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Three-Component Entanglements Consisting of Three Crescent-Shaped Bidentate Ligands Coordinated to an Octahedral Metal Centre

Fabien Durola,[a] Luca Russo,[b] Jean-Pierre Sauvage,*[a] Kari Rissanen,*[b] and Oliver S. Wenger[a]

Abstract: 3,3′-Biisoquinoline ligands (biiq) L, bearing aromatic substituents on their 8 and 8′ positions, have been used to generate interwoven systems consisting of three crescent-shaped ligands disposed around an octahedral metal centre. Mono-ligand complexes of the type $[ReL(CO)_3py]^+$ (py: pyridine) have also been prepared, leading to sterically non-hindering complexes in spite of the endotopic nature of the chelate used. The three-component entanglements have been prepared by using either Fe^{II} or Ru^{II} as gathering metal centre. The synthetic procedure is simple and efficient, affording fully characterised complexes as their PF_6 or $SbCl_6$ salts. X-ray crystallography clearly shows that the crescent-shaped ligands do not repel each other in the tris-chelate complexes. In an analogous way, the Re^I complexes show open structures with no steric repulsion between the L ligand and the ancillary CO or py groups. The FeL_3 or RuL_3 compounds are very unusual in the sense that, contrary to all the other tris-bidentate chelate complexes made till now, the three organic components are tangled up, in a situation which will be very favourable to the formation of new non trivial topologies of the catenane type.

Keywords: chelating ligands · entanglement · helical complexes · N ligands · supramolecular chemistry

Introduction

Transition metals with a preferred tetrahedral geometry are perfect gathering and orienting elements for tangling up two coordinating molecular threads easily and quantitatively, as shown in Figure 1. This is particularly well illustrated by the $[Cu(dpp)_2]^+$ and $[Cu(dap)_2]^+$ complexes (dpp: 2,9-diphenyl-1,10-phenanthroline; dap: 2,9-dianisyl-1,10-phenanthroline) which contain two entwined ligands.[1] This family of complexes constitutes the basis of a wide family of catenanes, rotaxanes and molecular knots.[2] The situation is with no doubt very different for pentacoordinated[3] and octahedrally coordinated[4] transition metal centres. Zn^{2+} has been used as a template assuming that this metal cation is preferably five-coordinate, although six-coordinate complexes can not be excluded. For instance, a [2]-catenane has been prepared by using a bidentate ligand and a ring-incorporated tridentate chelating unit.[3] Pd^{II}, with its preferred square-planar geometry, has also been used as template to afford rotaxanes and catenanes in very high yields.[5] In a spectacular piece of work, Stoddart and his co-workers prepared Borromean rings using six Zn^{2+} centres and combining bidentate and tridentate ligands.[6] The design of ligands capable of forming three-component entanglements by coordination to a given octahedral metal centre is less straightforward than for tetrahedral geometry. A few studies have demonstrated that three-chelate octahedral transition metals can also be used as templates for making catenanes[7] and knots[8] but the entanglement of three disconnected bidentate chelates has not been described as yet. In the previous examples of topologically non-trivial species built around transition metals, at least two chelates were interlinked prior to the final cyclisation reaction.

We report here a special family of ligands, namely 8,8′-diaryl-3,3′-biisoquinolines, which lead to such three-component entanglements by complexation to octahedral metals such as Fe^{II} and Ru^{II}. The synthesis of the complexes will be described as well as crystallographic studies which evidence

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[a] F. Durola, Prof. Dr. J.-P. Sauvage, Dr. O. S. Wenger
Laboratoire de Chimie Organo-Minérale
Institut de Chimie
Université Louis Pasteur
4 rue Blaise Pascal, 67070 Strasbourg Cedex (France)
Fax: (+33) 390-241-368)
E-mail: sauvage@chimie.u-strasbg.fr

[b] Dr. L. Russo, Prof. Dr. K. Rissanen
Nanoscience Center
Department of Chemistry
University of Jyväskylä
P.O. Box 35, 40014 Jyväskylä (Finland)

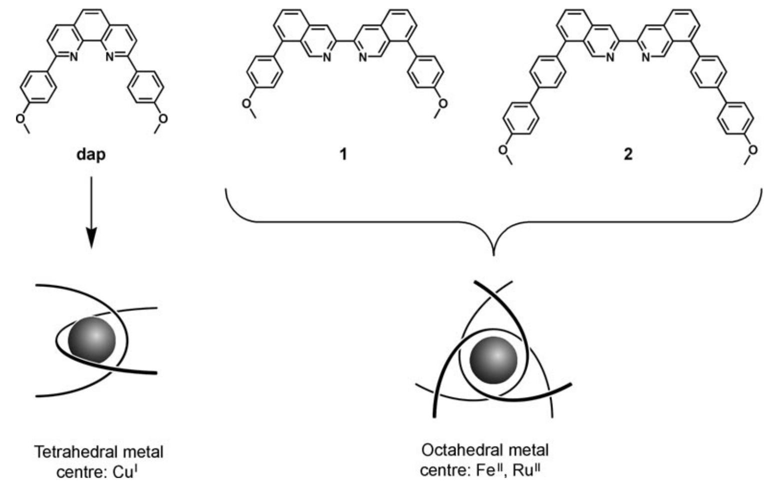


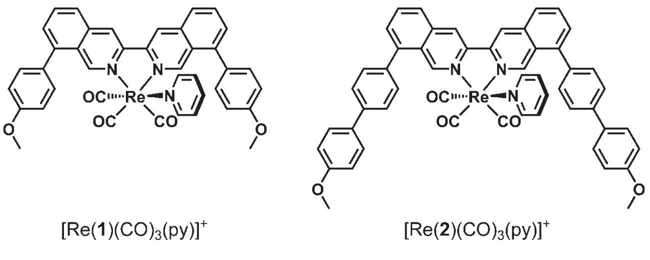
Figure 1. Schematic representation of two- or three-component entanglements obtained from the appropriate ligands and metal centres.

the endotopic nature of the ligands and the absence of repulsion between organic groups within the complexes, in spite of the pronounced entangled nature of the molecules.

Results and Discussion

As already pointed out, the two anisyl groups of the dap ligand constitute a steric barrier around the metal centre (see Figure 1). In order for the coordination sphere of the complexed metal to be less congested, a promising solution is to draw aside the two aromatic groups attached to the 3,3′-biisoquinoline (biiq) chelate itself. To keep the directionality of the system and, in particular, to make sure that the complexing site will be disposed in an endotopic fashion or endocyclic manner if the ligand is incorporated in a ring, we turned our attention to the 3,3′-biisoquinoline (biiq) family. As depicted in Figure 1, ligands **1** and **2** match these prerequisites: No or very limited steric hindrance occurs around the metal and unambiguous endotopic character of the chelate once complexed to a metal centre. In addition, the crescent shape of both compounds will be very favourable to the formation of an entangled ensemble once trischelate complexes are obtained, as represented in the Figure 1.

Ligands **1** and **2** were respectively prepared in five and seven steps from commercially available compounds, as recently described.[9] Two distinct families of complexes were synthesised which contain either one chelate (rhenium(I) complexes, Scheme 1) or three biiq ligands (iron(II) or ruthenium(II) complexes, Scheme 2).



Scheme 1. Rhenium(I) complexes [Re(**1**)(CO)$_3$(py)]$^+$ and [Re(**2**)(CO)$_3$(py)]$^+$.

These two complexes, [Re(**1**)(CO)$_3$(py)](PF$_6$) and [Re(**2**)(CO)$_3$(py)](PF$_6$) were prepared following a relatively classical experimental procedure.[10] Starting from pentacarbonylchlororhenium(I) and a free biisoquinoline chelate **1** or **2**, a triscarbonyl(biisoquinoline)chlororhenium complex is first obtained [Eq. (1); L = **1** or **2**]. Charged complexes can often be more easily crystallised and are more soluble. This is why the chloro ligand is then removed by using silver triflate and replaced by a molecule of pyridine, to give after subsequent anion exchange the charged complexes, [Re(**1**)(CO)$_3$(py)](PF$_6$) and [Re(**2**)(CO)$_3$(py)](PF$_6$), respectively [Eq. (2); L = **1** or **2**].

$$[\mathrm{Re(CO)_5Cl}] + \mathrm{L} \rightarrow [\mathrm{Re(CO)_3LCl}] \tag{1}$$

$$[\mathrm{Re(CO)_3LCl}] + \mathrm{py} \rightarrow [\mathrm{Re(CO)_3Lpy}]^+ \tag{2}$$

Crystallisation of the complexes, by slow diffusion of diisopropyl ether in acetone or 1,2-dichloroethane, respectively, afforded good diffraction quality crystals. The X-ray structures of the monomeric complexes proved the open cleft-like structure of the ligands (Figure 2). The endotopic cleft is defined by the distance between the anisolic O atoms in dap, **1** and **2** (Scheme 1.). In a Cu^{I}–dap complex,[11] the O···O distance is 10.64 Å, in the smaller biiq complex [Re(**1**)(CO)$_3$(py)]$^+$ the distance is 14.20 Å [O(4)···O(5)], whereas in the larger biiq complex [Re(**2**)(CO)$_3$(py)]$^+$ the corresponding distance is 18.05 Å [O(1)···O(2)]. Both Re complexes are slightly bent from planarity to a shallow V-shape. The angle between the planar quinolinic moieties bonding to the Re cation is 11.3° for [Re(**1**)(CO)$_3$(py)]$^+$ and 10.1° for [Re(**2**)(CO)$_3$(py)]$^+$. In spite of the slight distortion from planarity the Re atoms lie nearly in the plane defined by the O and N atoms. The deviation of the Re atoms from the plane O4-N2-N1-O5 for [Re(**1**)(CO)$_3$(py)]$^+$ is only 0.72 Å and the corresponding deviation for [Re(**2**)(CO)$_3$(py)]$^+$ is 0.58 Å [O1-N1-N2-O2].

The inspection of the above mentioned geometrical data and the X-ray plots with van der Waals radii (Figure 3) clearly shows the large size of the endotopic cleft and its ability to include two additional biiq ligands around an octahedral metal ion.

The two homoleptic octahedral complexes of ruthenium and iron, [Ru(**1**)$_3$](PF$_6$)$_2$ and [Fe(**2**)$_3$](SbCl$_6$)$_2$ (Scheme 2)

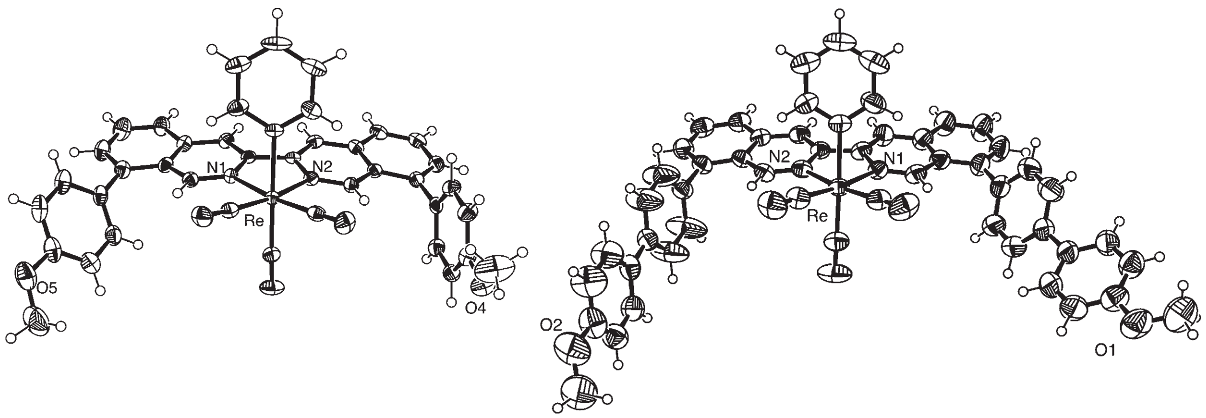


Figure 2. Plots of the X-ray structures of the monomeric cationic Re-complexes $[Re(\mathbf{1})(CO)_3(py)]^+$ (left) and $[Re(\mathbf{2})(CO)_3(py)]^+$ (right) with thermal ellipsoids at 50% probability level and selected atomic labels. The PF_6^- ions have been omitted for clarity.

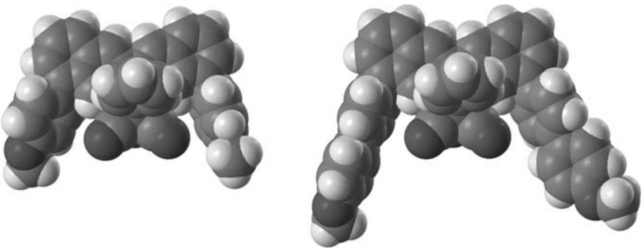
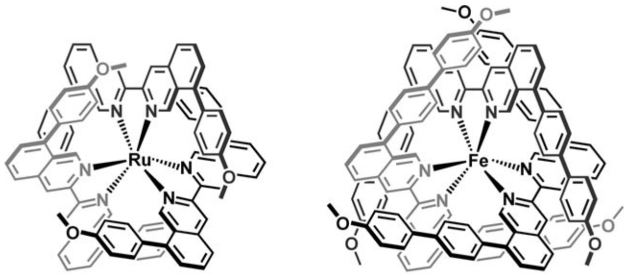


Figure 3. van der Waals plots of the X-ray structures of the monomeric cationic Re-complexes $[Re(\mathbf{1})(CO)_3(py)]^+$ (left) and $[Re(\mathbf{2})(CO)_3(py)]^+$ (right). The PF_6^- ions have been omitted for clarity.



$[Ru(\mathbf{1})_3]^{2+}$ $[Fe(\mathbf{2})_3]^{2+}$

Scheme 2. Chemical representation of homoleptic octahedral complexes $[Ru(\mathbf{1})_3](PF_6)_2$ and $[Fe(\mathbf{2})_3](SbCl_6)_2$.

were readily obtained by mixing in stoichiometric proportions free ligands **1** or **2** and ruthenium(II) tetra(dimethylsulfoxide) dichloride or iron(II) tetrafluoroborate tetrahydrate as metal sources [Eq. (3) and (4)]. After anion exchange the crystals of the ruthenium complex $[Ru(\mathbf{1})_3](PF_6)_2$ were obtained from acetone and diisopropyl ether, similarly to the iron complex $[Fe(\mathbf{1})_3](PF_6)_2$ described in a preliminary communication.[12] The crystallisation of homoleptic complexes from ligand **2** is more problematic and only after exchange of the BF_4^- ion for the larger $SbCl_6^-$ ion were very small crystals of moderate quality obtained from 1,2-dichloroethane and diisopropyl ether.

$$[Ru(dmso)_4Cl_2] + 3\,\mathbf{1} \rightarrow [Ru(\mathbf{1})_3]^{2+} \qquad (3)$$

$$Fe^{2+}(BF_4^-)_2 + 3\,\mathbf{2} \rightarrow [Fe(\mathbf{2})_3]^{2+} \qquad (4)$$

The X-ray structures[14] of the complexes $[Ru(\mathbf{1})_3](PF_6)_2$ and $[Fe(\mathbf{2})_3](SbCl_6)_2$ reveal a very appealing entanglement of the ligands around the metal centre. The smaller ligand **1** wraps around the Ru cation forming a symmetrical helical structure (Figure 4). The three anisyl groups occupy the top and bottom parts of the complex, the distances between the O atoms being 8.29, 8.38 and 8.63 Å in the top part and 7.97, 8.61 and 9.27 Å for the bottom part, manifesting the nearly symmetrical structure. The entanglement around the metal centre induces only slight changes to the endotopic cleft distance, the distances in $[Ru(\mathbf{1})_3]^+$ being 15.62 (green), 16.24 (red) and 15.88 Å (blue). These distances are approximately 2 Å wider than for the monomeric $[Re(\mathbf{1})(CO)_3(py)]^+$, this indicating that the biiq ligand is able to adapt its conformation upon octahedral entanglement.

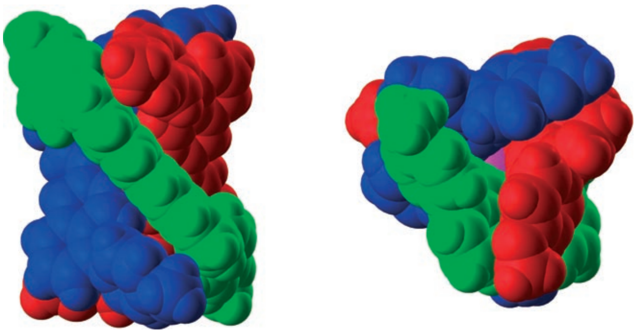


Figure 4. The van der Waals plot of the complex $[Ru(\mathbf{1})_3]^{2+}$ (anions and acetone molecules excluded) showing each ligand with a different colour. Side view (left) and top view (right).

The cleft in the larger biiq ligand **2** is much wider and leads to more "relaxed" entanglement of ligands around the octahedral Fe centre in $[Fe(\mathbf{2})_3]^{2+}$. The complex $[Fe(\mathbf{2})_3]^{2+}$ exhibits more dissymmetric overall structure (Figure 5), the top part inter-ligand O···O distances being 14.15, 14.85 and 15.44 Å, the corresponding bottom part being 11.42, 15.53 and 17.86 Å. The intra-chelate cleft O···O distances are

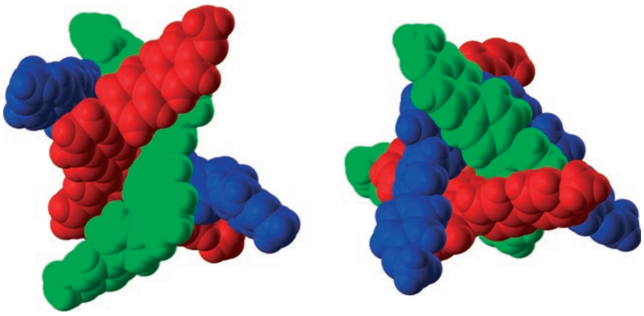


Figure 5. The van der Waals plots of the complex $[Fe(\mathbf{2})_3]^{2+}$ (anions and nitrobenzene molecules excluded) showing each ligand with a different colour. Side view (left) and top view (right).

18.70 (green), 20.86 (red) and 19.86 Å (blue), being quite close to the O···O distance of 18.05 Å in the monomer.

The coordination of three biiq ligands, **1** or **2**, around a Ru or Fe cation results in a more or less symmetrical helical pseudo-D_3 structure [the coordination sphere in both entangled complexes show slight deformation from the perfect D_3 symmetry, the N-M-N angles deviate 5–8° from the ideal 180° or 90° degree angles], where the biiq moiety assumes planarity in contrast to the monomeric biiq–Re complexes. The subsequent deprotection of the phenolic functions[13] at the ends of the endotopic cleft should lead to hexa-OH functionalised helical complexes, which upon alkylation with a proper bis-functionalised spacer would lead to new topologies.

Conclusion

The use of octahedral transition metals such as Fe^{II} or Ru^{II} in conjunction with new ligands containing a 3,3′-biisoquinoline chelate and aromatic groups attached on the 8 and 8′ positions led to the generation of unusual three-component entanglements. The endotopic nature of these ligands, in spite of their non sterically hindering character, is favourable to high yield synthesis of such interwoven systems. X-ray crystallography turned out to be particularly informative and demonstrated in a unambiguous fashion the desired entangled situation in the two cases studied, $[Ru(\mathbf{1})_3]^{2+}$ and $[Fe(\mathbf{2})_3]^{2+}$.

Another interesting feature of the ligands used is that the mono-chelate complexes do not experience steric congestion between the groups borne by the bidentate chelate and the ancillary ligands coordinated to the metal. This is again clearly demonstrated by X-ray diffraction on two rhenium(I) complexes, $[ReL(CO)_3(py)]^+$ (L = **1** or **2**).

The entangled nature of the three-chelate complexes will subsequently been taken advantage of to synthesise new interlocking ring topologies.

Experimental Section

General: The following chemicals were obtained commercially and were used without further purification: pentacarbonylchlororhenium(I) (Aldrich), silver trifluoromethanesulfonate (Aldrich), potassium hexafluorophosphate (Acros), iron(II) tetrafluoroborate tetrahydrate (Aldrich), triphenylcarbenium hexachloroantimonate (Acros).

All silica column chromatographies were performed by using Merck Silicagel 60 (0.063–0.200 mm).

^1H NMR spectra were recorded with a Bruker AVANCE 300 (300 MHz (^1H); 75 MHz (^{13}C)) spectrometer using deuterated solvent as the lock. The spectra were collected at 25 °C and the chemical shifts were referenced to residual solvent protons as internal standards. ^1H: CD_3CN 1.95 ppm, CD_2Cl_2 5.32 ppm, $[D_6]$dmso 2.50 ppm. Mass spectra were obtained with a VG ZAB-HF spectrometer (FAB) and a VG-BIOQ triple quadrupole in positive or negative mode (ES-MS).

[Re(1)(CO)$_3$(py)](PF$_6$): 8,8′-Dianisyl-3,3′-biisoquinoline (50 mg, 0.107 mmol) and pentacarbonylchlororhenium(I) (36.3 mg, 0.100 mmol) were suspended in toluene (5 mL). The reaction mixture was heated at 120 °C under argon for 5 h. The yellow precipitate was filtered, washed with toluene and purified by column chromatography (silica; eluent: dichloromethane, methanol 100:1 (v/v)). This gave $[Re(dabiiq)(CO)_3Cl]$ (50 mg) as a yellow powder. All this product was dissolved in pyridine (10 mL). After addition of silver triflate (0.646 mmol, 166 mg), the reaction mixture was refluxed overnight under argon. After pyridine evaporation and column chromatography (silica; eluent: acetonitrile, water, saturated aqueous potassium nitrate solution, 100:1:0.1 (v/v/v); re-precipitation with aqueous potassium hexafluorophosphate solution) (40 mg) of pure $[Re(dabiiq)(CO)_3(pyridine]](PF_6)$ (0.042 mg; 65 %) were obtained as a yellow powder. ^1H NMR (CD_2Cl_2): $\delta = 9.84$ (s, 2H), 9.11 (s, 2H), 8.25 (d, 2H, $J = 8.1$ Hz), 8.07 (m, 2H), 8.05 (dd, 2H, $J = 8.0$, 7.1 Hz), 7.83 (d, 2H, $J = 7.2$), 7.78 (m, 1H), 7.54 (d, 4H, $J = 9.0$ Hz), 7.24 (m, 2H), 7.20 (d, 4H, $J = 7.5$ Hz), 3.91 ppm (s, 6H). ES-MS: m/z: 818.1669 (calculated 818.1665 for $C_{40}H_{29}N_3O_5Re^+$). Crystals were grown by slow diffusion of diisopropyl ether in acetone. Crystal data: $M = 962.83$, orange prism, $0.12 \times 0.10 \times 0.10$ mm^3, monoclinic, space group $C2/c$, $a = 18.607(2)$, $b = 13.057(2)$, $c = 30.686(3)$ Å, $\beta = 93.775(7)°$, $V = 7439(2)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.719$ g cm^{-3}, $F_{000} = 3792$, $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, $\mu = 3.390$ mm^{-1}, $T = 173(2)$ K, $2\theta_{max} = 30.0°$, 18986 reflections collected, 10859 unique ($R_{int} = 0.0376$), 7857 with $I_o > 2\sigma(I_o)$, structure solved by using SHELXS and refined with SHELX-97 full-matrix least squares on F^2 within the SHELXTL[15] suite, 505 parameters, 0 restraints, $GoF = 1.001$, $R_1 = 0.0621$, $wR_2 = 0.0761$ (all reflections), $1.75 < \Delta\rho < -1.10$ eÅ^{-3}.

[Re(2)(CO)$_3$Cl]: 8,8′-Di(phenylanisyl)-3,3′-biisoquinoline (120 mg, 0.193 mmol) was suspended in 1,2-dichloroethane (60 mL). After addition of pentacarbonylchlororhenium(I) (50 mg, 0.138 mmol) the reaction mixture was heated to reflux under argon for 12 h. Then the solvent was evaporated and the yellow residue was subjected to column chromatography (silica; eluent: dichloromethane, methanol 50:1 (v/v)). This yielded pure $[Re(dpabiiq)(CO)_3Cl]$ (81 mg, 0.087 mmol; 53 %) as a yellow powder. ^1H NMR ($[D_6]$DMSO): $\delta = 9.67$ (s, 2H), 9.48 (s, 2H), 8.28 (d, 2H, $J = 8.1$ Hz), 8.17 (dd, 2H, $J = 8.1$, 7.2 Hz), 7.96–7.90 (m, 6H), 7.74 (d, 4H, $J = 8.7$ Hz), 7.72 (d, 4H, $J = 8.7$ Hz), 7.09 (d, 4H, $J = 8.7$ Hz), 3.83 ppm (s, 6H).

[Re(2)(CO)$_3$(py)](PF$_6$): $[Re(dpabiiq)(CO)_3Cl]$ (80 mg, 0.086 mmol) was dissolved in pyridine (10 mL). After addition of silver triflate (222 mg, 0.864 mmol) the reaction mixture was refluxed for 2 h under argon. After evaporation of pyridine and column chromatography (silica; eluent: acetonitrile, water, saturated aqueous potassium nitrate solution, 100:10:1 (v/v/v); re-precipitation with aqueous potassium hexafluorophosphate solution) pure $[Re(dpabiiq)(CO)_3(pyridine]](PF_6)$ (92 mg, 0.083 mg; 96 %) was obtained as a yellow powder. ^1H NMR (CD_3CN): $\delta = 9.89$ (s, 2H), 9.04 (s, 2H), 8.17 (d, 2H, $J = 8.4$ Hz), 8.15–8.11 (m, 2H), 8.10 (d, 2H, $J = 8.4$ Hz), 7.93 (dd, 2H, $J = 7.8$, 1.5 Hz), 7.89 (d, 4H, $J = 8.4$ Hz), 7.80 (tt, 1H, $J = 7.8$, 1.5 Hz), 7.73 (dd, 8H, $J = 8.7$, 8.4 Hz), 7.25 (dd, 2H, $J = 7.8$, 6.6 Hz), 7.07 (d, 4H, $J = 8.7$ Hz), 3.86 ppm (s, 6H). ES-MS: m/z: 970.2292 (calculated 970.2289 for $C_{52}H_{37}N_3O_5Re^+$). Crystals were grown by slow diffusion of diisopropyl ether in 1,2-dichloroethane. Crystal data: $M = 1115.03$, dark red prism, $0.10 \times 0.10 \times 0.10$ mm^3, monoclinic, space group $C2/c$, $a = 18.417(3)$, $b = 13.577(2)$, $c = 38.696(7)$ Å, $\beta = 103.300(6)°$, $V = 9416(3)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.565$ g cm^{-3}, $F_{000} = 4432$, $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, $\mu = 2.690$ mm^{-1}, $T = 173(2)$ K, $2\theta_{max} = 30.0°$, 21752 reflections collected, 13544 unique ($R_{int} = 0.0333$), 8565 with $I_o > 2\sigma(I_o)$, structure solved by using SHELXS and refined with SHELX-97 full-matrix least squares on F^2 within the SHELXTL[15] suite, 613 parameters, 0 restraints, $GoF=0.877$, $R_1=0.0898$, $wR_2=0.1525$ (all reflections), $0.65<\Delta\rho<-0.98$ eÅ^{-3}.

$[Ru(1)_3](PF_6)_2$: Ruthenium(II) tetra(dimethylsulfoxide) dichloride (10 mg, 0.020 mmol) and 8,8′-dianisyl-3,3′-biisoquinoline (29 mg, 0.062 mmol) were dissolved in ethylene glycol (5 mL). The resulting deep red solution was heated at 140 °C under argon overnight and then allowed to cool at room temperature. The crude product was precipitated by addition of a saturated aqueous solution of potassium hexafluorophosphate and cold distilled water. The orange precipitate was purified by column chromatography (silica; eluent: acetone, water, saturated aqueous solution of potassium nitrate, 100:5:0.5 (v/v/v); re-precipitation with a saturated aqueous solution of potassium hexafluorophosphate in water). This procedure yielded pure $[Ru(dabiiq)_3](PF_6)_2$ (30 mg, 0.017 mmol; 81 %) as an orange powder. ^{1}H NMR (CD_3CN): $\delta=8.93$ (s, 6H), 8.18 (s, 6H), 8.06 (d, 6H, $J=8.1$ Hz), 7.89 (dd, 6H, $J=8.1$, 7.2 Hz), 7.51 (d, 6H, $J=7.2$ Hz), 6.71 (d, 12H, $J=8.4$ Hz), 6.35 (d, 12H, $J=8.7$ Hz), 3.55 ppm (s, 18H). ES-MS: m/z: 753.2290 (calculated 753.2286 for $C_{96}H_{72}N_6O_6Ru^{2+}$). Crystals were grown by slow diffusion of diisopropyl ether in acetone. The accomplishment of the tris-chelate homoleptic complex is based on 222 non-crystallographic symmetry around the metal centre. Crystal data: $M=1912.76$, orange, $0.12\times0.10\times0.10$ mm^3, triclinic, space group $P\bar{1}$, $a=13.113(2)$, $b=16.382(2)$, $c=22.638(3)$ Å, $\alpha=105.88(5)$, $\beta=97.10(4)$, $\gamma=105.47(5)°$, $V=4405(2)$ Å^3, $Z=2$, $\rho_{calcd}=1.442$ g cm^{-3}, $F_{000}=1968$, $Mo_{K\alpha}$ radiation, $\lambda=0.71073$ Å, $\mu=0.303$ mm^{-1}, $T=173(2)$ K, $2\theta_{max}=30.0°$, 37 279 reflections collected, 25 718 unique ($R_{int}=0.0394$), 15 018 with $I_o>2\sigma(I_o)$, structure solved using SHELXS and refined with SHELX-97 full-matrix least squares on F^2 within the SHELXTL[15] suite, 1252 parameters, 1273 restraints, $GoF=0.992$, $R_1=0.1320$, $wR_2=0.1868$ (all reflections), $0.96<\Delta\rho<-0.93$ eÅ^{-3}.

$[Fe(2)_3](SbCl_6)_2$: 8,8′-Di(phenylanisyl)-3,3′-biisoquinoline (621 mg, 1 mmol) was suspended in a 1:1 (v/v) *n*-butanol–1,2-dichloroethane solvent mixture (50 mL). After addition of iron(II) tetrafluoroborate tetrahydrate (113 mg, 0.333 mmol), the reaction mixture was refluxed for 12 h during which time it turned red. Then the solvents were evaporated and the crude product was purified by column chromatography (silica; eluent: acetonitrile, water, saturated aqueous solution of potassium nitrate, 200:10:1 (v/v/v); re-precipitation with a saturated aqueous solution of potassium hexafluorophosphate in water). This yielded the pure iron(II) tris(biisoquinoline) complex (378 mg; 53 %) (counter anion is PF_6^-) as a red powder. ^{1}H NMR (CD_3CN): $\delta=8.84$ (s, 6H; H^1), 8.04 (s, 6H; H^4), 7.73 (d, 6H, $J=7.8$ Hz; H^7), 7.29 (d, 12H, $J=8.7$ Hz), 7.14 (dd, 6H, $J=7.8$, 7.2 Hz; H^6), 7.09 (dd, 6H, $J=7.2$, 0.9 Hz; H^5), 7.06–7.01 (m, 24H), 6.74 (d, 12H, $J=8.4$ Hz), 3.90 ppm (s, 18H, OCH_3). ES-MS: m/z: 958.842 (calculated 958.838 for $C_{132}H_{96}N_6O_6Fe^{2+}$). Anion exchange was then performed by mixing the resulting complex with triphenylcarbenium hexachloroantimonate in 1,2-dichloroethane, followed by a precipitation of the title compound with diethyl ether. Crystals were grown by slow diffusion of diisopropyl ether in 1,2-dichloroethane. The ligand arms are so easily accommodated within the complex that rotational disorder of the central phenyl ring in the ligand arm is observed for two of the three ligands in $[Fe(\mathbf{2})_3](SbCl_6)_2$. From another point of view, the disorder within the structure, only partially resolved, appears to be the main reason for the low precision of the final refined model. About 17 % of the volume of the unit cell is occupied by electron density that could not be modelled due to the presence of disordered solvent included in the structure, which has been excluded from the final refinement, by means of the SQUEEZE[16] routine. Crystal data: $M=2710.01$, orange-red plate, $0.20\times0.10\times0.03$ mm^3, monoclinic, space group $P2_1/n$, $a=19.692(4)$, $b=35.924(7)$, $c=21.297(4)$ Å, $\beta=113.76(3)°$, $V=13789(5)$ Å^3, $Z=4$, $\rho_{calcd}=1.305$ g cm^{-3}, $F_{000}=5496$, $Mo_{K\alpha}$ radiation, $\lambda=0.71073$ Å, $\mu=0.781$ mm^{-1}, $T=123(2)$ K, $2\theta_{max}=45.0°$, 87 136 reflections collected, 17 685 unique ($R_{int}=0.1094$), 6911 with $I_o>2\sigma(I_o)$, absorption corrections (SADABS[17]) $T_{min}/T_{max}=0.880$. Structure solved by using SHELXS and refined with SHELX-97 full-matrix least squares on F^2 within the SHELXTL[15] suite, 1423 parameters, 2731 restraints, $GoF=1.244$, $R_1=0.1522$, $wR_2=0.3859$ (all reflections), $1.91<\Delta\rho<-1.05$ eÅ^{-3}.

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