New synthesis of meso-free-[14]triphyrin(2.1.1) by McMurry coupling and its derivatization to Mn(I) and Re(I) complexes

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The metal-free and meso-free [14]triphyrin(2.1.1) were successfully prepared based on the intramolecular McMurry coupling reaction of diformyl-tripyrrane in 16% yield, and it was converted to the bawl-shaped Mn(I)(TriP)(CO)₃ and Re(I)(TriP)(CO)₃.

Triphyrins are porphyrin analogues which contain only three pyrrole or pyrrole related rings linked through meso-sp³ carbon atoms.⁵ There has been considerable interest because of their potential applications as the functional materials. In 2006, Osaka and coworkers reported the synthesis of [14]triphyrin(1.1.1), so-called tribenzosubporphyrins, as 14π-electron porphyrin analogues.⁶ Subsequently, Kobayashi and Osaka et al. independently developed synthetic protocols for meso-aryl substituted subporphyrins as their boron complexes.²⁻³ The triphyrins reported to date have all been boron complexes with highly nonplanar dome-shaped conformations, with the exception of subpyrroporphyrin⁵ and triphyrins with more than four meso carbons.⁵⁻⁶ In 2008, we have succeeded to prepare nearly planar metal-free meso-aryl-substituted [14]triphyrin(2.1.1) compounds by acid-catalyzed condensation of bicyclo[2.2.2]octadiene(BCOD)-fused pyrrole and aromatic aldehydes.⁶ These compounds had never been reported until they were found serendipitously during the synthesis of tetraarylporphyrins by the well-known Lindsey method. The [14]triphyrin(2.1.1) compounds represent the first examples of near planar metal-free contracted porphyrinoids with a 14π-electron aromatic system containing only the pyrrole moieties.

Including the [14]triphyrin(2.1.1), however, the previously reported triphyrins and their analogues have been mainly meso-substituted compounds. One exception is meso-free benzotriphyrin prepared by Osaka et al. heating of the mixture of 2-(3-oxo-2,3-dihydro-1H-isindol-1-yl)acetic acid and boric acid at 350 °C.² For the further generalization of the [14]triphyrin chemistry, their meso-free and/or metal complexes are desired. We will report here the new synthetic method of metal-free and meso-free [14]triphyrin(2.1.1)₁ basing on the intramolecular McMurry coupling reaction of diformyl-tripyrrane. The Mn(I) and Re(I) triphyrins were also successfully obtained by the reaction of triphyrin 1 with Mn(CO)₅Br or Re(CO)₅Cl, respectively.

Synthetic scheme is shown in Scheme 1. Intramolecular McMurry coupling of diformyltripyrane 37 was performed in THF and the reaction was quenched with 10% aqueous K₂CO₃. After a filtration by celite, the solvent of the organic layer was removed under a reduced pressure. The residue was purified on alumina column chromatography with CHCl₃ and the obtained green residue was oxidized by DDQ. The purification by silica gel column chromatography (20 % EtOAc in n-hexane) gave triphyrin 1 as red solid in 16 % yield. The triphyrin 1 is soluble in common organic solvents, such as CHCl₃, CH₂Cl₂, THF, n-hexane, and MeOH.

Scheme 1 Synthetic scheme of triphyrins 1, 1-Mn, and 1-Re.

The NMR spectrum of triphyrin 1 measured in CDCl₃ is shown in Figure 1a. It is symmetrical and shows peaks of two kinds of meso-H (8.88 and 8.87 ppm). Inner NH proton is observed at (7.25 ppm) as a broad signal. The FAB-mass spectrum shows the peak at 442, which corresponds to [M+H]⁺ of triphyrin 1 (Figure S1). The absorption spectrum of the triphyrin 1 was measured in CH₂Cl₂ (Figure 2). The intense peak (similar to Soret peak of porphyrins) is shown at 336 nm and the broad weaker bands (similar to Q bands) in the 440-560 nm with broad peaks at 470 and 550 nm. They are 20 nm
blue-shifted from those of meso-aryl-substituted [14]triphyrin(2.1.1). To clarify the reaction mechanism, the green intermediate after the rough purification by alumina chromatography was further purified by silica-gel column chromatography with CH$_2$Cl$_2$. The NMR spectrum of the intermediate 2 is shown in Figure 1b. It is not symmetrical and the meso-peaks of 1 at 8.87 and 8.88 ppm disappeared. Meso-methine proton is observed at 6.77 ppm as singlet and ethyl methyl protons at 5.90 and 6.66 ppm as doublets ($J = 12$ Hz). The singlet peak for 2H is observed at 4.31 ppm, which is characterized as methylen protons between pyrrole rings. The intermediate was not stable under air and the color changed gradually in solution. Small peaks of triphyrin 1 is observed in Figure 1b, which appeared during the measurement. These results suggested the structure of the intermediate 2 as shown in Scheme 1.

The crystals of triphyrin 1 were obtained in MeOH-ethylene glycol. The X-ray crystal structure of 1 is shown in Figure 3. The diethylypyrrole unit is slightly tilted with respect to macrocycle and the dihedral angle between the mean planes of diethylypyrrole and the other part of triphyrin plane is 10.68°. N-N distances are 2.504(2), 2.502(2), and 2.552(2) Å for N1-N2, N2-N3, and N3-N1, respectively. The four carbons, C2, C1, C14, and C13 are almost in line but the angles made by C7-C3-C4 was 20.01(9)°. This means hydrogen atom on N1 directed to N3 rather than to N2, and therefore NH hydrogen atom was mainly delocalized on the N1 and N3.

Fig 2 UV-vis spectra of 1 (red line), 1-Mn (blue line), and 1-Re (green line) in CH$_2$Cl$_2$.

To confirm the structure of 1, NMR spectra in CD$_2$Cl$_2$ were measured from room temperature to -90 °C (Figure S2). At room temperature the inner proton is broad at 6.68 ppm and disappeared by lowering the temperature. It re-observed at 7.27 ppm at -60 °C and shifted to 7.30 ppm at -90 °C. The peak at 6.68 ppm disappeared by addition of CD$_3$OD, to confirm the peaks to inner NH proton. At room temperature two singlet peaks due to meso-protons are observed at 8.90 and 8.82 ppm. The peak at 8.82 ppm was broadened at -40 °C with methylene qualtlet peaks at 3.2 ppm, but the other meso-peak remained sharp. The broadened peak was reobserved at 8.89 ppm at -90 °C. These results indicated that the diethylypyrrole flip-flipped at room temperature but methylbuthylpyrrole did not because of the hydrogen bonding between inner hydrogen and nitrogen atoms.

Electron distributions of LUMO and HOMO of tautomers of triphyrin 1 with inner proton on N1 or N2, estimated by density functional theory (DFT) calculations where the geometry optimization was carried out at the B3LYP/6-31G(*) level (Figure S3). When the inner proton located on N2, the triphyrin is flat. However when the proton is located on N1, diethylypyrrole is twisted and N2 is raised from the triphyrin plane. The latter structure is well-coincident with the crystal structure of 1 in Figure 1a.

We have also succeeded to prepare Mn(I)-coordinated triphyrin (MnTriP(CO))$_2$: 1-Mn and Re(I)-coordinated triphyrin (ReTriP(CO))$_2$: 1-Re. Triphyrin 1 was treated with MnBr(CO)$_5$ in toluene with the presence of NaOAc. After 1 h reflux of the solution, the solvent was removed and the residue was purified on silica-gel column chromatography (CH$_2$Cl$_2$) to give 1-Mn in 80% yield. For $^1$H-NMR, the NH proton of 1 disappeared. IR spectra showed clear absorptions at 2007 and 1889 cm$^{-1}$, due to typical symmetric and asymmetric vibration mode for three CO ligands which were not observed for free-base 1. UV-vis spectrum of 1-Mn is shown in Figure 1. The Soret-like peak is broadened and 5-nm blue-shifted. The Q-like band appears around 470 nm and the edge reaches around 750 nm.

In a similar procedure with the synthesis of 1-Mn, 1-Re was also prepared in 71% yield. The Soret peak is observed at 347 nm and 10 and 6 nm red-shifted from triphyrin 1 and 1-Mn, respectively. The Q-like band is very similar to that of 1-Mn and it appears around 470 nm and the edge reaches around 750 nm.

The crystals of triphyrin 1-Mn and 1-Re were obtained in MeOH-ethylene glycol. The structures are shown in Figure 4. Three inner nitrogen atoms and three CO moieties are coordinated to the Mn$^{I}$ and Re$^{I}$ ions, respectively. The triphyrin are bowl-shaped and Mn and Re ions are above the plane made by three inner nitrogens by 1.300 Å and 1.455 Å, respectively. The distances between C2-C13 and C7-C16 are 5.986(3) and 6.496(3) Å for 1-Mn and 5.981(3) and 6.383(3) Å for 1-Re, respectively. The nitrogen-nitrogen distances of N1-N2, N2-N3, and N3-N1 were 2.586(2), 2.594(2), and 2.696(2) Å for 1-Mn and 2.650(2), 2.654(2), and 2.779(2) Å for 1-Re, respectively. Each N-N length of 1-Mn is 0.06 Å shorter than that of 1-Re, because of the larger size of Re$^{I}$ ion than Mn$^{I}$ ion. This also influence the shape of the bawl: the curve of 1-Re is deeper than that of 1-Mn.
Fig 4 X-ray crystallographic structures of (a) 1-Mn and (b) 1-Re.

The cyclic voltammogram of 1 in CH2Cl2 containing 0.1 M Bu4NPF6 at room temperature consists of a single electron

- reduction process (Ep=red = -1.77 V vs Fe/Fe3+) and a single one-electron oxidation process (Ep=ox = 0.63 V vs Fe/Fe3+), as shown in Figure S4a and Table S1. The reduction was reversible but the oxidation was irreversible. The cyclic voltammogram of 1-Mn consists of a single electron reduction process (Ep=red = -1.79 V vs Fe/Fe3+) and two one-electron oxidation processes (Ep=ox = 0.25 V and Ep=ox = 0.97 V vs Fe/Fe3+). The reduction and the first oxidation reactions were reversible but the second oxidation was irreversible. The reversible first oxidation occurred at Mn(II) center. The cyclic voltammogram of 1-Re is very similar to that of 1-Mn: Ep=red = -1.63 V, Ep=ox = 0.48 and 1.10 V vs Fe/Fe3+. The reversible oxidation corresponded to the oxidation of Re(I) center.

In conclusion we have successfully prepared meso-free hexaalloy[14]triphyrin(2.1.1) from diformyltripyrane by McMurry coupling. The reaction mechanism of the reduction cyclization mechanism was clarified by the NMR measurement. The Mn(II) and Re(I) complexes were also prepared and the bowl-shaped structures were confirmed by the X-ray analysis. With this method we can freely design the substituents at β- and/or meso-positions of triphyrins. These triphyrins will be promising as new ligands in the coordination chemistry.

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Notes and references