. Guisado-Barrios, M. Soleilhavoup and G. Bertrand, *Acc. Chem. Res.*, 2018, **51**, 3236–3244.
- 25 H. V. Huynh, *Chem. Rev.*, 2018, **118**, 9457–9492.
- 26 A. Gomez-Suarez, D. J. Nelson and S. P. Nolan, *Chem. Commun.*, 2017, **53**, 2650–2660.



- 27 D. Janssen-Muller, C. Schleppehorst and F. Glorius, *Chem. Soc. Rev.*, 2017, **46**, 4845–4854.
- 28 R. Savka, M. Bergmann, Y. Kanai, S. Foro and H. Plenio, *Chem. – Eur. J.*, 2016, **22**, 9667–9675.
- 29 R. Savka, S. Foro and H. Plenio, *Dalton Trans.*, 2016, **45**, 11015–11024.
- 30 S. Roy and H. Plenio, *Adv. Synth. Catal.*, 2010, **352**, 1014–1022.
- 31 D. J. Nelson, *Eur. J. Inorg. Chem.*, 2015, 2012–2027.
- 32 M. Poyatos, J. A. Mata and E. Peris, *Chem. Rev.*, 2009, **109**, 3677–3707.
- 33 D. M. Khramov, A. J. Boydston and C. W. Bielawski, *Angew. Chem., Int. Ed.*, 2006, **45**, 6186–6189.
- 34 K. A. Williams and C. W. Bielawski, *Chem. Commun.*, 2010, **46**, 5166–5168.
- 35 A. J. Boydston, K. A. Williams and C. W. Bielawski, *J. Am. Chem. Soc.*, 2005, **127**, 12496–12497.
- 36 M. Poyatos and E. Peris, *Dalton Trans.*, 2021, **50**, 12748–12763.
- 37 Y. Li, Y.-Y. An, J.-Z. Fan, X.-X. Liu, X. Li, F. E. Hahn, Y.-Y. Wang and Y.-F. Han, *Angew. Chem., Int. Ed.*, 2020, **59**, 10073–10080.
- 38 S. Ibáñez, M. Poyatos and E. Peris, *Acc. Chem. Res.*, 2020, **53**, 1401–1413.
- 39 A. J. Caruso and J. L. Lee, *J. Org. Chem.*, 1997, **62**, 1058–1063.
- 40 D. Takeuchi, Y. Chiba, S. Takano and K. Osakada, *Angew. Chem., Int. Ed.*, 2013, **52**, 12536–12540.
- 41 F. B. Schwarz, T. Heinrich, J. O. Kaufmann, A. Lippitz, R. Puttreddy, K. Rissanen, W. E. S. Unger and C. A. Schalley, *Chem. – Eur. J.*, 2016, **22**, 14383–14389.
- 42 M. R. D. Gatus, I. Pernik, J. A. Tompsett, S. C. Binding, M. B. Peterson and B. A. Messerle, *Dalton Trans.*, 2019, **48**, 4333–4340.
- 43 S. Saito, T. Kobayashi, T. Makino, H. Yamaguchi, H. Muto, I. Azumaya, K. Katagiri and R. Yamasaki, *Tetrahedron*, 2012, **68**, 8931–8936.
- 44 L. Hintermann, *Beilstein J. Org. Chem.*, 2007, **3**, 22–26.
- 45 E. A. Martynova, N. V. Tzouras, G. Pisanò, C. S. J. Cazin and S. P. Nolan, *Chem. Commun.*, 2021, **57**, 3836–3856.
- 46 R. Savka and H. Plenio, *Dalton Trans.*, 2015, **44**, 891–893.
- 47 S. Leuthäuser, D. Schwarz and H. Plenio, *Chem. – Eur. J.*, 2007, **13**, 7195–7203.
- 48 S. Wolf and H. Plenio, *J. Organomet. Chem.*, 2009, **694**, 1487–1492.
- 49 O. Halter, I. Fernández and H. Plenio, *Chem. – Eur. J.*, 2017, **23**, 711–719.
- 50 M. Bergmann, R. Savka, S. Foro and H. Plenio, *Eur. J. Inorg. Chem.*, 2017, **2017**, 3779–3786.
- 51 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **64**, 112–122.
- 52 S. Ando, M. Otsuka and T. Ishizuka, *Organometallics*, 2020, **39**, 3839–3848.
- 53 P. J. Rayner, P. Norcott, K. M. Appleby, W. Iali, R. O. John, S. J. Hart, A. C. Whitwood and S. B. Duckett, *Nat. Commun.*, 2018, **9**, 4251.
- 54 H. Valdés, M. Poyatos and E. Peris, *Organometallics*, 2013, **32**, 6445–6451.
- 55 S. Burling, M. F. Mahon, S. P. Reade and M. K. Whittlesey, *Organometallics*, 2006, **25**, 3761–3767.
- 56 T. Makino, R. Yamasaki, I. Azumaya, H. Masu and S. Saito, *Organometallics*, 2010, **29**, 6291–6297.
- 57 T. Makino, H. Masu, K. Katagiri, R. Yamasaki, I. Azumaya and S. Saito, *Eur. J. Inorg. Chem.*, 2008, 4861–4865.
- 58 The plate-like shape of the crystals result in a poor quality of the respective diffraction data, which is the reason why the data were not deposited.
- 59 S. Gaillard, P. Nun, A. M. Z. Slawin and S. P. Nolan, *Organometallics*, 2010, **29**, 5402–5408.
- 60 F. Lazreg, D. B. Cordes, A. M. Z. Slawin and C. S. J. Cazin, *Organometallics*, 2015, **34**, 419–425.
- 61 G. Sipos, P. Gao, D. Foster, B. W. Skelton, A. N. Sobolev and R. Dorta, *Organometallics*, 2017, **36**, 801–817.
- 62 D. J. Nelson and S. P. Nolan, *Chem. Soc. Rev.*, 2013, **42**, 6723–6753.
- 63 S. Popov and H. Plenio, *Eur. J. Inorg. Chem.*, 2021, **22**, 3708–3718.

