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A new cyclam with a triphenylphosphine-pendant and its metal complexes

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Abstract

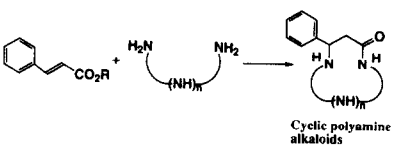
A new triphenylphosphine-pendant cyclam (triphenylphosphine = TPP; cyclam = 1,4,8,11-tetraazacyclotetradecane) was synthesized by reaction of an ethyl cinnamate derivative bearing a diphenylphosphine group at the *ortho* position of the phenyl group with 2,3,2-tetraamine (= 1,9-diamino-3,7-diazanonane) in refluxing MeOH, followed by BH_3 reduction. Triphenylphosphine oxide-pendant cyclam (triphenylphosphine oxide = TPPO) was derived by treatment of TPP-pendant cyclam with benzyl alcohol in CCl_4. The TPP-pendant cyclam formed stable 1:1 metal inclusion complexes with Ni^{II} and Mn^{III}. The TPPO-pendant cyclam yielded a 1:1 Ni^{II} complex which was the best catalyst among the cyclam-Ni^{II} and -Mn^{III} complexes for epoxidation of *trans*-stilbene with NaClO in CH_2Cl_2. Gold(I) reacted with TPP-pendant cyclam to yield a stable 1:1 complex, in which Au^{I} binds only to the pendant phosphine. On the other hand, gold(III) reacted with TPP-pendant cyclam to give an Au^{III}-inclusion complex with the pendant TPP coordination. The Au^{I} complex reacted with $[Au^{III}(dien)Cl]^{2+}$ in CH_3CN to yield an Au^{I}(out)–Au^{III}(in-cyclam) mixed complex. The Ni^{II} complex with TPP-pendant cyclam reacted with $Au^{I}(PEt_3)Cl$ in CH_2Cl_2, yielding a novel Au^{I}(out)–Ni^{II}(in-cyclam) binuclear complex.

Keywords: Triphenylphosphine-pendant cyclam; Nickel complexes; Gold complexes; Cyclam complexes; Epoxidation

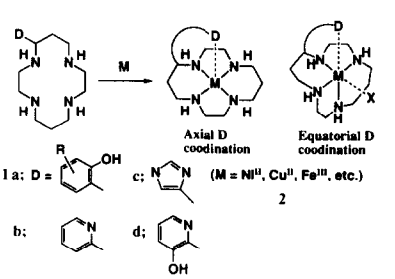
1. Introduction

Saturated macrocyclic polyamines are extremely useful and versatile ligands [1–3]. Recently we have developed a new synthetic route to new series of macrocyclic polyamines that are functionalized with C-tethered donors. Thus, we have introduced phenol- (**1a**) [4], pyridine- (**1b**) [4h,5], imidazole- (**1c**) [6], 3-hydroxypyridine-pendant (**1d**) [7] in cyclam (= 1,4,8,11-tetraazacyclotetradecane) or its homologues, using a biosynthetic pathway of cyclic biogenic polyamine (such as spermine and spermidine) alkaloids (Scheme 1). All pendant functions interact with metal ions (e.g. Ni^{II} [4b–f,5a,6a,7], Cu^{II} [4d–f,6c,7], Zn^{II} [4d,g,i,6c,7], Co^{II} [4d,6a], Fe^{II} [4a,e,f,5a], Mn^{III} [6b], Au^{III} [4h,5b], etc.), participating in coordination either as an axial donor [4–6] or an equatorial donor [4c,g,6a,c,7], depending on the size of the cyclam cavity (Scheme 2). The resulting complexes **2** are gifted with new properties leading to novel application, which has led to our conceptual development of intelligent molecules [2].

We now have extended our original biosynthetic method to the synthesis of a new triphenylphosphine-pendant cyclam **3**. Our interest with **3** were (i) how triphenylphosphine (TPP) stabilizes the entrapped metals M_1 (**4**) to favor the lower or higher oxidation states, (ii) whether TPP axially coordinates with metal ions M_2 (**5**)



Scheme 1.



Scheme 2.

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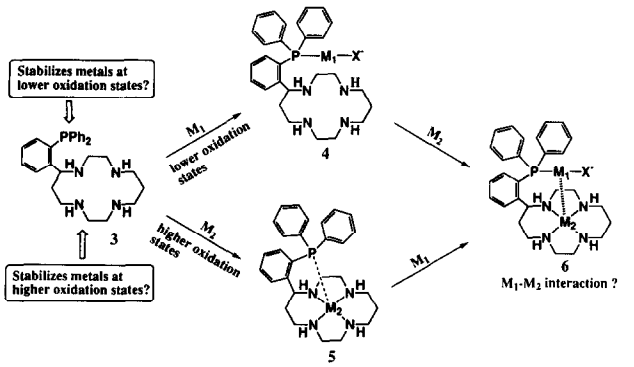


Scheme 3.

entrapped in the cyclam, (iii) whether soft metal ions M_1 exclusively bind to TPP, and hard metal ions M_2 (**6**) can subsequently go into the cyclam cavity (Scheme 3), and (iv) catalytic activity of Ni^{II}- and Mn^{III}-cyclam complexes in epoxidation of olefins [6b,8] can be improved with the intramolecular presence of TPP.

2. Experimental section

2.1. General information

All reagents and solvents used were of analytical grade. CH_3CN was distilled over CaH_2 and stored in the dark. All aqueous solutions were prepared using deionized and distilled water. Tetra-n-butylammonium hexafluorophosphate (n-Bu_4NPF_6) was recrystallized from ethyl acetate. *trans*-Stilbene and *trans*-stilbene oxide were purchased from Tokyo Chemical Industry. [Ni^{II}-cyclam]·$(ClO_4)_2$ was prepared by recrystallization of [Ni^{II}-cyclam]·Cl_2 [9] from water in the presence of 10 times excess amount of $NaClO_4$. [Mn^{III}-cyclam·(ClO_4)]·$(ClO_4)_2$ was prepared by the reported method [10a].

IR and UV spectra were respectively recorded on Shimadzu FTIR-4200 and Hitachi U-3200 spectrophotometers. Melting points were determined on a micro melting apparatus. Thin layer chromatography (TLC) was carried out on Merck Art. 5554 (silica gel) TLC plates. ^1H (400 MHz), ^{13}C (100 MHz), and ^{31}P (162 MHz) NMR spectra were recorded on a JEOL α-400 spectrometer at 25.0 ± 5°C. 3-(Trimethylsilyl)-propionic-2,2,3,3-d_4 acid sodium salt (Merck) in D_2O and tetramethylsilane (Merck) in organic solvent were used as internal references for ^1H and ^{13}C NMR measurements. A D_2O solution of 80% phosphoric acid was used as an external reference for ^{31}P NMR measurements.

2.2. Synthesis of triphenylphosphine-pendant cyclam: 5-(2-diphenylphosphinophenyl)-1,4,8,11-tetraazacyclotetradecane, 3 (see Scheme 4)

A toluene solution (270 ml) of 2-(diphenylphosphino)-benzaldehyde (19.6 g, 67.5 mmol) [11] and (carbethoxymethylene)triphenylphosphorane (Wittig reagent) (23.5 g, 67.5 mmol) was heated at reflux for 3 h. The reaction mixture was evaporated to dryness. The residue was purified by silica gel column chromatography (eluent CH_2Cl_2) and crystallization from n-hexane/ethyl acetate (1:1) to obtain ethyl 3-(2-diphenylphosphinophenyl)-2-propenate **7** as colorless prisms (21.7 g, 60.3 mmol, 89% yield). m.p. = 71.0–72.0°C. IR (KBr pellet) 3056, 2986, 1709 (C=O), 1635 (C=C), 1458, 1436, 1314, 1265, 1181, 1092, 1028, 899, 730, 706 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.27 (3H, t, J = 7.1 Hz, CCH_3), 4.19 (2H, q, J = 7.1 Hz, OCH_2C), 6.25 (1H, dd, J = 15.7, 1.2 Hz, C = CHC), 6.94 (1H, ddd, J = 7.7, 4.2, 0.9 Hz, ArH), 7.24–7.38 (12H, m, ArH), 7.62 (1H, ddt, J = 7.7, 4.2, 0.6 Hz, ArH), 8.40 (1H, dd, J = 15.7, 4.4 Hz, ArCHC).

A MeOH solution (1.10 l) of 1,9-diamino-3,7-diazanonane (2,3,2-tetraamine) (**8**) (9.66 g, 60.3 mmol) and **7** (21.7 g, 60.3 mmol) was heated under reflux for 20 days. After the mixture was evaporated to dryness, the residue was dissolved in 500 ml of CH_2Cl_2 and unreacted **8** was removed by extraction with 28% aqueous NH_3 (200 ml × 2). The water layer was extracted with CH_2Cl_2 (100 ml × 3). After all organic layers were combined and dried over Na_2SO_4, the solvent was evaporated to dryness. The residue was taken up in CH_3CN (100 ml) and a colorless powder precipitated. Crystallization from CH_3CN yielded 7-(2-diphenylphosphinophenyl)-5-oxo-1,4,8,11-tetraazacyclotetradecane (**9**) as colorless needles (4.54 g, 9.57 mmol, 16% yield). m.p. = 188.0–189.0°C. IR (KBr pellet) 3430, 3299, 3054, 2924, 2911, 2820, 1645 (C=O), 1539, 1476, 1458, 1435, 1364, 1339, 1306, 1291, 1183, 1132, 1090, 1068, 1051, 1024, 891, 866, 842, 768, 744, 698, 503 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.68–1.76 (2H, m, CCH_2C), 2.30–2.86 (14H, m, NCH_2, $COCH_2$), 3.20–3.28 (1H, m, CHNCO), 3.47–3.56 (1H, m, CHNCO), 4.66–4.82 (2H, br, ArCHN), 6.97–7.02 (1H, m, ArH), 7.17 (1H, dt, J = 2.5, 7.7 Hz, ArH), 7.21–7.39 (12H, m, ArH).

Monooxomacrocycle **9** (2.00 g, 4.21 mmol) was added to a THF solution (150 ml) of BH_3–THF (150 mmol) at 0°C [7]. The solution was stirred at room temperature for 1 h and then heated at 65°C for 1 day. After decomposition of excess amount of BH_3 with 6 M aqueous HCl at 0°C, the solvent was evaporated. The residue was dissolved in water (100 ml) and washed with CH_2Cl_2 (50 ml × 2). The aqueous layer pH was adjusted to 12 with 3 M NaOH and then extracted with CH_2Cl_2 (50 ml × 3). After all organic layers were combined and dried over Na_2SO_4, the solvent was evaporated to dryness. Crystallization of the residue from CH_3CN yielded **3** as colorless prisms (1.45 g, 3.15 mmol, 75% yield). m.p. 149.5–150.5°C. IR (KBr pellet) 3650, 3291, 3052, 2926, 2818, 1478, 1465, 1435, 1337, 1183, 1117, 1092, 1068, 1020, 999, 959, 912, 829, 797, 745, 698, 544, 503 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.58–1.63 (2H, m, CH_2CAr), 1.67–

1.74 (2H, m, CCH_2C), 2.20 (1H, ddd, J = 2.6, 9.5, 11.9 Hz, NCH_2), 2.35–2.51 (3H, m, NCH_2), 2.55–2.82 (11H, m, NCH_2), 4.56–4.63 (1H, m, NCHAr), 6.87 (1H, ddd, J = 1.3, 4.4, 7.8 Hz, ArH(4)), 7.11 (1H, dt, J = 1.3, 7.4 Hz, ArH(3)), 7.24–7.37 (11H, m, ArH), 7.52–7.56 (1H, m, ArH); ^{13}C NMR ($CDCl_3$): δ 29.6, 38.1, 46.7, 49.4, 49.6, 49.7, 49.8, 50.86, 50.92, 61.3 (J_{PC} = 23.5 Hz), 126.0 (J_{PC} = 5.1 Hz), 126.7, 128.46 (J_{PC} = 6.6 Hz), 128.49 (J_{PC} = 7.3 Hz), 128.6, 128.8, 129.2, 133.4, 133.9 (J_{PC} = 19.8 Hz), 134.3 (J_{PC} = 19.8 Hz), 135.2 (J_{PC} = 13.2 Hz), 136.7 (J_{PC} = 10.3 Hz), 137.0 (J_{PC} = 11.0 Hz), 149.4 (J_{PC} = 22.0 Hz); ^{31}P NMR ($CDCl_3$): δ −16.5. *Anal.* Calc. for $C_{28}H_{37}N_4P_1 \cdot 1/2H_2O$: C, 71.6; H, 8.2; N, 11.9. Found: C, 71.4; H, 8.1; N, 12.1%.

2.3. Synthesis of triphenylphosphine oxide-pendant cyclam: 5-(2-diphenylphosphinylphenyl)-1,4,8,11-tetraazacyclotetradecane, **10**

A CCl_4 solution (50 ml) of benzyl alcohol (35 ml) and **3** (500 mg, 1.09 mmol) was heated at reflux for 12 h. After the mixture was evaporated to dryness, the residue was purified by silica gel chromatography (eluent CH_2Cl_2/MeOH/28% aqueous NH_3, 10:4:1) and crystallization from CH_3CN yielded **10** as colorless prisms (388 mg, 0.76 mmol, 75% yield). m.p. 174.0–175.0°C. IR (KBr pellet) 3335, 3055, 2926, 2876, 2811, 1482, 1466, 1437, 1364, 1190 (P=O), 1119, 756, 721, 698, 532 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.49–1.59 (1H, m, CHCAr), 1.64–1.71 (2H, m, CCH_2C), 1.80–1.93 (2H, m, CHCAr, NCH), 2.12–2.18 (1H, m, NCH), 2.37–2.77 (12H, m, NCH_2), 4.53–4.70 (1H, m, NCHAr), 7.00 (1H, ddd, J = 1.1, 7.7, 14.3 Hz, ArH(4)), 7.15 (1H, ddt, J = 1.3, 2.6, 7.5 Hz, ArH(3)), 7.43–7.56 (7H, m, ArH), 7.64–7.81 (4H, m, ArH), 7.77–7.81 (1H, m, ArH); ^{13}C NMR ($CDCl_3$): δ 29.4, 38.7, 46.3, 49.0, 49.1, 49.39, 49.44, 50.1, 50.4, 60.8 (J_{PC} = 5.1 Hz), 125.8 (J_{PC} = 13.2 Hz), 127.7 (J_{PC} = 10.3 Hz), 128.47 (J_{PC} = 11.7 Hz), 128.49 (J_{PC} = 12.5 Hz), 130.7 (J_{PC} = 102.0 Hz), 131.7 (J_{PC} = 2.9 Hz), 131.8 (J_{PC} = 2.2 Hz), 131.9 (J_{PC} = 9.5 Hz), 132.1 (J_{PC} = 9.5 Hz), 132.4 (J_{PC} = 2.2 Hz), 133.3 (J_{PC} = 7.2 Hz), 133.3 (J_{PC} = 104.2 Hz), 133.4 (J_{PC} = 102.0 Hz), 151.4 (J_{PC} = 8.1 Hz); ^{31}P NMR ($CDCl_3$): δ 31.2. *Anal.* Calc. for $C_{28}H_{37}N_4O_1P_1 \cdot 1/2CH_3CN$: C, 70.1; H, 7.8; N, 12.7. Found: C, 69.7; H, 7.9; N, 12.5%.

2.4. Synthesis of Ni^{II} complex with **3**, **11**

A MeOH solution (5 ml) of **3** (92.1 mg, 0.20 mmol) and $Ni^{II}(ClO_4)_2 \cdot 6H_2O$ (76.7 mg, 0.2 mmol) was heated at reflux for 30 min. Orange powder precipitated at room temperature. Crystallization of the powder from MeOH yielded **11**·$(ClO_4)_2$ as orange prisms (95.1 mg, 0.13 mmol, 65% yield). IR (KBr pellet) 3202, 2928, 2876, 1468, 1435, 1310, 1120, 1091, 1024, 743, 702, 627, 504 cm^{-1}. *Anal.* Calc. for $C_{28}H_{37}N_4O_8P_1Cl_2Ni_1$: C, 46.8; H, 5.2; N, 7.8. Found: C, 47.0; H, 5.2; N, 7.8%.

2.5. Synthesis of Ni^{II} complex with **10**, **13**

A MeOH solution (5 ml) of **10** (23.8 mg, 0.05 mmol) and $Ni^{II}Cl_2 \cdot 6H_2O$ (18.3 mg, 0.05 mmol) was heated at reflux in MeOH (5 ml) for 30 min. After addition of 10 times excess amount of NH_4PF_6, **13**·$ClO_4 \cdot PF_6$ was obtained as orange prisms (22.4 mg, 0.03 mmol, 60% yield). IR (KBr pellet) 3256, 2998, 2870, 1456, 1439, 1179, 1121, 843, 768, 750, 723, 696, 623, 559, 545 cm^{-1}. *Anal.* Calc. for $C_{28}H_{37}N_4O_4P_2F_6Cl_1Ni_1 \cdot CH_3OH$: C, 42.9; H, 5.1; N, 6.9. Found: C, 43.2; H, 5.3; N, 6.9%.

2.6. Synthesis of Mn^{III} complex with **3**, **14**

A MeOH solution (25 ml) of **3** (100 mg, 0.22 mmol) and $Mn^{III}(AcO)_3 \cdot 2H_2O$ (38.4 mg, 0.14 mmol) was heated under reflux for 10 min. After the solution was evaporated to dryness, conc. HCl aqueous solution (5 ml) was added to the residue to yield a green powder that was recrystallized from MeOH to yield **14**·Cl_3 as yellow needles (63.2 mg, 0.10 mmol, 71% yield). IR (KBr pellet) 3142, 2942, 2853, 1474, 1458, 1435, 1113, 1092, 1051, 1032, 1017, 1001, 883, 800, 763, 757, 752, 701, 511, 486 cm^{-1}. *Anal.* Calc. for $C_{28}H_{37}N_4P_1Cl_3Mn_1$: C, 54.1; H, 6.0; N, 9.1. Found: C, 54.2; H, 6.0; N, 9.1%.

2.7. Synthesis of Au^{I} complex with **3**, **17**

To a toluene solution (7 ml) of **3** (92.1 mg, 0.2 mmol) was added an EtOH solution (1 ml) of $Au^{I}(Et_3P)Cl$ (70.1 mg, 0.2 mmol) [12] at room temperature. After stirring for 5 h, the mixture was evaporated to dryness. The residue was crystallized from toluene to yield **17** as colorless needles (52.2 mg, 0.075 mmol, 38% yield). IR (KBr pellet) 3271, 2920, 2886, 2793, 2731, 1480, 1464, 1437, 1335, 1184, 1125, 1101, 752, 694, 550, 507 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.48–1.84 (4H, m, CCH_2C), 2.07–2.16 (2H, m, NCH_2), 2.40–2.82 (12H, m, NCH_2), 4.77–4.83 (1H, m, NCHAr), 6.78 (1H, ddd, J = 1.2, 7.8, 12.3 Hz, ArH(4)), 7.17 (1H, tt, J = 1.6, 7.6 Hz, ArH(3)), 7.44–7.63 (11H, m, ArH), 7.79–7.83 (1H, m, ArH); ^{31}P NMR ($CDCl_3$): δ 25.4. *Anal.* Calc. for $C_{28}H_{37}N_4P_1Cl_1Au_1$: C, 48.5; H, 5.4; N, 8.1. Found: C, 48.6; H, 5.4; N, 8.0%.

2.8. Synthesis of Au^{III} complex with **3**, **18**

To a suspension of $Au^{III}(dien)Cl_3$ [13] (40.6 mg, 0.1 mmol) in CH_3CN (15 ml) was added a MeOH solution (3 ml) of **3** (46.0 mg, 0.1 mmol). After stirring for 3 h, $Au^{III}(dien)Cl_3$ was dissolved in the solution, the solution color changed to yellow. After the mixture was evaporated to dryness, the residue was dissolved in MeOH (1 ml). To the solution was added 60% aqueous $HClO_4$ (1 ml) to yield a yellow powder. The powder was crystallized from MeOH to obtain **18**·Cl·$(ClO_4)_2$ as yellow prisms (71.7 mg, 0.078 mmol, 78% yield). IR (KBr

pellet) 3291, 3017, 2957, 1456, 1437, 1120, 872, 763, 709, 694, 625, 546 cm^{-1}. ^1H NMR (DMSO-d_6): δ 1.66–1.96 (4H, m, CCH_2C), 2.22–2.38 (2H, m, NCH_2), 2.52–3.16 (12H, m, NCH_2), 4.56–4.64 (1H, m, NCHAr), 6.76–6.82 (1H, m, ArH), 7.42–7.78 (13H, m, ArH); ^{31}P NMR ($CDCl_3$): δ 32.6. *Anal.* Calc. for $C_{28}H_{37}N_4O_8P_1Cl_3Au_1 \cdot CH_3OH$: C, 37.7; H, 4.5; N, 6.1. Found: C, 37.6; H, 4.7; N, 6.1.

2.9. Synthesis of Au^{I}-Au^{III} complex with 3, 20

To a suspension of $Au^{III}(dien)Cl_3$ (29.3 mg, 0.072 mmol) in CH_3CN (8 ml) was added a MeOH solution (1 ml) of **17** (50.0 mg, 0.072 mmol) at room temperature. After stirring for 2 h, $Au^{III}(dien)Cl_3$ was dissolved and the solution color changed to yellow. After the mixture was evaporated to dryness, the residue was dissolved in MeOH (1 ml). To the solution was added 1 M aqueous $HClO_4$ (1 ml) to yield an orange power that crystallized from MeOH/CH_3CN (1:1) to obtain **20**·Cl_2·$(ClO_4)_3$ as orange prisms (23.3 mg, 0.011 mmol, 31% yield). IR (KBr pellet) 3058, 2926, 2851, 1456, 1437, 1101, 1001, 756, 710, 694, 545, 513 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.45–2.22 (8H, m, CCH_2C), 2.15–2.25 (4H, m, NCH_2), 2.60–3.45 (24H, m, NCH_2), 4.57–4.63 (2H, m, NCHAr), 6.73–6.78 (2H, m, ArH(4)), 7.05–7.10 (2H, m, ArH(3)), 7.40–7.85 (24H, m, ArH). *Anal.* Calc. for $C_{56}H_{72}N_8O_{12}P_2Cl_5Au_3$: C, 35.8; H, 4.0; N, 6.0. Found: C, 35.7; H, 4.4; N, 5.9%.

2.10. Synthesis of Au^{I}-Ni^{II} complex with 3, 21

A MeOH solution (10 ml) of **3** (35.9 mg, 0.05 mmol) and $Au^{I}(Et_3P)Cl$ (17.6 mg, 0.05 mmol) was stirred at room temperature for 2 h. After the mixture was evaporated to dryness, the residue was dissolved in MeOH (3 ml), and diethyl ether (5 ml) was added to the solution to yield a purple powder that was crystallized from H_2O/MeOH (1:1) to yield **21**·Cl_2·ClO_4 as orange prisms (18.3 mg, 0.021 mmol, 43% yield). IR (KBr pellet) 3225, 2953, 2868, 1460, 1437, 1144, 1090, 997, 754, 696, 627, 545, 509 cm^{-1}. *Anal.* Calc. for $C_{28}H_{37}N_4O_4P_1Cl_3Ni_1Au_1 \cdot CH_3OH$: C, 37.9; H, 4.5; N, 6.1. Found: C, 37.5; H, 4.5; N, 6.1%.

2.11. Catalytic oxygenation of trans-stilbene with Ni^{II} or Mn^{III} complex

A CH_2Cl_2 solution (0.4 ml) of *trans*-stilbene (0.16 mmol), catalyst (4 μmol; **11**, Ni^{II}-cyclam complex **12**, **13**, **14**, and Mn^{III}-cyclam complex **16**), and benzyl tri-*n*-butyl ammonium chloride (6 μmol, phase-transfer agent) was stirred vigorously with 0.74 M NaClO (Antiformin, pH 12.7, 0.8 ml) at 25°C for 1 h. The reaction was quenched with 10% aqueous Na_2SO_3 (5 ml) and extracted with ethyl acetate (2 ml × 3). After all organic layer was combined and dried over Na_2SO_4. The solution was diluted to 10 ml with ethyl acetate and analyzed. Identification of reaction products was performed by conjunction of reaction mixtures with standards onto HPLC column. HPLC analysis was performed with a 5 μm Lichrospher Si60 column (250 × ϕ 4 mm) eluted with n-hexane/ethyl acetate (10:1) at 1.5 ml min^{-1} with detector at 258 nm. A Shimadzu SPD-6A UV spectrophotometric detector and a Shimadzu C-R6A Chromato PAC were used. The retention time for *trans*-stilbene, *trans*-stilbene oxide, and benzaldehyde is 4.4, 6.3, and 7.8 min, respectively. *cis*-Stilbene oxide (5.0 min) was not detected. The results are summarized in Table 3.

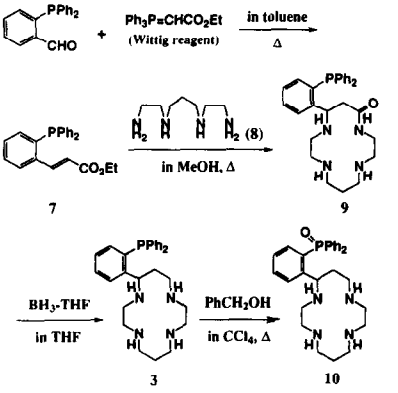
2.12. Electrochemical measurement

Cyclic voltammetry in CH_3CN or H_2O was carried out using a Yanaco P-1100 polarographic analyzer. A three-electrode system was employed. In H_2O, either a glassy carbon, hanging mercury electrode, or gold electrode were used as the working electrode, along with a Pt-wire coil, or glassy carbon as the auxiliary electrode and saturated calomel electrode (SCE) as the reference electrode (0.2412 V versus NHE). In CH_3CN, a glassy carbon electrode was used as the working electrode, along with a glassy carbon as the auxiliary electrode and saturated calomel electrode (SCE) as the reference electrode. The reference electrode was separated from the bulk of the solution by a glass frit and was immersed in an CH_3CN solution containing 0.1 M n-Bu_4NPF_6. All experiments were carried out at 25.0 ± 0.1°C under Ar. Potentials are reported versus SCE, the scan rates were 500 mV s^{-1} and 100 mV s^{-1} for cyclic voltammetry in H_2O and CH_3CN, respectively. Experimental errors were within ±10 mV.

3. Results and discussion

3.1. New ligands 3 and 10

The synthetic route to the target ligand **3** involved an condensation of unsaturated ester **7** and a tetraamine **8**, as



Scheme 4.

shown in Scheme 4. Compound **3** was obtained as prismatic crystals. Unlike any previous homologous pendant cyclams, **3** is more soluble in organic solvents such as $CHCl_3$ than in water. The triphenylphosphine oxide-pendant cyclam **10** was synthesized from the reaction of **3** with equimolar benzyl alcohol in refluxing CCl_4 in 75% yield. Triphenylphosphine oxide (TPPO) was confirmed by strong IR stretching frequency at 1190 cm^{-1} (in KBr pellet), characteristic of $\nu_{P=O}$ [14].

3.2. Interaction of Ni^{II} with 3

Treatment of **3** with equimolar $Ni^{II}(ClO_4)_2$ in MeOH for 30 min at reflux temperature and concentration of the solvent precipitated orange prisms **11**. This metal complex **11** fits to the 1:1 Ni^{II}-**3** complex formula as $2ClO_4$ salt. We assigned the Ni^{II} complex to the non-interacting triphenylphosphine (TPP) structure **11** (mostly four-coordinate, diamagnetic Ni^{II}) from UV-visible absorption (λ_{max} 450 nm, ε 60 in MeOH) and electrochemical redox potentials. Earlier, all the other pendant cyclams **1a–d** yielded only pink (paramagnetic) Ni^{II} complexes **2a–d**, which were shown by X-ray analysis to be axially coordinated with the pendants [4b,c,5a,6a,7]. Ni^{II}-(pendant-free) cyclam complex **12** is orange (λ_{max} 452 nm, ε 57 M^{-1} cm^{-1}) in MeOH, indicating a diamagnetic Ni^{II} complex form, although the equilibrium of four-coordinate diamagnetic ⇌ six-coordinate paramagnetic Ni^{II} exists depending on the conditions [15]. Electrochemical redox potential on cyclic voltammograms (CV) was −1.52 versus saturated calomel electrode (SCE) for Ni^{II}/Ni^{I} (at hanging mercury electrode) and +0.52 for Ni^{II}/Ni^{III} (at glassy carbon electrode) for **11** (Table 1) with $I = 1.5$ (Na_2SO_4) at 25°C in H_2O (scan rate 500 V s^{-1}). For reference, **12** showed almost the same $E_{1/2}$ values of −1.56 V and +0.50 V, respectively, under the same conditions. In the previous 5-coordinate Ni^{II} complexes with the pendant donors axially coordinated, the Ni^{I} state was less stabilized; i.e. the $E_{1/2}$ for $Ni^{II}/Ni^{I} < -1.6$ V.

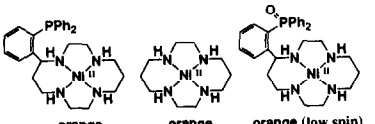
Table 1
Redox properties of the Ni^{II} and Mn^{III} complexes

Complex		$E_{1/2}$ (V versus SCE)
Ni^{II} complex[a]	Ni^{II}/Ni^{III} (ΔE_p, mV)[b]	Ni^{I}/Ni^{II} (ΔE_p, mV)[c]
11	+0.53 (58)	−1.52 (28)
13	+0.54 (55)	−1.55 (73)
12	+0.50	−1.56
Mn^{III} complex[d]	Mn^{III}/Mn^{II}	
14	−0.12	
16[e]	−0.04	
15[e]	+0.09	

[a]At 25°C with $I = 1.5$ (Na_2SO_4) in H_2O.
[b]At glassy carbon electrode (scan rate 500 mV s^{-1}).
[c]At hanging mercury electrode (scan rate 500 mV s^{-1}).
[d]At 25°C with $I = 0.1$ ($NaClO_4$) in H_2O (pH 3.6) at gold electrode.
[e]From Ref. [6b].

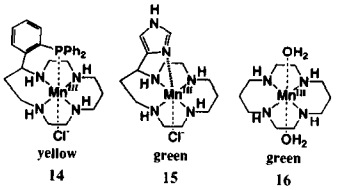
3.3. Interaction of Ni^{II} with 10

Refluxing **10** with equimolar $Ni^{II}Cl_2$ in MeOH for 30 min, followed by addition of NH_4PF_6 precipitated orange prisms **13**. We again assigned the four-coordinate, uncoordinating TPPO structure **13**, as suggested by the similar electrochemical redox behaviors (Table 1) and UV-visible absorption (λ_{max} 455 nm, ε 90 in MeOH) to those of **12**. The $\nu_{P=O}$ occurs at 1179 cm^{-1} (in KBr pellet), almost the same wave number as with the free ligand.



3.4. Interaction of Mn^{III} with 3

Ligand **3** and one equivalent of $Mn^{III}(OAc)_3$ were heated at reflux in MeOH for 10 min. After addition of a small amount of conc. HCl aqueous solution to the resulting solution, yellow needles **14** were obtained (λ_{max} 355 nm, ε 2100 (sh) in H_2O, pH 3.5). In our previous X-ray study, the imidazole pendant cyclam **2c** formed a green-colored, 6-coordinate Mn^{III} complex **15** with the imidazole N and Cl^- coordinating from axial sites (λ_{max} 350 nm, ε 1600 (sh) in H_2O) [6b]. For another reference, the pendant-free cyclam complex **16** (six-coordinate with two axial water) [10] showed λ_{max} 340 nm (ε 2300 (sh)) in H_2O (green color). The $E_{1/2}$ values for Mn^{III}/Mn^{II} on CV of **15** and **16** at gold electrode were respectively +0.09 V and −0.04 V versus SCE with $I = 0.1$ ($NaClO_4$) at 25°C in H_2O (pH 3.6, scan rate = 500 mV s^{-1}) (Table 1) [6b]. It was therefore concluded that the imidazole axial ligation gives little contribution to the stabilization of the Mn^{II} state with respect to Mn^{III}. Under the same conditions, CV of **14** showed a quasi-reversible Mn^{III}/Mn^{II} couple at $E_{1/2}$ −0.12 V, implying practically little stabilization of Mn^{III}.



3.5. Interaction of Au^{I} with 3

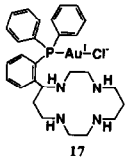
Stirring **3** with $Au^{I}(Et_3P)Cl$ in toluene for 10 min yielded **17** as colorless prisms. The evidence for Au^{I} (out) structure **17** comes from the ^1H and ^{31}P NMR measurements, where the TPP proton signals move from δ 7.2–

Table 2
Reduction properties of the Au^{III} or Au^{I} complexes in CH_3CN at 25°C[a]

Complex	Peak potential (V versus SCE)		
	$Au^{III} \rightarrow Au^{II}$	$Au^{II} \rightarrow Au^{I}$	$Au^{I} \rightarrow Au^{0}$
17	_[b]	_[b]	−1.89
18	−1.28	−1.42	−1.89
19	−0.16	−0.62	−0.98
20	−0.26	−0.72	−1.26, −1.80

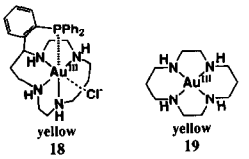
[a]With 0.1 M n-Bu_4NPF_6 at glassy carbon electrode.
[b]No observed.

7.4 (for **3**) to δ 7.4–7.6 (for **17**) and the ^{31}P signal moves from δ −16.5 to δ 25.4, while the methylenes on the cyclam undergo no shifts upon Au^{I} complexation. CV of **17** (Table 2) in CH_3CN (25 °C, I = 0.1 (n-Bu_4NPF_6)) showed an irreversible reduction peak at −1.89 V versus SCE for the $Au^{I} \rightarrow Au^{0}$ at glassy carbon electrode (scan rate 100 mV s^{-1}). It is similar to the value of Au^{I}(TPP)Cl (−1.86 V) under the same conditions.



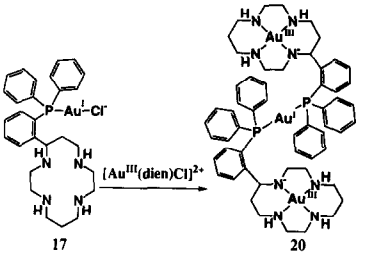
3.6. Interaction of Au^{III} with 3

Upon treatment of **3** with $[Au^{III}(dien)Cl]Cl_2$ in CH_3CN/MeOH (5:1) at room temperature for 3 h, smooth ligand replacement took place, to yield a yellow Au^{III}(in cyclam) complex **18**, which was recrystallized from MeOH and isolated as $Cl\cdot(ClO_4)_2$ salt. We tentatively assigned the Au^{III} complex to the folded cyclam and coordinating TPP structure **18** from the following results. The proton and ^{31}P NMR measurements showed the multiplet of the TPP protons shifting from δ 7.2–74 (for **3**) to δ 7.4–7.8 (for **18**) and ^{31}P shifting from δ −16.5 to δ 32.6. Earlier, the square-planar Au^{III}-cyclam complex **19** was shown to have a CT absorption band ($N^{-} \rightarrow Au^{III}$) at λ_{max} 382 nm (ε 1907) in DMF [4h]. Since the present Au^{III} complex **18** possesses a much weaker CT band at λ_{max} 391 nm (ε 182) in the same solvent, it is suggested that the interaction between Au^{III} and the nitrogen donors of cyclam is weaker, leading to a postulated less strained cyclam *cis* configuration. CV of **18** (Table 2) in CH_3CN (25°C, 0.1 M n-Bu_4NPF_6) showed irreversible reduction peaks at −1.28, −1.42 and −1.89 V versus SCE for $Au^{III} \rightarrow Au^{II}$, $Au^{II} \rightarrow Au^{I}$ and $Au^{I} \rightarrow Au^{0}$ at glassy carbon electrode (scan rate 100 mV s^{-1}), respectively, that were very different from the values with **19** (−0.16, −0.62 and −0.98 V, respectively), but **18** showed the same value for $Au^{I} \rightarrow Au^{0}$ as **17**. It is supposed that the Au^{III} in **18** was greatly stabilized with respect to Au^{III} in **19**, but upon reduction to Au^{I}, demetallation of **18** was observed, leading to **17**.



3.7. Au^{III}–Au^{I} complex with 3

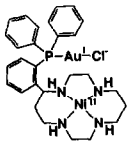
Refluxing the Au^{I} complex **17** with $[Au^{III}(dien)Cl]Cl_2$ in CH_3CN for 2 days produced an Au^{I}(out)–Au^{III}(in cyclam) mixed complex **20** (as $Cl_2(ClO_4)_3$ salt) as orange prisms. The structural assignment is based on elemental analysis (C, H, N) and proton NMR (the N–CH_2 signals for cyclam shift from δ 2.4–2.8 for **17** to δ 2.6–3.1 for **20** as found for **19** [4e]; no such shift is observed for the Ph_3P multiplet). The UV spectroscopic measurements of **20** in DMF showed λ_{max} 387 nm (ε 3722) to be compared with λ_{max} 382 nm (ε 1907) for **19** in the same solvent, where the easy deprotonation of the cyclam NH occurred (the pK_a value of 5.4 for **19** in H_2O with I = 0.1 ($NaClO_4$) at 25°C) [4h]. CV of **20** (Table 2) in CH_3CN (25°C, 0.1 M n-Bu_4NPF_6) showed irreversible reduction peaks at −0.26, −0.72, −1.26 and −1.80 V versus SCE for $Au^{III} \rightarrow Au^{II}$, $Au^{II} \rightarrow Au^{I}$, $Au^{I} \rightarrow Au^{0}$(in cyclam), and $Au^{I} \rightarrow Au^{0}$(out cyclam) at glassy carbon electrode (scan rate 100 mV s^{-1}), which were similar to the combined values for **19** and **17**.



3.8. Ni^{II}–Au^{I} complex with 3

The orange Ni^{II} complex **11** was reacted with $Au^{I}(Et_3P)Cl$ in CH_2Cl_2, yielding an Au^{I}(out)–Ni^{II}(in cyclam) complex **21**. The structure assignment is based on elemental analysis (C, H, N) and the following data. The UV spectroscopic measurement in MeOH showed λ_{max} 460 nm (ε 50), almost the same for **11** (λ_{max} 450 nm, ε 60). CV of **21** in CH_3CN (25°C, I = 0.1 (n-Bu_4NPF_6)) showed a quasi-reversible redox wave at $E_{1/2}$ +1.27 V versus SCE for Ni^{II}/Ni^{III} couple and an irreversible reduction peak at −1.56 V for $Ni^{II} \rightarrow Ni^{I}$ at glassy carbon electrode (scan rate 100 mV s^{-1}). For comparison, unsubstituted Ni^{II}-cyclam **12** showed a quasi-reversible redox wave at $E_{1/2}$ +1.16 V and an irreversible peak at −1.50 V, respectively, under the same condition. According to

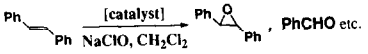
these results, it is considered that Au^{I} and Ni^{II} have little interaction in **21**.



21

3.9. Catalytic oxygenation of trans-stilbene with Ni^{II} (11,12,13) and Mn^{III} complexes (14,16)

Like the previous reaction conditions [8a], the catalytic oxygenation of *trans*-stilbene was carried out under uniform conditions with **11–14** and **16** at 25°C (see Section 2).

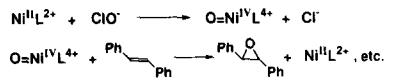


The results (Table 3) showed that the Ni^{II}-TPPO-pendant cyclam complex **13** was the most efficient catalyst for the oxygen atom transfer reaction from NaClO to the substrate *trans*-stilbene and also the most selective catalyst for the epoxidation among the cyclam complexes tested. The TPP-cyclam in **11** was first converted into the phosphine oxide to yield **13**, as demonstrated on TLC. In 1987, Kochi reported that in norbornene (1 mmol) oxygenation with Ni^{II}-cyclam **12** (0.01 mmol) and iodosylbenzene (0.03 mmol) in CH_2Cl_2 (1 ml) at 25°C for 2 h, addition of 2 equiv. of triethylphosphine oxide increased the epoxide yield from 24 to 42% (based on iodobenzene formed) [8b]. In order to check the intermolecular TPPO effect, we added 10 equiv. of TPPO to the Ni^{II}-cyclam **12** under the present conditions and we indeed observed an increase in the yield and selectivity of epoxide formation over product (entry 4 in Table 3). However, our intramolecular TPPO of **13** is more efficient due to the proximate TPPO effect and probably higher solubility in CH_2Cl_2 than the pendantless complex **12** [16]. In another experiment, with 5 equiv. of **13** (against the substrate) or Ni^{II}-cyclam and TPPO, but without NaClO, no epoxide product was detected on HPLC, implying that the oxygen to be transferred to stilbene did not come from TPPO, but came from NaClO. We tentatively postulate an oxenoid intermediate, (TPPO-cyclam) Ni^{IV}=O species, like the previously proposed (cyclam) Ni^{IV}=O [8b,c].

Table 3
Catalytic oxidation of *trans*-stilbene with Ni^{II} and Mn^{III} cyclam complexes[a]

Cyclam complex	Turnover for product[b]		
	trans-epoxide (A)	PhCHO (B)	A/B
Ni^{II} complex			
11 (TPP-pendant)	16.2	1.6	10.1
13 (TPPO-pendant)	17.1	1.7	10.1
12 (free)[c]	11.2	2.3	4.9
12 + TPPO (10 equiv.)	12.1	1.4	8.6
Mn^{III} complex			
14 (TPP-pendant)	10.4	1.8	5.8
16 (free)	6.0	1.3	4.6

[a]0.16 mmol of *trans*-stilbene, 4 μmol of the cyclam complex, and 6 μmol of benzyl tri-n-butyl ammonium chloride (phase-transfer agent) in 0.4 ml of CH_2Cl_2 with 0.8 ml of 0.74 M NaClO (Antiformin, pH 12.7) at 25°C for 1 h.
[b]Mole of product/mole of catalyst in 1 h. Other minor unidentified products were also detected.
[c]In ref 8a, the total yield of *trans*-epoxide was 4.7% (0.33 mol/mol of **12**) the reaction time 6 h, using the same ratio reaction mixture.



4. Conclusions

New macrocyclic tetraamine ligands, triphenylphosphine-pendant and triphenylphosphine oxide-pendant cyclams, were synthesized. They formed stable 1:1 complexes with Ni^{II}, Au^{III}, and Mn^{III}. The triphenylphosphine-pendant may (in the case of Au^{III} and Mn^{III}) or may not (in the case of Ni^{II}) bind to the cyclam-incorporated metal ions. Little effects of the triphenylphosphine-pendant on the metal redox properties were seen. Gold(I) ion interacted only with the triphenylphosphine pendant. To the resulting complex, Ni^{II} or Au^{III} further interacted only with the cyclam moiety to yield each hetero dimetallic complexes. The Ni^{II} complex with the triphenylphosphine oxide-pendant was the most effective catalyst for epoxidation of *trans*-stilbene with NaClO as an oxygenation source.

Acknowledgements

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References

[1] E. Kimura, in, M. Hiraoka, (ed.), *Studies in Organic Chemistry*, Vol. 45, Elsevier, Amsterdam, 1992, p. 381.
[2] E. Kimura, *Tetrahedron*, *48* (1992) 6175.
[3] E. Kimura, in, S.R. Cooper (ed.), *Crown Compounds Toward Future Applications*, VCH, New York, 1992, p. 81.
[4] (a) E. Kimura, T. Koike and M. Takahashi, *J. Chem. Soc., Chem. Commun.*, (1985) 385; (b) Y. Iitaka, T. Koike and E. Kimura, *Inorg. Chem.*, *25* (1986) 402; (c) E. Kimura, T. Koike, K. Uenishi and R.B. Davidson, *J. Chem. Soc., Chem. Commun.*, (1986) 1110; (d) E. Kimura, M. Yamaoka, M. Morioka and T. Koike, *Inorg.*

Chem., *25* (1986) 3883; (e) E. Kimura, T. Koike, K. Uenishi, M. Hediger, M. Kuramoto, S. Joko, Y. Arai, M. Kodama and Y. Iitaka, *Inorg. Chem.*, *26* (1987) 2975; (f) E. Kimura, S. Joko, T. Koike and M. Kodama, *J. Am. Chem. Soc.*, *109* (1987) 5528; (g) E. Kimura, T. Koike and T. Toriumi, *Inorg. Chem.*, *27* (1988) 3687; (h) E. Kimura, Y. Kurogi and M. Takahashi, *Inorg. Chem.*, *30* (1991) 4117; (i) E. Kimura, H. Kurosaki, T. Koike and K. Toriumi, *J. Inclusion Phenom.*, *12* (1992) 377.

[5] (a) E. Kimura, T. Koike, H. Nada and Y. Iitaka, *J. Chem. Soc., Chem. Commun.*, (1986) 1322; (b) E. Kimura, Y. Kurogi, T. Koike, M. Shionoya and Y. Iitaka, *J. Coord. Chem.*, *28* (1993) 33.

[6] (a) E. Kimura, M. Shionoya, T. Mita and Y. Iitaka, *J. Chem. Soc., Chem. Commun.*, (1987) 1712; (b) E. Kimura, M. Shionoya, T. Yamauchi and M. Shiro, *Chem. Lett.*, (1991) 1217; (c) E. Kimura, Y. Kurogi, M. Shionoya and M. Shiro, *Inorg. Chem.*, *30* (1991) 8935.

[7] E. Kimura, Y. Kotake, T. Koike, M. Shionoya and M. Shiro, *Inorg. Chem.*, 29 (1990) 4991.

[8] (a) H. Yoon and C.J. Burrows, *J. Am. Chem. Soc.*, *110* (1988) 4087; (b) J.D. Koola and J.K. Kochi, *Inorg. Chem.*, *26* (1987) 908; (c) J.F. Kinneary, J.S. Albert and C. Burrows, *J. Am. Chem. Soc.*, *110* (1988) 6124.

[9] B. Bosnich, M.L. Tobe and G.A. Webb, *Inorg. Chem.*, *4* (1965) 1109.

[10] (a) P.K. Chan and C.K. Poon, *J. Chem. Soc., Dalton Trans.*, (1976) 858; (b) T.W. Hambly, G.A. Lawrance, D.F. Sangster and C.B. Ward, *Aust. J. Chem.*, *40* (1987) 883.

[11] J.E. Hoots, T.B. Rauchfuss and D.A. Warobleski, *Inorg. Synth.*, *21* (1982) 175.

[12] H. Schmidbaur and A. Shiotani, *Chem. Ber.*, *104* (1971) 2821.

[13] (a) W.H. Baddley, F. Basolo, H.B. Gray, C. Nölting and A. Pöi, *Inorg. Chem.*, *2* (1963) 921; (b) G. Nardin, L. Randaccio, G. Annibale, G. Natile and B. Pitteri, *J. Chem. Soc., Dalton Trans.*, (1980) 220.

[14] K. Nakanishi, P.H. Solomon and N. Furutachi, in, J. Kotachi (ed.), *Infrared Absorption Spectroscopy*, Nankodo, Tokyo, 1978, p. 55.

[15] A. Anichini, L. Fabbrizzi and P. Paoletti, *Inorg. Chem. Acta*, *24* (1977) L21.

[16] T.R. Wagler, Y. Fang and C.J. Burrows, *J. Org. Chem.*, *54* (1989) 1584.