



Synthesis and structural characterization of magnesium complexes bearing phenanthrene imine derivative ligands



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ABSTRACT

Reduction reactions of the phenanthrene-*o*-aryliminoquinone with 0.5 equiv of magnesium in tetrahydrofuran afford the bisligated magnesium complexes [^{Ar}piq]₂Mg(thf) (**1a**, Ar = 2,6-Me₂C₆H₃; **1b**, Ar = 2,6-ⁱPr₂C₆H₃). **1a** can be further reduced by magnesium to oxygen-bridged dinuclear complex [(μ-O)^{Ar}piqMg(thf)₂]₂ (**2**). Similar reduction reactions of the N,N-bis(arylimino)phenanthrene with magnesium give bis(arylimino)phenanthrene magnesium complexes ^{Ar1,Ar2}bipMg(thf)₃ (**3**, Ar₁ = Ar₂ = 2,6-Me₂C₆H₃; **4**, Ar₁ = Ar₂ = 2,6-ⁱPr₂C₆H₃; **5**, Ar₁ = 2,6-Me₂C₆H₃, Ar₂ = 2,6-ⁱPr₂C₆H₃). All the complexes were well characterized and the molecular structures of **1b**, **2**, **3**, and **5** were established by X-ray diffraction analysis.

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1. Introduction

In the past decades, the α -diimine ligands represented by diazabutadiene (**dad**) and bis(N-arylimino)acenaphthene (**bian**), have received considerable attention and were widely used as chelating ligands in transition-metal chemistry due to their rigidities and easy modification of the N-substituents [1]. In addition to being used as neutral ligands, they can also be reduced with alkali or alkaline-earth metals, forming monoanionic or enediamido ligands [2]. Using these reduced monoanionic or enediamido ligands as starting reactants, some Al, Ca, and Ge complexes were also reported [3]. On the other hand, the α -diimine ligands can also be reduced by low-value organometallic precursors, such as metallic samarium [4] and CrCl₂ [5]. The π acceptor properties of the monoanionic and enediamido ligands cause electron deficiency at the coordinated metal and render these complexes highly reactive towards organic substrates. For example, Ar-**bian** enediamido magnesium complexes are very active to the unsaturated organic substrates and acid compounds [6], and show moderate activities in the lactide polymerization [7]. The monoanionic **bian** chromium complexes show high activities in diene polymerization affording *cis*-1,4 enriched polymer [5]. As one of our continuing research work on α -diimine complexes, we are very interested in exploring the phenanthrene-imine derivative ligands which have larger delocalized π systems compared to that of Ar-**bian** analogues. The neutral bis(arylimino)phenanthrene ligands (Ar-**bip**) have been used in supporting the nickel and diethylpalladium

complexes [1e,8]. Some rare earth metal complexes with monoanionic radical phenanthrene-*o*-aryliminoquinone ligands (Ar-**piq**) were prepared by reacting the ligands with either metallic or low value rare-earth-metal precursors [9]. More recently, we have demonstrated that the phenanthrene-imine derivatives (Ar-**bip** and Ar-**piq**) can also be reduced by CrCl₂ affording corresponding monoanionic Ar-**bip** and Ar-**piq** Cr(III) complexes [10]. To the best of our knowledge the main group complexes, especially the magnesium complexes based on phenanthrene-imine derivative ligands have not been reported so far. Herein we wish to report the synthesis and structural characterization of the phenanthrene-imine magnesium complexes.

2. Experimental

2.1. Materials and measurements

All manipulations involving air and moisture-sensitive compounds were carried out under an atmosphere of dried and purified nitrogen using standard Schlenk and vacuum-line techniques. Toluene and hexane were dried over sodium metal and distilled under nitrogen. Elemental analyses were performed on a Varian EL microanalyzer. NMR spectra were carried out on Varian 300 MHz instrument at room temperature in CDCl₃ solution for ligand, and in C₆D₆ or C₇D₈ solution for complexes. The EPR spectra were recorded on a JES-FA 200 ESR spectrometer at X-band. FT-IR was performed on a Nicolet FT-IR 360 spectrometer (Nicolet, USA). 9,10-Phenanthrenequinone, 1,4-diazabicyclo[2.2.2]octane (dabco), 2,6-dimethylaniline, and 2,6-diisopropylaniline were bought from

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Aldrich Chemical Co. and used without further purification. The ligand N-(2,6-dimethylphenyl)-9,10-iminophenanthraquinone, N-(2,6-diisopropylphenyl)-9,10-iminophenanthraquinone, N,N'-bis(2,6-dimethylphenyl)-phenanthrenediimine, N,N'-bis(2,6-diisopropylphenyl)-phenanthrenediimine and N-(2,6-dimethylphenyl)-N'-(2,6-diisopropylphenyl)-phenanthrenediimine were synthesized according to the literature [10].

2.2. Synthesis of complex 1a

A solution of N-(2,6-dimethylphenyl)-9,10-iminophenanthraquinone (1.55 g, 5.0 mmol) in thf (30 mL) was added to magnesium turnings (0.06 g, 2.50 mmol), and the mixture was stirred for 40 min, during which time the mixture turned deep red. Filtration and evaporation of the solvent afford **1a** as deep red powder (1.95 g, 87%). Crystals of **1a** suitable for X-ray structural determination was grown in thf solution. M.p. 157 °C. *Anal. Calc.* for $C_{48}H_{42}MgN_2O_3$: C, 80.16; H, 5.89; N, 3.38. Found: C, 80.25; H, 5.79; N, 3.31%. IR(KBr): ν (cm^{-1}) 3306m, 3068w, 2972s, 2871s, 1579s, 1471s, 1450s, 1419s, 1378s, 1341m, 1280m, 1249s, 1227m, 1180m, 1121w, 1104w, 1065s, 1032m, 938w, 920m, 803w, 758s, 724s, 656m, 616w, 572w, 508w.

2.3. Synthesis of complex 1b

Complex **1b** was prepared in a similar method to that for **1a**, using N-(2,6-diisopropylphenyl)-9,10-iminophenanthraquinone (1.85 g, 5.0 mmol) and Mg (0.06 g, 2.5 mmol). Yield 1.70 g (82%). M.p. 190 °C. *Anal. Calc.* for $C_{56}H_{58}MgN_2O_3$: C, 80.90; H, 7.03; N, 3.37. Found: C, 80.78; H, 7.09; N, 3.31%. IR(KBr): ν (cm^{-1}) 3088m, 3061m, 2960s, 2866s, 1677w, 1618m, 1593s, 1505w, 1465s, 1447s, 1383m, 1345w, 1323w, 1296s, 1526m, 1230w, 1160w, 1093m, 1043w, 795w, 762s, 721m, 615w, 492m.

2.4. Synthesis of complex 2

The mixture of **1a** (0.36 g, 5 mmol) and activated magnesium turnings (0.24 g, 10 mmol) in thf (30 mL) was stirred for 40 min giving deep red mixture. Filtrating and evaporating the solvent afford complex **2** as deep red powder (0.39 g, 82%). Crystals of **2** suitable for X-ray structural determination was grown in thf solution. M.p. 208 °C. 1H NMR (300 MHz, C_6D_6 , 25 °C): δ 1.09 (bs, 16H, thf), 2.34 (s, 12H, CH_3), 3.59 (b, 16H, thf), 6.94 (t, $J_{H-H} = 6.0$ Hz, 2H, *p*- C_6H_3), 7.11 (d, $J_{H-H} = 6.0$ Hz, 4H, *m*- C_6H_3), 7.20 (br s, 4H, Ar-H), 7.30 (m, 2H, Ar-H), 7.45 (m, 2H, Ar-H), 8.16 (m, 4H, Ar-H), 8.75 (m, 4H). ^{13}C NMR (75 MHz, toluene- d_8): δ 21.01, 25.55, 68.55, 118.46, 119.50, 120.10, 121.69, 123.08, 123.34, 123.85, 124.17, 124.55, 124.81, 125.46, 126.40, 127.66, 128.56, 129.19, 129.67, 131.23, 133.09, 139.49, 139.79, 156.79. *Anal. Calc.* for $C_{60}H_{66}Mg_2N_2O_6$: C, 75.08; H, 6.93; N, 2.92. Found: C, 75.06; H, 7.11; N, 2.85%. IR(KBr): ν (cm^{-1}) 3386s, 3069m, 2971s, 2870s, 1593m, 1578s, 1520w, 1486m, 1472s, 1450s, 1419s, 1378s, 1341m, 1293w, 1279w, 1248w, 1208w, 1181w, 1163w, 1120w, 1099w, 1054m, 1019m, 938w, 920w, 758s, 724s, 638m, 574m.

2.5. Synthesis of complex 3

Complex **3** was prepared in a similar method to that for **1**, using N,N'-bis(2,6-dimethylphenylimine)phenanthrene (0.41 g, 1.0 mmol) and Mg turnings (2.40 g, 1.0 mmol). Yield 0.61 g (93%). Crystals of **3** suitable for X-ray structural determination was grown in thf solution. M.p. 211 °C. 1H NMR (300 MHz, C_6D_6 , 25 °C): δ 1.33 (bs, 12H, thf), 1.77 (s, 12H, CH_3), 3.50 (bs, 12H, thf), 6.81–6.86 (m, 4H), 7.27 (m, 4H), 7.34 (t, $J_{H-H} = 6.0$ Hz, 2H), 7.94 (d, $J_{H-H} = 9.0$ Hz, 2H), 8.52 (d, $J_{H-H} = 6.0$ Hz, 2H). ^{13}C NMR (75 MHz, C_6D_6 , 25 °C): δ 19.19 (s, 4C, CH_3), 26.01 (s, 6C, thf), 68.57 (s, 6C, thf), 116.92,

121.20, 122.25, 123.74, 123.92, 125.17, 127.34, 129.83, 130.05, 143.08, 156.26 ppm. *Anal. Calc.* for $C_{42}H_{50}MgN_2O_3$: C, 77.00; H, 7.69; N, 4.28. Found: C, 77.05; H, 7.72; N, 4.21%. IR(KBr): ν (cm^{-1}) 3389s, 3063m, 2961s, 2867m, 1643w, 1620w, 1591s, 1471s, 1449s, 1396s, 1336m, 1288m, 1258m, 1241m, 1227m, 1204w, 1176w, 1160w, 1092m, 1066m, 1027m, 987w, 939w, 918w, 760s, 725m, 616w, 593w, 574m, 533m.

2.6. Synthesis of complex 4

Complex **4** was prepared in a similar method to that for **3**, using N,N'-bis(2,6-diisopropylphenylimine)phenanthrene (0.53 g, 1.0 mmol) and Mg (2.40 g, 100 mmol). Yield 0.63 g (82%). M.p. 247 °C. 1H NMR (300 MHz, C_6D_6 , 25 °C): δ 0.82–1.09 (m, 24H, $CH(CH_3)_2$), 1.40 (b, 12H, thf), 3.20 (m, 4H, $CH(CH_3)_2$), 3.56 (b, 12H, thf), 7.01–7.32 (m, 10H, Ar), 8.02 (d, $J_{H-H} = 9.0$ Hz, 2H, Ar), 8.54 (d, $J_{H-H} = 9.0$ Hz, 2H, Ar). ^{13}C NMR (75 MHz, toluene- d_8 , 25 °C): δ 23.93 (CH_3), 25.82 (thf), 30.32 (s, 2C, $CH(CH_3)_2$), 68.41 (thf), 122.86, 123.59, 123.88, 124.57, 127.20, 131.20, 131.94, 135.61, 135.85, 137.20, 145.38, 147.30, 160.29. *Anal. Calc.* for $C_{50}H_{66}MgN_2O_3$: C, 78.26; H, 8.67; N, 3.65. Found: C, 78.34; H, 8.62; N, 3.60%. IR(KBr): ν (cm^{-1}) 3389s, 3063m, 2960s, 2925s, 2865s, 1640m, 1615m, 1595s, 1449s, 1434s, 1381s, 1360s, 1327m, 1287m, 1253m, 1219w, 1190w, 1099w, 1057w, 1042w, 940m, 794m, 777m, 760s, 728s, 691w, 615w, 520w.

2.7. Synthesis of complex 5

Complex **5** was prepared in a similar method to that for **3**, using N-(2,6-dimethylphenylimine)-N-2,6-(diisopropylphenylimine)phenanthrene (0.47 g, 1.0 mmol) and magnesium turnings (2.40 g, 100 mmol). Yield 0.61 g (93%). Crystals of **5** suitable for X-ray structural determination was grown in thf solution. M.p. 223 °C. 1H NMR (300 MHz, C_6D_6 , 25 °C): δ 0.96 (d, $J_{H-H} = 9.0$ Hz, 6H, $CH(CH_3)_2$), 1.02 (d, $J_{H-H} = 6.0$ Hz, 6H, $CH(CH_3)_2$), 1.44 (b, 12H, thf), 1.94 (s, 6H, CH_3), 3.25 (m, 2H, $CH(CH_3)_2$), 3.62 (b, 12H, thf), 6.85–6.87 (m, 2H, Ar), 6.89–7.00 (m, 2H, Ar), 7.10–7.40 (m, 11H), 8.01 (d, $J_{H-H} = 6.0$ Hz, 1H, Ar), 8.12 (d, $J_{H-H} = 9.0$ Hz, 1H, Ar), 8.61 (t, $J_{H-H} = 9.0$ Hz, 1H, Ar). ^{13}C NMR (75 MHz, C_6D_6 , 25 °C): δ 19.93 (s, CH_3), 23.44 (s, $CH(CH_3)_2$), 23.83 (s, $CH(CH_3)_2$), 26.11 (b, thf), 28.80 (s, $CH(CH_3)_2$), 68.34 (b, thf), 121.70, 123.50, 123.67, 123.91, 124.09, 124.29, 124.88, 125.06, 125.20, 125.28, 125.96, 126.97, 127.53, 129.28, 130.26, 132.23, 132.78, 136.28, 139.92, 143.02, 143.12 ppm. *Anal. Calc.* for $C_{42}H_{50}MgN_2O_3$: C, 77.00; H, 7.69; N, 4.28. Found: C, 77.12; H, 7.75; N, 4.32%. IR(KBr): ν (cm^{-1}) 3059s, 2961s, 2866s, 1677m, 1594s, 1505m, 1465s, 1446s, 1383m, 1361w, 1346m, 1296s, 1245m, 1231m, 1196w, 1160m, 1094m, 1120w, 1094m, 1042w, 968w, 934w, 923w, 850w, 794m, 763s, 720s, 627w, 614w, 492m.

2.8. X-ray crystal structural determination

The crystals were mounted on a glass fiber using the oil drop. Data obtained with the ω – 2θ scan mode were collected on a Bruker SMART 1000 CCD diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The structures were solved using direct methods, while further refinement with full-matrix least squares on F^2 was obtained with the SHELXTL program package [11]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced in calculated positions with the displacement factors of the host carbon atoms. Complex **3** is in relative low quality and some B alerts were reported in Checkcif.

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