Supplementary Material

Preparation: Complexes **2** - **8** were prepared in a very similar way; only a representative method is described. An argon-scrubbed solution of 2-(3,5-disubstituted aniline)-4,6-di-*tert*-butylphenol H_2L^R (3 mmol) in freshly distilled acetonitrile (25 mL) was stirred with either $Co(ClO_4)_2 \bullet 6H_2O$ or $GaCl_3$ (1 mmol) and triethylamine (0.5 mL) for 0.5 h under argon. The resulting solution was refluxed for 1 h under argon. The cooled solution was exposed to air and stirred further for 1 h upon which a dark green solid separated out. The microcrystalline solid was recrystallized from Et_2O-CH_3CN to yield dark green or deep red-brown crystals.

Complex 2: Yield: 72%. Anal. calcd for $C_{66}H_{87}O_9N_3Co$: C, 70.44; H, 7.79; N, 3.73; Co, 5.24. Found: C, 70.0; H, 7.8; N, 3.6; Co, 5.4. ESI (pos.)-MS in CH_2Cl_2: *m/z* 1124.6 (100%) $[M]^+$, 769.4 (~67%) $[M\text{-}L]^+$. Cyclic voltammetry in CH_2Cl_2: $E^1_{1/2}$(ox), 0.198 V; $E^2_{1/2}$(ox), -0.325 V; $E^1_{1/2}$(red), 0.947 V; $E^2_{1/2}$(red), -1.286 V vs. Fc^+/Fc. IR(KBr, cm^{-1}): 3418, 2953, 2905, 1610, 1586, 1462, 1422, 1245, 1195, 1153, 1121, 1061, 844, 856. UV-vis in THF (λ, nm; ε, M^{-1} cm^{-1}): 480 (5.6 x 10^3), 666 (5.9 x 10^3), 888 (6.5 x 10^3).

Complex 3: Yield: 60%. Anal. calcd for $C_{84}H_{123}N_3O_3Co$: C, 78.71; H, 9.67; N, 3.28; Co, 4.60. Found: C, 78.8; H, 9.5; N, 3.7; Co, 4.7. EI-MS: *m/z*, 1280 (0.69%), 1281 (0.62%) $[M]^+$, 873 (100%), 874 (61.8%) $[M\text{-}L]^+$. Cyclic voltammetry in CH_2Cl_2: $E^1_{1/2}$(ox), 0.226, $E^2_{1/2}$(ox), -0.387; $E^3_{1/2}$(red), -1.255 V; vs. Fc^+/Fc. IR(KBr, cm^{-1}): 3420, 2961, 2905, 2868, 1594, 1578, 1478, 1462, 1432, 1361, 1247, 1200, 1040, 1006, 953, 877, 852, 707. UV-vis in CH_2Cl_2 (λ, nm; ε, M^{-1} cm^{-1}): 312 (28.6 x 10^3), 381sh (~14.1 x 10^3), 477 (5.7 x 10^3), 661 (6.9 x 10^3), 883 (7.6 x 10^3).

Complex 4: Yield: 38%. Anal. calcd for $C_{66}H_{69}F_{18}N_3O_3Co$: C, 58.58; H, 5.14; N, 3.11; Co, 4.36. Found: C, 59.0; H, 5.1; N, 3.1; Co, 4.5. ESI(pos.)-MS in CH_2Cl_2: 1352.4 (~60%) $[M]^+$, 921.3 (100%), $[M\text{-}L]^+$. Cyclic and square-wave voltammetry in CH_2Cl_2: $E^1_{1/2}$(ox), 0.469, $E^2_{1/2}$(ox), -0.04; $E^3_{1/2}$(red), -0.812; $E^4_{1/2}$(red), -1.128 V vs. Fc^+/Fc. IR(KBr, cm^{-1}): 3456, 2959, 1617, 1582, 1478, 1431, 1380, 1364, 1325, 1278, 1173, 1138, 1036, 1005, 949, 894, 847, 717, 701, 682. UV-vis in THF (λ, nm; ε, M^{-1} cm^{-1}): 372 (11.3 x 10^3), 655 (4.08 x 10^3), 913 (5.2 x 10^3).

Complex 5: Yield: 35%. Anal. calcd for $C_{60}H_{69}F_6N_3O_3Co$: C, 68.43; H, 6.60; N, 3.99; Co, 5.60. Found: C, 68.6; H, 6.6; N, 4.0; Co, 5.7. ESI(pos.)-MS in $C_2H_5OC_2H_5$: 1052.6 (100%) $[M]^+$, 721.3 $[M\text{-}L]^+$. Cyclic and square-wave voltammetry in CH_2Cl_2: $E^1_{1/2}$(ox), 0.334, $E^2_{1/2}$(ox), -0.193; $E^3_{1/2}$(red), -0.802; $E^4_{1/2}$(red), -1.168 V vs. Fc^+/Fc. IR(KBr, cm^{-1}): 3418, 3115, 3089, 2952, 2906, 2867, 1612, 1591, 1461, 1447, 1427, 1387, 1361, 1337, 1246, 1195, 1135, 1117, 1038, 1013, 993, 962, 830, 768, 682, 661, 641. UV-vis in CH_2Cl_2 (λ, nm; ε, M^{-1} cm^{-1}): 918 (11.5 x 10^3), 685 (7.6 x 10^3), 367 (12.1 x 10^3).

Complex 6: Yield: 70%. Anal. calcd for $C_{84}H_{123}N_3O_3Ga$: C, 78.05; H, 9.59; N, 3.25; Ga, 5.39. Found: C, 77.7; H, 9.6; N, 3.0; Ga, 5.5. EI-MS: *m/z* 1292 (3.76%) $[M^+]$, 883 (100%) $[M\text{-}L]^+$. Cyclic voltammetry in CH_2Cl_2: $E^1_{1/2}$(ox) = 0.445, $E^2_{1/2}$(ox) = +0.152, $E^3_{1/2}$(ox) = -0.240 V vs. Fc^+/Fc. IR(KBr, cm^{-1}): 3418, 3080, 2961, 2905, 2868, 1581, 1469, 1439, 1421, 1386, 1362, 1334, 1248, 1200, 1038, 1004, 953, 875, 856, 833, 721, 707, 645, 630, 608. UV-vis in CH_2Cl_2 (λ, nm; ε, M^{-1} cm^{-1}): 767 (3.5 x 10^3), 510 (1.98 x 10^3), 321 (20.4 x 10^3).

Complex 7: Yield: 30%. Anal. calcd for $C_{66}H_{69}F_{18}N_3O_3Ga$: C, 58.12; H, 5.10; N, 3.08; Ga, 5.11. Found: C, 58.0; H, 5.1; N, 3.1; Ga, 5.0. EI-MS: *m/z* 1364 (14.4%) $[M]^+$, 931 (100%) $[M\text{-}L]^+$. IR(KBr, cm^{-1}): 3463, 2963, 1584, 1477, 1439, 1381, 1365, 1353, 1277, 1176, 1143, 1130, 1003, 947, 893, 851, 712, 702, 683, 621. UV-vis in CH_2Cl_2 (λ, nm; ε, M^{-1} cm^{-1}): 805 (3.7 x 10^3), 365 (16.7 x 10^3), 288 (21.3 x 10^3).

Complex 8: Yield: 40%. Anal. calcd for $C_{60}H_{69}Cl_6N_3O_3Ga$: C, 61.98; H, 5.98; N, 3.61; Ga, 6.00. Found: C, 61.8; H, 6.0; N, 3.7; Ga, 5.8. EI-MS: *m/z* 1162 (100%) $[M]^+$, 797 (~30%) $[M\text{-}L]^+$. IR(KBr, cm^{-1}): 3421, 3081, 2958, 2906, 2869, 1573, 1560, 1467, 1440, 1420, 1388, 1356, 1333, 1257, 1107, 1033, 1003, 940, 850, 799, 718, 675, 647.

Crystallographic Data.

Complex **2**: $[C_{66}H_{87}O_9N_3Co] \bullet {}^1/_2(C_2H_5)_2O$; M_f = 1161.38, T = 100(2) K, monoclinic, a = 12.9603(6) Å, b = 22.0793(12) Å, c = 22.8771(12) Å, β = 95.07(1)°, V = 6520.8(6) Å^3, space group $P2_1/c$, Z = 4, D_c = 1.184 g cm^{-3}, F(000) = 2496, $\lambda(MoK_\alpha)$ = 0.71073 Å, μ = 0.320 mm^{-1}. A total of 15482 independent reflections was used for solution and refinement (SHELX97) by full-matrix least squares on F^2; no absorption correction. Final R indices: R_1 = 0.0363, R_1 (all data) = 0.0478.

Complex **3**: $C_{84}H_{123}N_3O_3Co$, M_f = 1281.78, T = 100(2) K, monoclinic, a = 16.1355(4) Å, b = 14.5516(4) Å, c = 34.0664(8) Å, β = 97.77(1)°, V = 7925.3(3) Å^3, space group $P2_1/c$, Z = 4, D_c = 1.074 g cm^{-3}, F(000) = 2796, $\lambda(MoK_\alpha)$ = 0.71073 Å, μ = 0.263 mm^{-1}. A total of 18094 independent reflections was used for solution and refinement (SHELX97) by full-matrix least squares on F^2; no absorption correction, Gaussian, face-indexed. Final R indices: R_1 = 0.0480, R_1 (all data) = 0.0674.

Complex **4**: $C_{66}H_{69}F_{18}ON_3O_3Co$, M_f = 1353.17, T = 100(2) K, monoclinic, a = 13.3974(3) Å, b = 22.8936(9) Å, c = 21.4790(9) Å, β = 90.494(5)°, V = 6587.7(4) Å^3, space group $P2_1/n$, Z = 4, D_c = 1.364 g cm^{-3}, F(000) = 2796, $\lambda(MoK_\alpha)$ = 0.71073 Å, μ = 0.358 mm^{-1}. A total of 19130 independent reflections was used for solution and refinement (SHELX97) by full-matrix least squares on F^2; absorption correction, Gaussian. Final R indices: R_1 = 0.0503, R_1 (all data) = 0.0656.

Complex **5**: $C_{60}H_{69}F_6N_3O_3Co$, M_f = 1053.11, T = 100(2) K, triclinic, a = 10.6439(3) Å, b = 14.7847(4) Å, c = 17.7515(6) Å, α = 96.64(1)°, β = 94.02(1)°, γ = 94.25(1)°, V = 2758.4(1) Å^3, space group P-1, Z = 2, D_c = 1.268 g cm^{-3}, F(000) = 1110, $\lambda(MoK_\alpha)$ = 0.71073 Å, μ = 0.378 mm^{-1}. A total of 17661 independent reflections was used for solution and refinement (SHELX97) by full-matrix least squares on F^2; absorption correction, Gaussian, face indexed. Final R indices: R_1 = 0.0457, R_1 (all data) = 0.0647.

Complex **6**: $C_{84}H_{123}N_3O_3Ga$, M_f = 1292.57, T = 100(2) K, monoclinic, a = 16.4504(3) Å, b = 14.6410(3) Å, c = 33.8237(6) Å, β = 96.57(1)°, V = 8092.9(3) Å^3, space group $P2_1/c$, Z = 4, D_c = 1.061 g cm^{-3}, F(000) = 2812, $\lambda(MoK_\alpha)$ = 0.71073 Å, μ = 0.385 mm^{-1}. A total of 19839 independent reflections was used for solution and refinement (SHELX97) by full-matrix least squares on F^2; no absorption correction. Final R indices: R_1 = 0.0443, R_1 (all data) = 0.0554.

Complex **8**: $C_{63}H_{76.5}Cl_6N_{3.5}O_3Ga$, M_f = 1213.20, T = 100(2) K, monoclinic, a = 18.2999(9) Å, b = 19.7567(9) Å, c = 35.0963(15) Å, β = 93.22(1)°, V = 12668.9(10) Å^3, space group C2/c, Z = 8, D_c = 1.272 g cm^{-3}, F(000) = 5088, $\lambda(MoK_\alpha)$ = 0.71073 Å, μ = 0.733 mm^{-1}. A total of 8277 independent reflections was used for solution and refinement (SHELX97) by full-matrix least squares on F^2; no absorption correction. Final R indices: R_1 = 0.1143, R_1 (all data) = 0.1368.

Supplementary Material

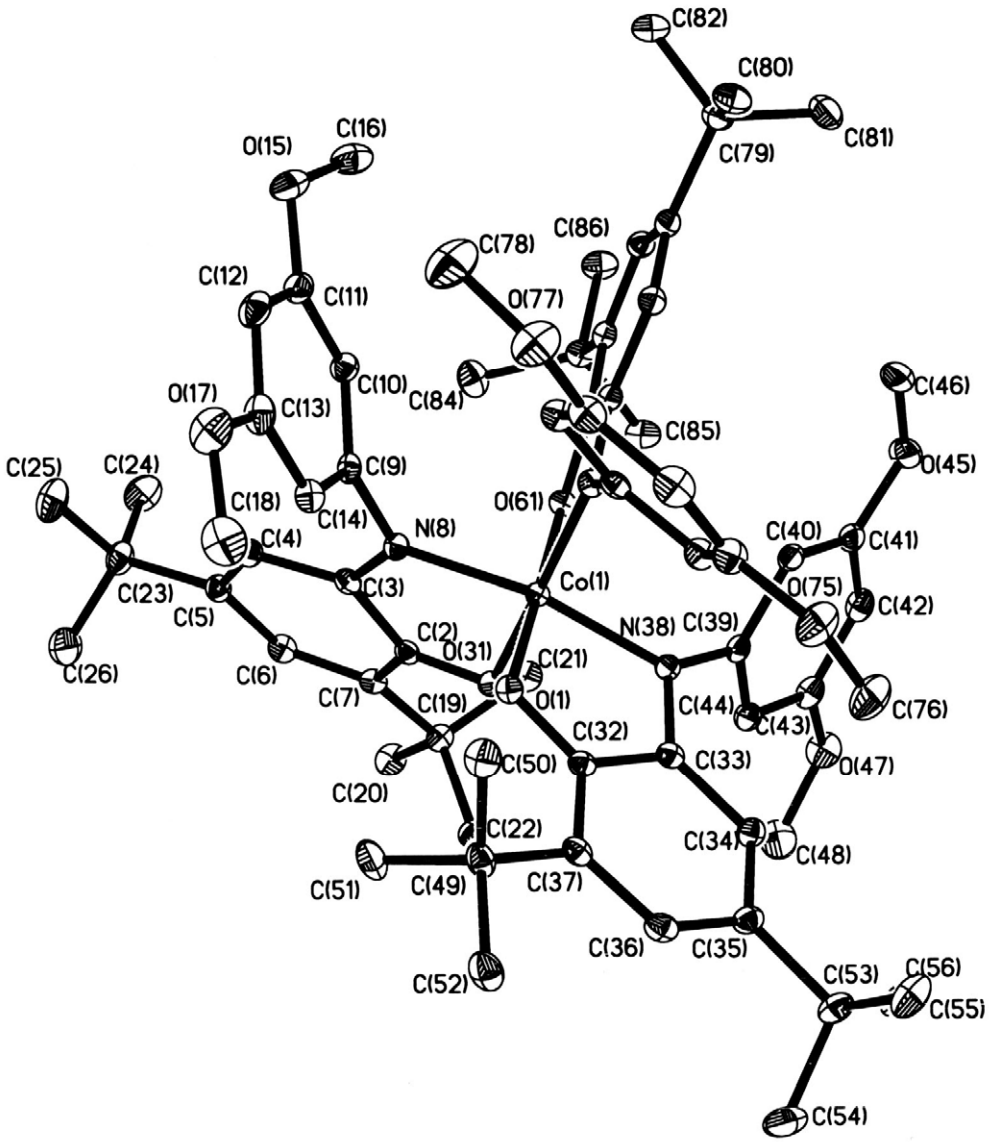

Figure S1. Molecular structure of complex **2**, [$Co^{III}(L^{OCH_3\bullet}$) with selected bond lengths (Å) and angles (^{o}): Co(1)-O(61) 1.8848(9), Co(1)-O(31) 1.8893(9), Co(1)-O(1) 1.9039(9), Co(1)-N(68) 1.9187(11), Co(1)-N(8) 1.9249(11), Co(1)-N(38) 1.9302(11), N(8)-C(9) 1.4236(17), N(8)-C(3) 1.3432(17), C(2)-O(1) 1.3046(16), C(32)-O(31) 1.3047(16), C(62)-O(61) 1.3053(16), O(61)-Co(1)-O(31) 178.90(4), O(1)-Co(1)-N(68) 170.58(4), N(8)-Co(1)-N(38) 168.54(5).

Supplementary Material

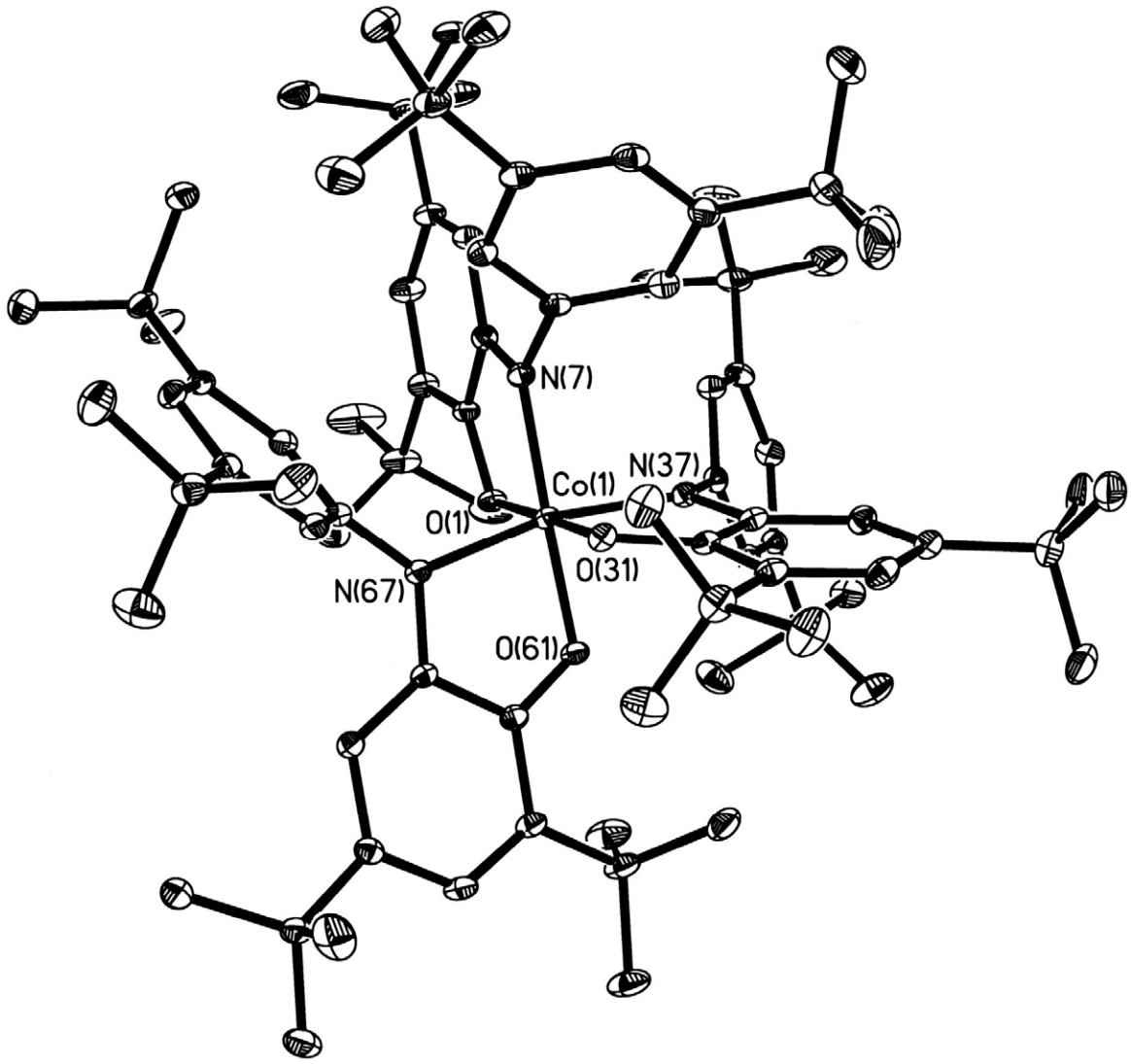

Figure S2. Molecular structure of complex **3**, $[Co^{III}(L^{t\text{-}Bu\bullet})_3]$ with selected bond lengths (Å) and angles (°): Co(1)-O(31) 1.8754(11), Co(1)-O(1) 1.8818(11), Co(1)-O(61) 1.8896(11), Co(1)-N(37) 1.9118(14), Co(1)-N(7) 1.9177(13), Co(1)-N(67) 1.9389(14), C(6)-N(7) 1.346(2), C(8)-N(7) 1.433(2), O(31)-C(31) 1.3020(19), O(1)-C(1) 1.3007(19), O(61)-C(61) 1.296(2), O(31)-Co(1)-O(1) 178.65(5), O(61)-Co(1)-N(7) 173.17(5), N(37)-Co(1)-N(67) 165.24(6).

Supplementary Material

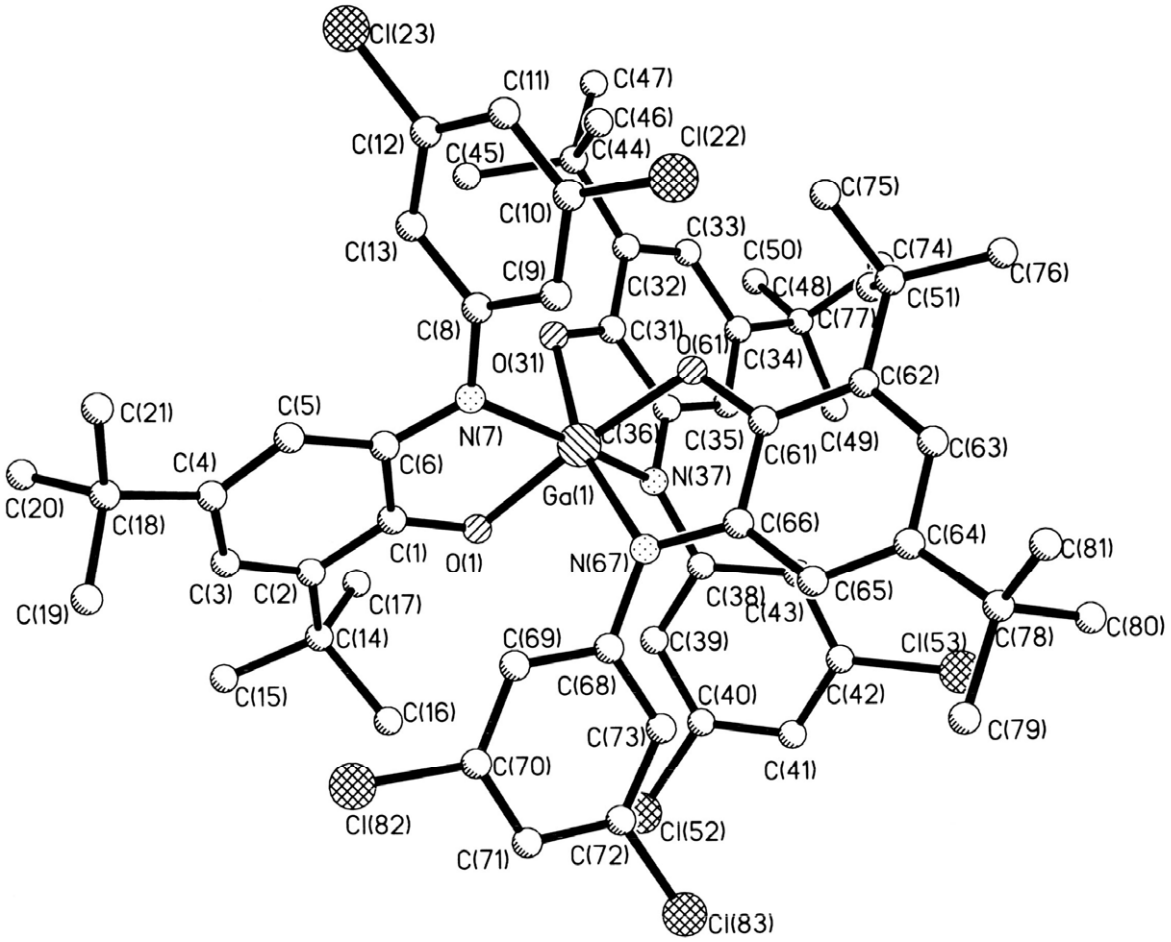

Figure S3. Molecular structure of complex **8** [$Ga^{III}(L^{Cl\bullet})_3$] with selected bond lengths (Å) and angles (^{o}): Ga(1)-O(1) 1.935(8), Ga(1)-O(61) 1.954(8), Ga(1)-O(31) 1.965(8), Ga(1)-N(7) 2.027(10), Ga(1)-N(37) 2.044(10), Ga(1)-N(67) 2.068(10), O(1)-C(1) 1.316(15), O(1)-Ga(1)-O(61) 174.4(3), N(7)-Ga(1)-N(37) 164.0(4), O(31)-Ga(1)-N(67) 164.2(4).