Linkage and Redox Isomerism in Ruthenium Complexes of Catecholate, Semi-quinone, and *o*-Acylphenolate Ligands Derived from Tri- and Tetrahydroxy-9,10-anthracenediones

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The complexes $Ru(CO)_2L_2$(PHAQ-2H) (PHAQ = 1,2,4-trihydroxy-9,10-anthracenedione (PUR), 1,2,3- trihydroxy-9,10-anthracenedione (AG), and 1,2,5,8-tetrahydroxy-9,10-anthracenedione (QAL); L = PPh_3, PCy_3, PBu_3), and Ru(CO)(dppe)(PBu_3)(PHAQ-2H), containing catecholate-type ligands were prepared. The complex $Ru(CO)_2(PBu_3)_2$(AG-2H) crystallizes in the space group $P2_1/n$ (No. 14 *var*) with $a = 13.317(2)$, $b = 15.628(2)$, $c = 21.076(3)$ Å, $\beta = 101.660(10)°$, Z = 4; the crystal structure shows it to contain a 2,3-catecholate ligand. The electrochemistry of these complexes was examined, and the semi-quinone complexes $[Ru(CO)_2L_2(PHAQ\text{-}2H)]^{1+}$ and $[Ru(CO)(dppe)(PBu_3)(PHAQ\text{-}2H)]^{1+}$ were generated by chemical oxidation. One example of an *o*-acylphenolate complex, $HRu(CO)(PCy_3)_2$(PUR-H), is also reported.

Introduction

Metal complexes of polyhydroxy-9,10-anthracenediones (PHAQs)[1] have been used as dyes and as indicators.[2,3] Relatively few organometallic complexes have been reported. As ligands PHAQs offer three features of interest to organometallic chemistry. (1) They can exhibit linkage isomerism, acting as chelates via the 1,2-, 2,3-, or the 1,9-oxygen atoms and other adjacent oxygen atoms. (2) As 1,2-chelates they display ligand-based redox chemistry. (3) The complexes are deeply colored, allowing for applications of the complexes as optical sensor components or as molecular recognition elements. We recently reported some ruthenium complexes of 1,2-dihydroxy-9,10-anthracenedione (alizarin), including 1,2-catecholate, 1,9-acylphenolate, and 1,2-semi-quinone complexes.[4] In this paper we present the syntheses and characterizations of ruthenium complexes (Figure 1) of the PHAQs purpurin, anthragallol, and quinalizarin.

Experimental Section

Starting Materials. Dichloromethane was distilled under nitrogen from calcium hydride before use. Purpurin was obtained from Aldrich. Quinalizarin was obtained from Pfaltz & Bauer. Anthragallol was prepared according to a literature procedure.[5] $Ru_3(CO)_{12}$ was obtained from Strem. Other chemicals were of reagent grade purity and were used as received. All reactions were carried out under a blanket of nitrogen and with nitrogen-saturated solvents using standard Schlenk procedures. However, workup and spectral analyses were conducted without exclusion of air.

Physical Methods of Characterizations. Infrared spectra were recorded on a Nicolet Magna 550 spectrophotometer. ^{1}H NMR spectra were obtained on Varian Associates Gemini 300 or Varian Associates VXR-400S instruments, using deuteriochloroform as solvent and TMS as reference. ^{13}C NMR spectra were recorded on the Gemini 300 or the VXR-400S instrument in deuteriochloroform and referenced to TMS. ^{31}P NMR spectra were recorded on the VXR-400S instrument in deuteriochloroform, and chemical shifts are reported relative to *o*-phosphoric acid. UV/visible spectra (300−800 nm) were recorded using a Hewlett-Packard 8452A diode array spectrophotometer. EPR spectra were recorded on an IBM/Bruker X-band ER-200 SRC spectrometer, with a microwave power of 20 mW, in dichloromethane solutions. Spectral parameters were determined by comparison of experimental spectra with spectra simulated using Bruker WINEPR Simfonia (ver. 1.25) software.

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(1) Throughout this paper the following abbreviations are used: purpurin (1,2,4-trihydroxy-9, 10-anthracenedione), PUR; anthragallol (1,2,3-trihydroxy-9, 10-anthracenedione), AG; quinalizarin (1,2,5,8-tetrahydroxy-9, 10-anthracenedione), QAL. The removal of one hydroxyl proton is indicated by “-H” and of two hydroxyl protons as “-2H”; removal of three hydroxyl protons and O-methylation is indicated by “-3H+Me”.

(2) For example, see: (a) Capitan, F.; Roman, M. *Inf. Quim Anal.* **1967**, *21*, 208. (b) Roman, M.; Fernandez-Gutierrez, A. *Bol. Soc. Quim. Peru* **1975**, *41*, 1. (c) Maties, R.; Jimenez, F.; Arias, J. J.; Roman, M. *Anal. Let.* **1997**, *30*, 2059. (d) Capitan, F.; Arrebola Ramirez, A.; Jimenez Linares, C. *Analyst (London)* **1986**, *111*, 739. (e) Fieser, L. F. *J. Chem. Educ.* **1930**, *7*, 2609.

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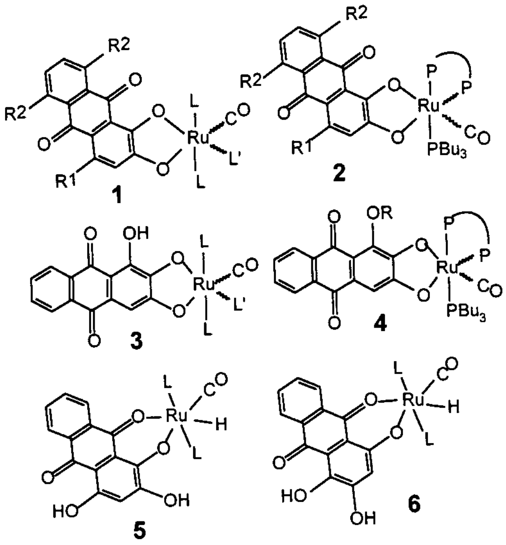

Figure 1. Structures of complexes derived from purpurin (PUR), anthragallol (AG), and quinalizarin (QAL). **1**: Ru(CO)$_2$(PR$_3$)$_2$(PUR-2H) (R^1 = OH, R^2 = H, L′ = CO); Ru(CO)$_{2-n}$(PR$_3$)$_{2+n}$(QAL-2H) (R^1 = H, R^2 = O H, L′ = CO or PR$_3$). **2**: Ru(CO)(PBu$_3$)(dppe)(PUR-2H) (R^1 = OH, R^2 = H); Ru(CO)(PBu$_3$)(dppe)(QAL-2H) (R^1 = H, R^2 = OH); Ru(CO)(PBu$_3$)(dppe)(PUR-3H+Me) (R^1 = OMe, R^2 = H). **3**: Ru(CO)$_{2-n}$(PR$_3$)$_{2+n}$(AG-2H) (L′ = CO or PR$_3$). **4**: Ru(CO)(PBu$_3$)(dppe)(AG-2H) (R = H); Ru(CO)(PBu$_3$)(dppe)(AG-3H+Me) (R= Me). **5**: HRu(CO)(PCyc$_3$)$_2$(1,9-PUR−H). **6**: HRu(CO)(PCyc$_3$)$_2$(4,10-PUR−H).

Electrochemistry. The electrochemical procedures were conducted as described previously.[4] All potentials are reported relative to the ferrocene/ferrocinium couple as 0 V.

Ru(CO)$_2$(PBu$_3$)$_2$(PUR-2H). A solution of Ru$_3$(CO)$_{12}$ (103 mg, 161 μmol), PBu$_3$ (240 μL, 960 μmol), and purpurin (126 mg, 492 μmol) in toluene (30 mL) was heated at reflux under an argon atmosphere for 14 h. The resulting red solution was evaporated to dryness, and the residue was applied as a dichloromethane solution to a silica gel preparative TLC plate. Elution with first dichloromethane and then 3% acetone in dichloromethane gave a red colored leading band, which was extracted with acetone. Yield: 136 mg, 167 μmol, 35%. Recrystallization from methanol gave red crystals.

Ru(CO)$_2$(PBu$_3$)$_2$(PUR-2H). IR (hexanes): 2037.6 vs, 1973.1 s cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 15.642 (s, 1 H), 8.274 (m, 2 H), 7.604 (m, 2 H), 6.182 (s, 1 H), 1.705 (m, 12 H), 1.49 (br, 12 H), 1.353 (m, 12 H), 0.874 (t, 18 H, J = 7 Hz) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$): δ 197.2 (br, 2 C), 179.79 (1 C), 179.69 (1 C), 176.64 (1 C), 165.25 (1 C), 164.55 (1 C), 136.16 (1 C), 134.38 (1 C), 131.60 (1 C), 131.24 (1 C), 126.40 (1 C), 125.26 (1 C), 114.45 (1 C), 106.19 (1 C), 105.84 (1 C), 25.12 (6 C), 24.27 (t, 6 C, J_{PC} = 7 Hz), 22.85 (t, 6 C, J_{PC} = 13 Hz), 13.42 (6 C) ppm. ^{31}P{^{1}H} NMR (CDCl$_3$): δ 20.56 ppm. UV/vis (CH$_2$Cl$_2$): $\lambda_{max}(\epsilon)$ 512 (1.2 × 10^4), 542 (2.0 × 10^4), 582 (1.7 × 10^4) nm. Anal. Calcd for C$_{40}$H$_{60}$O$_7$P$_2$Ru: C, 58.88; H, 7.41. Found: C, 59.53; H, 7.49.

Ru(CO)$_2$(PCy$_3$)$_2$(PUR-2H) and HRu(CO)(PCy$_3$)$_2$(PUR-H). A solution of Ru$_3$(CO)$_{12}$ (108 mg, 170 μmol), PCy$_3$ (400 mg, 1.42 mmol), and purpurin (182 mg, 707 μmol) in toluene (30 mL) was heated at reflux under an argon atmosphere for 11 h. The resulting red solution was evaporated to dryness, and the residue was applied as a dichloromethane solution to silica gel preparative TLC plates. Elution with dichloromethane gave a green colored leading band, which overlapped with a brown band, a blue band, and a trailing red band. Extraction of the green/brown band with ethyl acetate gave 147 mg (31%) HRu(CO)(PCy$_3$)$_2$(PUR-H). Extraction of the red band with ethyl acetate gave 85 mg, 17%, of Ru(CO)$_2$(PCy$_3$)$_2$(PUR-2H).

HRu(CO)(PCy$_3$)$_2$(PUR-H). IR (CH$_2$Cl$_2$): 1898.1 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 15.550 (s, 1 H), 8.308 (m, 2 H), 8.040 (s, 1 H), 7.682 (m, 2 H), 6.546 (s, 1 H), 2.0−0.9 (m, 66 H), −15.283 (t, 1 H, J_{PH} = 19.6 Hz) ppm; minor isomer, −15.440 (t, P$_{PH}$ 19.6 Hz) ppm; major/minor = 11.7. ^{31}P{^{1}H} NMR (CDCl$_3$): δ 43.713 ppm. UV/vis (CH$_2$Cl$_2$): $\lambda_{max}(\epsilon)$ 498 (8.5 × 10^3) nm. Anal. Calcd for C$_{51}$H$_{73}$O$_6$P$_2$Ru: C, 64.81; H, 7.78. Found: C, 65.01; H, 7.88.

Ru(CO)$_2$(PCy$_3$)$_2$(PUR-2H). IR (CH$_2$Cl$_2$): 2031.6 s, 1966.4 s cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 15.937 (s, 1 H), 8.279 (m, 2 H), 7.598 (m, 2 H), 6.135 (s, 1 H), 2.2−1.0 (m, 66 H) ppm. ^{31}P{^{1}H} NMR (CDCl$_3$): δ 38.22 ppm. UV/vis (CH$_2$Cl$_2$): $\lambda_{max}(\epsilon)$ 362 (2.0 × 10^4), 512 (4.8 × 10^3), 546 (8.0 × 10^3), 586 (7.1 × 10^3) nm. Anal. Calcd for C$_{52}$H$_{72}$O$_7$P$_2$Ru: C, 64.25; H, 7.46. Found: C, 64.39; H, 7.65.

Ru(CO)(dppe)(PBu$_3$)(PUR-2H). A solution of Ru$_3$(CO)$_{12}$ (247.7 mg, 539 μmol), dppe (650 mg, 1.63 mmol), and purpurin (418 mg, 1.63 mmol) in toluene (30 mL) was heated at reflux under a nitrogen atmosphere for 3.5 h. Then PBu$_3$ (411 μL, 1.65 mmol) was added, and the solution was heated at reflux for 8 more hours. The products were separated by TLC on silica eluting with 2% ethyl acetate in dichloromethane. The second, purple band was extracted with ethyl acetate. Yield, 532 mg, 33%.

Ru(CO)(dppe)(PBu$_3$)(PUR-2H). IR (CH$_2$Cl$_2$): 1948.0 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 16.12 (s, 1 H), 8.94 (dd, 2 H, J = 8, 11 Hz), 8.54 (m, 1 H), 8.26 (m, 1 H), 7.86 (m, 2 H), 7.68 (m, 1 H), 7.64−7.42 (m, ca. 11 H), 7.37 (d, 1 H, J = 6 Hz), 6.94 (m, 1 H), 6.71 (m, 3 H), 6.01 (s, 1 H), 3.05 (m, 1 H), 2.60 (m, 1 H), 2.47 (m, 1 H), 2.05 (m, 1 H), 1.26 (m, 6 H), 1.05 (m, 6 H), (m, 6 H), 0.71 (t, 9 H, J = 7 Hz) ppm. ^{31}P{^{1}H} NMR (CDCl$_3$): δ 60.55 (dd, 1 P$_A$), 44.98 (dd, 1 P$_B$), 18.00 (dd, 1 P$_C$) ppm, J_{AB} = 12 Hz, J_{AC} = 23 Hz, J_{BC} = 334 Hz. UV/vis (CH$_2$Cl$_2$): $\lambda_{max}(\epsilon)$ 520 (1.2 × 10^4), 552 (1.7 × 10^4), 592 (1.5 × 10^4) nm. Anal. Calcd for C$_{53}$H$_{57}$O$_6$P$_3$Ru: C, 64.69; H, 5.84. Found: C, 64.60; H, 5.80.

Ru(CO)(dppe)(PBu$_3$)(PUR-3H+Me). A solution of Ru(CO)(dppe)(PBu$_3$)(PUR-2H) (51.5 mg, 52.4 μmol), potassium *t*-butoxide (57 mg, 520 μmol), and methyl iodide (150 μL, 240μmol) in 5 mL of THF was stirred under argon for 5 days. The solution was evaporated, and the residue was separated by TLC on silica eluting with 10% ethyl acetate in dicloromethane. The second, blue band was extracted with ethyl acetate, yielding 29.3 mg, 56%, upon evaporation.

Ru(CO)(dppe)(PBu$_3$)(PUR-3H+Me). IR (CH$_2$Cl$_2$): 1943.3 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 8.94 (dd, 2 H, J = 8, 11 Hz), 8.30 (m, 1 H), 8.25 (m, 1 H), 8.03 (m, 1 H), 7.82 (m, 2 H), 7.66 (m, 1 H), 7.6−7.3 (m, 10 H), 7.20 (m, 1 H), 6.95 (m, 2 H), 6.67 (m, 2 H), 6.18 (s, 1 H), 3.78 (s, 3 H), 3.02 (dm, 1 H), 2.57 (dm, 1 H), 2.42 (m, 1 H), 2.07 (m, 1 H), 1.26 (m, 6 H), 1.15 (m, 6 H), 1.06 (m, 6 H), 0.68 (t, 9 H, J = 7 Hz) ppm. ^{31}P{^{1}H} NMR (CDCl$_3$): δ 60.04 (dd, 1 P$_A$), 43.48 (dd, 1 P$_B$), 17.79 (dd, 1 P$_C$) ppm, J_{AB} = 12 Hz, J_{AC} = 23 Hz, J_{BC} = 348 Hz. UV/vis (CH$_2$Cl$_2$): $\lambda_{max}(\epsilon)$ 384 (3800), 562 (1.2 × 10^4), 594 (1.0 × 10^4) nm. Anal. Calcd for C$_{54}$H$_{59}$O$_6$P$_3$Ru: C, 64.99; H, 5.96. Found: C, 65.27; H, 6.15.

Ru(CO)(dppe)(PBu$_3$)(QAL-2H). A solution of Ru$_3$(CO)$_{12}$ (104.5 mg, 163.4 μmol), dppe (197 mg, 495 μmol), and quinalizarin (133 mg, 489 μmol) in toluene (30 mL) was heated at reflux under a nitrogen atmosphere for 4.5 h. Then PBu$_3$ (140 μL, 560 μmol) was added, and the solution was heated at reflux for 8 more hours. The products were separated by TLC on silica eluting with 2% ethyl acetate in dichloromethane. The second, blue-green band was extracted. Recrystallization from dichloromethane/methanol yielded 146 mg, 30%.

Ru(CO)(dppe)(PBu$_3$)(QAL-2H). IR (CH$_2$Cl$_2$): 1946.9 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 15.080 (s, 1 H), 14.014 (s, 1 H), [8.991 (dd, 2 H, J = 7.6, 10.8 Hz), 8.142 (m, 2 H), 7.780 (m, 2 H), 7.707 (m, 1 H), 7.634 (m, 2 H), 7.472 (m, 6 H), 7.111 (d, 2 H), 6.840 (m, 2 H), 6.756 (m, 4 H), 6.452 (d, 1 H, J = 8.0 Hz), 2.99 (m, 1 H), 2.78 (m, 1 H), 2.40 (m, 1 H), 1.87 (m, 1 H), 1.4−1.1 (m, 18 H), 0.757 (t, 9 H, J = 7.2 Hz) ppm;] minor − 14.873 (s, 1 H), 14.137 (s, 1 H), 6.000 (d, 1 H, J = 8.4 Hz), ^{31}P{^{1}H} NMR (CDCl$_3$): δ major isomer, 60.437 (dd, 1 P$_A$), 46.081 (dd, 1 P$_B$), 18.819 (dd, 1 P$_C$), J_{AB} = 11.5 Hz, J_{AC} = 22.5 Hz, J_{BC} = 339.1 Hz; minor isomer, 60.466 (dd, 1 P$_A$), 45.167 (dd, 1 P$_B$), 19.526 (dd, 1 P$_C$) ppm, J_{AB} = 11.5 Hz, J_{AC} = 21.4 Hz, J_{BC} = 339.5 Hz; major/minor = 3.9. UV/vis (CH$_2$Cl$_2$): $\lambda_{max}(\epsilon)$ 410 (5800), 584 (1.4 × 10^4), 622 (2.2 × 10^4), 674 (1.9 × 10^4) nm. Anal. Calcd for C$_{53}$H$_{57}$O$_7$P$_3$Ru: C, 63.66; H, 5.74. Found: C, 63.36; H, 5.85.

Ru(CO)(mer-PBu$_3$)$_3$(QAL-2H) and Ru(cis-CO)$_2$(trans-PBu$_3$)$_2$(QAL-2H). A solution of Ru$_3$(CO)$_{12}$ (101.5 mg, 159 μmol), PBu$_3$ (240 μL, 960 μmol), and quinalizarin (127.7 mg, 469 μmol) in toluene (20 mL) was heated at reflux under an argon atmosphere for 6 h. The resulting blue solution was evaporated to dryness, and the residue was applied as a dichloromethane solution to a silica gel preparative TLC plate. Elution with dichloromethane gave purple, blue, red, and purple bands; the blue band was extracted with ethyl acetate, 357 mg. Repeated TLCs were necessary to separate the bis- and trisphosphine complexes.

Ru(CO)$_2$(PBu$_3$)$_2$(QAL-2H). IR (CH$_2$Cl$_2$): 2036.1 vs, 1970.8 s cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 14.18 (s, 1 H), 13.72 (s, 1 H), 7.63 (d, 1 H, J = 8 Hz), 7.05 (s, 2 H), 6.60 (d, 1 H, J = 8 Hz), 1.68 (m 12 H), 1.45 (dm, 12 H), 1.34 (m, 12 H), 0.89 (t, 18 H, J = 7 Hz) ppm. ^{31}P{^{1}H} NMR (CDCl$_3$): δ 21.90 (s) ppm. UV/vis (CH$_2$Cl$_2$): $\lambda_{max}(\epsilon)$ 584 (2.3 × 10^4), 622 (1.9 × 10^4) nm.

Ru(CO)(mer-PBu$_3$)$_3$(QAL-2H). IR (CH$_2$Cl$_2$): 1928.0 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ **a**, 14.70 (s, 1 H), 13.98 (s, 1 H), 7.60 (d, 1 H, J = 8 Hz), 7.01 (m, 2 H), 6.40 (d, 1 H, J = 8 Hz) ppm; **b**, 14.72 (s, 1 H), 13.96 (s, 1 H), 7.62 (d, 1 H, J = 8 Hz), 7.01 (m, 2 H), 6.47 (d, 1 H, J = 8 Hz) ppm; 2.0−1.2 (m, 54 H), 1.0−0.8 (m, 27 H) ppm. ^{31}P{^{1}H} NMR (CDCl$_3$): δ **a** (62%), 26.098 (t, J_{PP} = 23.1 Hz, 1 P), 15.494 (d, 2 P) ppm; **b** (38%), 26.75 (t J_{PP} = 24 Hz, 1 P), 15.30 (d, 2 P) ppm.

Ru(CO)(dppe)(PBu$_3$)(AG-2H). A solution of Ru$_3$(CO)$_{12}$ (243 mg, 379 μmol), dppe (457 mg, 1.15 mmol), and anthragallol (299 mg, 1.17 mmol) in toluene (30 mL) was heated at reflux under a nitrogen atmosphere for 3 h. Then PBu$_3$ (100 μL, 396 μmol) was added, and the solution was heated at reflux for 4 more hours. The products were separated by TLC on silica eluting with dichloromethane. Two green bands and a pine green band trailed by a dark green band were extracted with ethyl acetate. The pine green band was predominantly Ru(CO)$_2$(PBu$_3$)$_2$(AG-2H). The dark green band yielded 262 mg, 23%.

Ru(CO)(dppe)(PBu$_3$)(AG-2H). IR (CH$_2$Cl$_2$): 1944.2 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 12.218 (s, 1 H), 8.679 (m, 2 H), 8.111 (m, 4 H), 7.7−7.4 (m, 15 H), 7.052 (s, 1 H), 7.036 (m, 1 H), 6.915 (m, 2 H), 2.974 (dm, 1 H), 2.668 (dm, 1 H), 2.431 (m, 1 H), 2.010 (m, 1 H), 1.4−1.1 (m, 18 H), 0.780 t, 9 H, J = 7 Hz) ppm; minor isomer resonances were not assigned. ^{31}P{^{1}H} NMR (CDCl$_3$): δ minor isomer, 59.691 (dd, 1 P$_A$), 42.072 (dd, 1 P$_B$), 16.409 (dd, 1 P$_C$), J_{AB} = 11.6 Hz, J_{AC} = 23.3 Hz, J_{BC} = 358.7 Hz; major isomer, 59.207 (dd, 1 P$_A$), 40.142 (dd, 1 H$_B$), 18.498 (dd, 1 P$_C$), J_{AB} = 11.5 Hz, J_{AC} = 22.5 Hz, J_{BC} = 359.5 Hz, major/minor = 4.2. UV/vis (CH$_2$Cl$_2$): $\lambda_{max}(\epsilon)$ 316 (1.2 × 10^4), 394 (3.0 × 10^4), 472 (6.8 × 10^3), 498 (5.8 × 10^3) nm. Anal. Calcd for C$_{53}$H$_{57}$O$_6$P$_3$Ru: C, 64.692; H, 5.839. Found: C, 64.50; H, 6.09.

Ru(CO)(dppe)(PBu$_3$)(AG-3H+Me). A solution of Ru(CO)(dppe)(PBu$_3$)(AG-2H) (52 mg, 53 μmol), potassium *t*-butoxide (59 mg, 560 μmol), and methyl iodide (150 μL, 240 μmol) in 8 mL of THF was stirred under argon for 46 h. The solution was evaporated, and the residue was separated by TLC on silica eluting with 3% ethyl acetate in dichloromethane. The top, green band was extracted with ethyl acetate, yielding 25 mg, 46%, upon evaporation. The second green band contained 7 mg, 13%, of recovered starting material.

Ru(CO)(dppe)(PBu$_3$)(AG-3H+Me). IR (CH$_2$Cl$_2$): 1943.9 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 8.712 (dd, 2 H), 8.14 (m, 4 H), 7.7−7.4 (m, 13 H), 7.230 (s, 1 H), 6.991 (m, 2 H), 6.926 (m, 3 H), 3.789 (s, 3 H), 2.920 (m, 1 H), 2.715 (m, 1 H), 2.400 (m, 1 H), 1.990 (m, 1 H), 1.4−1.1 (m, 18 H), 0.758 (t, 9 H, J = 7 Hz) ppm. ^{31}P{^{1}H} NMR (CDCl$_3$): δ 59.06 (dd, 1 P$_A$), 40.43 (dd, 1 H$_B$), 20.91 (dd, 1 P$_C$), J_{AB} = 12 Hz, J_{AC} = 23 Hz, J_{BC} = 360 Hz. UV/vis (CH$_2$Cl$_2$): $\lambda_{max}(\epsilon)$ 324 (1.6 × 10^4), 388 (2.3 × 10^4), 606 (2.7 × 10^3) nm. Anal. Calcd for C$_{54}$H$_{59}$O$_6$P$_3$Ru: C, 64.99; H, 5.96. Found: C, 64.89; H, 5.84.

Ru(CO)$_2$(PPh$_3$)$_2$(AG-2H). A solution of Ru$_3$(CO)$_{12}$ (102.4 mg, 160 μmol), PPh$_3$ (265.3 mL, 1040 μmol), and anthragallol (119.9 mg, 468 μmol) in toluene (20 mL) was heated at reflux under an argon atmosphere for 3.5 h. The resulting green solution was evaporated to dryness, and the residue was applied as a dichloromethane solution to a silica gel preparative TLC plate. Elution with 4% ethyl acetate in dichloromethane gave four bands; the third, green one was extracted with ethyl acetate. Evaporation gave Ru(CO)$_2$(PPh$_3$)$_2$(AG-2H) (188.8 mg, 43%).

Ru(CO)$_2$(PPh$_3$)$_2$(AG-2H). IR (CH$_2$Cl$_2$): 2044.4 vs, 1982.1 s w cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 12.306 (s, 1 H), 8.107 (m, 2 H), 7.706 (m, 1 H), 7.578 (m, 12 H), 7.370 (m, 18 H), 7.277 (m, 1 H), 6.608 (s, 1 H) ppm. ^{31}P{^{1}H} NMR (CDCl$_3$): δ 18.94 (s) ppm. UV/vis (CH$_2$Cl$_2$): $\lambda_{max}(\epsilon)$ 382 (2.3 × 10^4), 462 (8.4 × 10^3), 492 sh nm.

Ru(CO)(mer-PBu$_3$)$_3$(AG-2H) and Ru(CO)$_2$(PBu$_3$)$_2$(AG-2H). A solution of Ru$_3$(CO)$_{12}$ (105.1 mg, 164 μmol), PBu$_3$ (234 μL, 940 μmol), and anthragallol (122 mg, 476 μmol) in toluene (30 mL) was heated at reflux under an argon atmosphere for 7 h. The resulting green solution was evaporated to dryness, and the residue was applied as a dichloromethane solution to a silica gel preparative TLC plate. Elution with 2% ethyl acetate in dichloromethane gave two green bands, which were extracted with ethyl acetate. The top band (89 mg, 18%) was identified as a mixture of two isomers of Ru(CO)(mer-PBu$_3$)$_3$(AG-2H). The second band (149 mg, 37% based on Ru) was Ru(CO)$_2$(PBu$_3$)$_2$(AG-2H).

Ru(CO)$_2$(PBu$_3$)$_2$(AG-2H). IR (CH$_2$Cl$_2$): 2035.4 vs, 1968.0 s cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 12.640 (s, 1 H), 8.14 (m, 2 H), 7.59 (m, 2 H), 7.14 (s, 1 H), 1.72 (m, 12 H), 1.39 (br, 24 H), 0.875 (t, 18 H, J = 7 Hz) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$): δ 198.26 (br, 2 C), 187.02 (1 C), 182.85 (1 C), 169.57 (1 C), 156.20 (1 C), 154.11 (1 C), 135.50 (1 C), 135.38 (1 C), 133.48 (1 C), 133.21 (1 C), 127.19 (1 C), 126.49 (1 C), 123.71 (1 C), 112.40 (1 C), 110.44 (1 C), 26.07 (6 C), 25.09 (t, 6 C, J_{PC} = 6 Hz), 23.50 (t, 6 C, J_{PC} = 13 Hz), 14.31 (6 C) ppm. ^{31}P{^{1}H} NMR (CDCl$_3$): δ 18.67 ppm. UV/vis (CH$_2$Cl$_2$): $\lambda_{max}(\epsilon)$ 372 (3.0 × 10^4), 456 (6.7 × 10^3) nm.

Ru(CO)(mer-PBu$_3$)$_3$(AG-2H). IR (CH$_2$Cl$_2$): 1922.8 cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 12.544 (s, 0.34 H, **a**), 12.475 (s, 0.66 H, **b**), 8.152 (**a** and **b**, m, 2 H), 7.571 (**a** and **b**, m, 2 H), 7.122 (s, 0.66 H, **b**), 7.070 (s, 0.34 H, **a**), 1.9−1.25 (m, 48 H), 1.001 (t, 8.2 H, J = 7 Hz), 0.953 (t, 2.9 H, J = 7 Hz), 0.893 (t, 15.8 H, J = 7 Hz) ppm. ^{31}P{^{1}H} NMR (CDCl$_3$): δ **a** (34%), 24.54 (t, J_{PP} = 24 Hz, 1 P), 13.20 (d, 2 P) ppm; **b** (66%), 24.36 (t, J_{PP} = 24 Hz, 1 P), 14.38 (d, 2 P) ppm.

[Ru(CO)(dppe)(PBu$_3$)(QAL-2H)]SbCl$_6$, [Ru(CO)(dppe)(PBu$_3$)(PUR-2H)]PF$_6$, [Ru(CO)(dppe)(PBu$_3$)(AG-2H)]PF$_6$, [Ru(CO)$_2$(PBu$_3$)$_2$(QAL-2H)]SbCl$_6$, [Ru(CO)$_2$(PBu$_3$)$_2$(PUR-2H)]SbCl$_6$, and [Ru(CO)$_2$(PBu$_3$)$_2$(AG-2H)]SbCl$_6$. Semi-quinone complexes were prepared by adding a stoichiometric amount of ferrocinium hexafluorophosphate or tris(4-bromophenyl)ammoniumyl hexachloroantimonate to a dichloromethane solution of the appropriate complex. IR and EPR spectra were then immediately recorded. IR (CH$_2$Cl$_2$): [Ru(CO)(dppe)(PBu$_3$)(QAL-2H)]SbCl$_6$, 1977.5 cm^{-1}; [Ru(CO)(dppe)(PBu$_3$)(PUR-2H)]PF$_6$, 1975.9 cm^{-1}; [Ru(CO)(dppe)(PBu$_3$)(AG-2H)]PF$_6$, 1976.8 cm^{-1}; [Ru(CO)$_2$(PBu$_3$)$_2$(QAL-2H)]SbCl$_6$, 2062.7 s, 2009.7 s cm^{-1}; [Ru(CO)$_2$(PBu$_3$)$_2$(PUR-2H)]SbCl$_6$, 2059.8 vs, 2002.2 s cm^{-1}; and [Ru(CO)$_2$(PBu$_3$)$_2$(AG-2H)]SbCl$_6$, 2063.6 vs, 2010.5 s cm^{-1}. EPR (CH$_2$Cl$_2$): [Ru(CO)(dppe)(PBu$_3$)(QAL-2H)]SbCl$_6$, g 2.004, $A(^{31}P)$ = 26.0, 23.5 G, $A(^1H$ or $^{31}P)$ = 1.5 G, $A(^{101}Ru) = A(^{99}Ru)$ = 4 G; [Ru(CO)(dppe)(PBu$_3$)(PUR-2H)]PF$_6$, g 2.005, $A(^{31}P)$ = 19.0, 21.0 G, $A(^1H$ or $^{31}P)$ = 1.2 G, $A(^{101}Ru) = A(^{99}Ru)$ = 3.5 G; [Ru(CO)(dppe)(PBu$_3$)(AG-2H)]PF$_6$, g 2.004, $A(^{31}P)$ = 26.0, 24.0 G, $A(^1H$ or $^{31}P)$ = 2.0 G, $A(^{101}Ru) = A(^{99}Ru)$ = 4.5 G; [Ru(CO)$_2$(PBu$_3$)$_2$(QAL-2H)]SbCl$_6$, g 2.005, $A(^{31}P_2)$ = 25.6 G, $A(^1H)$ = 2.4 G, $A(^{101}Ru) = A(^{99}Ru)$ = 4 G; [Ru(CO)$_2$(PBu$_3$)$_2$(PUR-2H)]SbCl$_6$, g 2.004, $A(^{31}P)$ = 20.1 G, $A(^{101}Ru) = A(^{99}Ru)$ = ca. 4 G; [Ru(CO)$_2$(PBu$_3$)$_2$(AG-2H)]SbCl$_6$, g 2.004, $A(^{31}P)$ = 25 G, $A(^{101}Ru) = A(^{99}Ru)$ = ca. 4 G.

Crystal Structure Analysis of *trans*-Ru(CO)$_2$(PBu$_3$)$_2$(AG-2H). Crystals suitable for X-ray diffraction studies were obtained by vapor diffusion of 2,2,3-trimethylbutane into a toluene solution of the complex. The crystal chosen for the analysis, a thick green plate of dimensions 0.38 × 0.46 × 0.72 mm, was sealed into a thin-walled glass capillary and mounted on a Siemens R3m/V diffractometer. The crystal belongs to the monoclinic system (2/m symmetry) in space group $P2_1/n$. Cell constants were derived from a least-squares fit to 50 carefully centered reflections, chosen as $\{hkl\}$ sets with 2θ(Mo Kα) = 24−30° and well-dispersed in reciprocal space. Data were collected as described previously[6] and were collected for Lorentz and polarization factors and for absorption ($T = 0.647 \rightarrow 0.698$).

All calculations were performed under the SHELXTL PLUS (Release 4.11 VMS) program package.[7] The analytical scattering factors for

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(6) Churchill, M. R.; Lashewycz, R. A.; Rotella, F. J. *Inorg. Chem.*, **1977**, *16*, 265.

(7) Sheldrick, G. M. *SHELXTL PLUS (Release 4.11 VMS)*; Siemens Analytical Instruments Inc.; Madison, WI, 1990. (See also Siemens SHELXTL PLUS Manual, 2nd ed., 1990).

Table 1. Crystallographic Data for $Ru(CO)_2(PBu_3)_2((AG-2H)$

empirical formula	$C_{40}H_{60}O_7P_2Ru$
fw	815.9
wavelength, Å	0.710730
space group	$P2_1/n$ (No. 14 *var*)
a, Å	13.317(2)
b, Å	15.628(2)
c, Å	21.076(3)
β, deg	101.660(10)
vol, Å^3	4295.9(11)
Z	4
calcd density, Mg/m^3	1.261
μ(mm^{-1})	0.472
final R indices [$I > 2\sigma(I)$][a]	R = 8.68%, wR = 11.82%
R indices (all data)[a]	R = 11.77%, wR = 12.21%

[a] $R(\%) = 100\ \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR(\%) = 100\ [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$

neutral atoms[8a] were corrected for anomalous dispersion.[8b] The structure was solved by direct methods, difference-Fourier techniques, and least-squares refinement. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms of the PBu_3 ligands and those four bonded to atoms C(5) → C(8) were included in optimized positions with d(C−H) = 0.96 Å.[9] The molecule is well defined but (using the usual crystallographic parlance, *vide infra*) one OH group of the anthragallol-2H is disordered and occupies two alternative sites, defined as O(1X) and O(1Y).

Data for the crystallographic study are collected in Table 1.

Results

Coordination chemistry of hydroxyanthraquinones has not received much attention recently. A 1,2- versus 1,9-chelation has previously been established for alizarin.[3a−c,4] The PHAQs used in this study offer a variety of additional coordination modes. In particular, purpurin and anthragallol both can act as 1,2- or 1,9-chelates, but the former can additionally act as a 4,10-univalent chelate and the latter as a 2,3-divalent chelate. Quiinalizarin can act as a 1,9-, 8,9-, or 5,10- univalent chelate. All of these, in principle, can act as bimetallic, dual compartment ligands.

1,2-Catecholate Complexes. Reaction of $Ru_3(CO)_{12}$, PR_3, and PHAQ in the ratios 1:3:6 in refluxing toluene generate $Ru(CO)_2(PR_3)_2$(PHAQ-2H) (PHAQ = PUR, R = Bu, Cyc; PHAQ= AG, R = Bu, Ph; PHAQ = QAL, R = Bu) and $Ru(CO)(PR_3)_3$(PHAQ-2H) (PHAQ = QAL, AG; R = Bu) (Figure 1). Characterizations of $Ru(CO)_2L_2$(PHAQ-2H) are straightforward, by comparison to previously reported catecholate complexes. The observation of two CO stretches in the IR spectra and a single ^{31}P resonance for each complex indicate that all are Ru(cis-CO)$_2$(trans-PR$_3$)$_2$(chelate) complexes. The ^1H NMR spectra show the expected numbers of free O−H resonances, and the expected aromatic proton resonances can be observed for the PBu_3 and PCy_3 complexes, although the aromatic region is largely obscurred for the PPh_3 complex. Proton resonances for hydroxy substituents in the 1-, 4-, 5-, or 8- positions have chemical shifts of 14−16 ppm, which is due to hydrogen bonding to the central quinone oxygens. $Ru(CO)(PBu_3)_3$(PHAQ-2H) exists as mixtures of two meridianal isomers in a ca. 6:4 ratio.

Anthragallol could form 1,2- or 2,3-catecholate products. The main product was shown to have 2,3-coordination in the case of $Ru(CO)_2(PBu_3)_2$(AG-2H) (vide infra) (Figure 2). The factors which give rise to 2,3-chelation are unknown at this time. This isomeric form maintains the hydrogen bond to the 9-oxo moiety and also would appear to be favored on steric grounds. However, electronic stabilization or kinetic control are also possible.

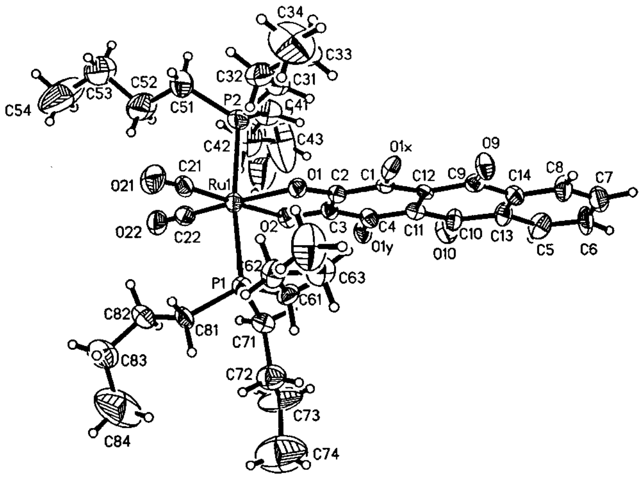

Figure 2. Molecular geometry of $Ru(CO)_2(PBu_3)_2$(AG-2H). Hydrogen atoms in the disordered portion of the structure, i.e., those on O(1X), O(1Y), C(1), and C(4), are not shown.

The products formed from dppe were too insoluble to allow for facile characterization, so further substitution using PBu_3 was accomplished (Figure 1). Ru(CO)(dppe)(PBu_3)(QAL-2H) is a highly soluble, deep blue compound, while Ru(CO)(dppe)(PBu_3)(AG-2H) is dark green, and Ru(CO)(dppe)(PBu_3)(PUR-2H) is red. The ^{31}P NMR spectrum of each indicates predominantly one isomer with PBu_3 occupying one site cis to the PAHQ chelate and one end of the dppe ligand occupying the other. The large trans P−P coupling constant of 350 Hz, compared with the small cis values of 12 and 23 Hz, is diagnostic.

The complexes are highly stable to heat, water, and air. All are quite soluble in dichloromethane, and the PBu_3 complexes are soluble in hydrocarbons.

The *o*-methylated complexes Ru(CO)(dppe)(PBu_3)(AG-3H+Me) and Ru(CO)(dppe)(PBu_3)(PUR-3H+Me) were prepared by reaction with methyl iodide and potassium *t*-butoxide. Thus, base-promoted reactions of the remaining phenolic hydroxyls are feasible to further functionalize these complexes.

Description of the Molecular Structure for $Ru(CO)_2(PBu_3)_2$(AG-2H). Figure 2 shows the overall disordered structure and the atomic labeling scheme. Selected bond lengths and angles are collected in Table 2.

As mentioned above, the crystal structure suffers from disorder. The final model has the rather high discrepancy index of R = 8.68% for the observed data ($I > 2\sigma(I)$ or $|F_o| > 4\sigma(|F_o|)$). The averaging of intensities of common reflections yields a value of R_{int} = 0.86%, indicating that the intensities have been measured with precision. The crystallographic model is clearly subject to some problems, which are caused, no doubt, by disorder. One may loosely define the disorder in the following fashion. There are two possible sites for the OH group adjacent to the O(1)−Ru(1)−O(2) chelate system, that centered on O(1X) has an occupancy of 0.341(18) while that centered on O(1Y) has an occupancy of 0.659(18). *This description is, of course, facile*. It must be recognized that each crystallographic site may be occupied by an entire molecule in one of two possible orientations (the two being inter-related by a C_2 rotation about the bisector of the O(1)−Ru(1)−O(2) chelate "bite"). The outer surfaces of the two such orientations must have approximately the same energy profile, and the sites of the outermost atoms

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[8] *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. 4 (a) pp 99−101, (b) pp 149−150.

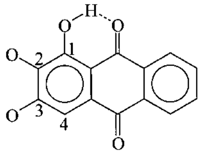
[9] Churchill, M. R. *Inorg. Chem.* **1973**, *12*, 1213.

Table 2. Selected Bond Lengths (Å) and Angles (Deg) for $Ru(CO)_2(PBu_3)_2$(AG-2H)

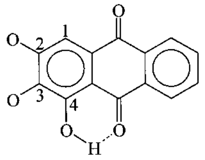
(A) Ruthenium−Ligand Bond Lengths			
Ru(1)−P(1)	2.405(4)	Ru(1)−O(2)	2.098(8)
Ru(1)−P(2)	2.407(4)	Ru(1)−C(21)	1.905(14)
Ru(1)−O(1)	2.084(8)	Ru(1)−C(22)	1.844(14)
(B) Carbon−Oxygen Distances			
O(1)−C(2)	1.306(14)	O(1X)−C(1)[a]	1.270(31)
O(2)−C(3)	1.295(14)	O(1Y)−C(4)[a]	1.304(19)
O(9)−C(9)	1.225(17)	O(21)−C(21)	1.104(18)
O(10)−C(10)	1.218(19)	O(22)−C(22)	1.171(18)
(C) Carbon−Carbon Distances In the Anthragallol-2H Ligand			
C(1)−C(2)	1.407(17)	C(5)−C(6)	1.351(23)
C(2)−C(3)	1.476(16)	C(6)−C(7)	1.324(31)
C(3)−C(4)	1.389(18)	C(7)−C(8)	1.414(23)
C(4)−C(11)	1.399(18)	C(8)−C(14)	1.391(20)
C(11)−C(12)	1.498(17)	C(14)−C(13)	1.356(21)
C(12)−C(1)	1.374(17)	C(13)−C(5)	1.402(21)
C(9)−C(12)	1.442(17)	C(10)−C(13)	1.502(19)
C(12)−C(11)	1.498(17)	C(13)−C(14)	1.356(21)
C(11)−C(10)	1.433(19)	C(14)−C(9)	1.509(19)
(D) Angles Around the Ruthenium Atom			
P(1)−Ru(1)−P(2)	171.9(1)	P(2)−Ru(1)−C(22)	93.4(5)
P(1)−Ru(1)−O(1)	86.5(2)	O(1)−Ru(1)−O(2)	80.6(3)
P(1)−Ru(1)−O(2)	86.8(2)	O(1)−Ru(1)−C(21)	98.1(5)
P(1)−Ru(1)−C(21)	93.9(4)	O(1)−Ru(1)−C(22)	173.5(5)
P(1)−Ru(1)−C(22)	93.6(5)	O(2)−Ru(1)−C(21)	178.4(5)
P(2)−Ru(1)−O(1)	86.1(3)	O(2)−Ru(1)−C(22)	93.0(5)
P(2)−Ru(1)−O(2)	88.8(2)	C(21)−Ru(1)−C(22)	88.3(6)
P(2)−Ru(1)−C(21)	90.3(4)		

[a] O(1X) and O(1Y) represent the two sites for the disordered oxygen atoms. Occupancies are 0.341(18) for O(1X) and 0.659(18) for O(1Y).

in the two orientations should, in general, coincide. To a first approximation, the $Ru(PBu_3)_2(CO)_2$ moieties of the two overlapping images overlap well, although the ends of the *n*-butyl groups do show substantial excursions (treated as "thermal motion"), with *U*(eq) values (in $Å^2$) of 0.29(3) for C(44), 0.27(3) for C(54), 0.26(3) for C(74), etc. The two possible orientations of the anthragallol-2H ligand are shown below. That designated **A** has a 34% occupancy and that designated **B** a 66% occupancy.



A



B

While we have not located the hydrogen atoms on atoms O(1X) in **A** or O(1Y) in **B**, they are probably involved in hydrogen bonding to the nearby quinonic oxygen atoms. The disordered OH groups will probably result in imprecise overlap of the two orientations of this ligand at other atomic sites. Therefore, all bond lengths in this ligand, and even more, the esd's on these bond lengths, should be taken *cum grano salis.*

The central ruthenium(II) moiety has a slightly distorted octahedral coordination environment with mutually trans PBu_3 ligands (Ru(1)−P(1) = 2.405(4), Ru(1)−P(2) = 2.407(4) Å, and ∠P(1)−Ru(1)−P(2) = 171.9(1)°) and mutually cis carbonyl ligands (Ru(1)−C(21) = 1.905(14), Ru(1)−C(22) = 1.844(14) Å, and ∠C(21)−Ru(1)−C(22) = 88.3(6)°). The anthragallol-2H ligand is bonded to the ruthenium(II) center via the oxygen atoms associated with C(2) and C(3) (Ru(1)−O(1) = 2.084(8), Ru(1)−O(2) = 2.098(8) Å, with the chelate "bite angle" ∠O(1)−Ru(1)−O(2) = 80.6(3)°), rather than via the possible, but less symmetrical, coordination through those oxygen atoms on C(1) [O(1x), see structure **A**] and C(2) [O(1)].

Oxygen−carbon distances within the disordered anthragallol-2H system include O(1)−C(2) = 1.306(14) and O(2)−C(3) = 1.295(14) Å, each of which is essentially a single bond. These bond lengths are shorter than those found for most catecholates (cf. $Ru(CO)_2(PPh_3)_2(O_2C_6H_4)$,[10c] 1.347(4) Å), However, the values are very similar to those found in two aluminum complexes derived from1,2-dihydroxy- and 1,2,4-trihydroxyanthraquinone (1.30−1.32 Å).[3e] Also, comparison of the single bonds for the free C−OH (1.349(7) Å) and the phenolate C−ORu (1.308(8) Å) of $HRu(CO)(PPh_3)_2$(alizarinate) suggests that this distance of 1.3 Å is the norm for phenolate C−O single bonds of hydroxyanthraquinone ligands.[4] The linkages O(9)−C(9) = 1.225(17) and O(10)−C(10) = 1.218(19) Å are clearly typical C═O double bonds. The final oxygen atom occupies two possible sites with O(1X)−C(1) = 1.270(31) and O(1Y)−C(4) = 1.304(19) Å, occupancies being 0.341(18) for O(1X) and 0.659(18) for O(1Y). These bond lengths are consistent with C−OH systems.

The crystal structure is stabilized by the stacking of anthragallol-2H systems (see Figure 1S in Supporting Information).

1,9-Complex. Reaction of $Ru_3(CO)_{12}$, PCy_3, and PUR in the ratios 1:6:3 generates two significant products, $Ru(CO)_2(PCy)_2$-(PUR-2H) and $HRu(CO)(PCy_3)_2$(PUR-H) (Figure 1). The latter complex has a acylphenolate ligand, as we have shown previously for $RuH(CO)(PPh_3)_2$(1,9-AL-H).[4] However, there are two possible linkage isomers for purpurin, via the 1,9- or 4,-10-oxygen atoms. The singlet ^{31}P signal indicates a trans arrangment of PCy_3 ligands. The ^1H NMR and IR spectra are similar to those of $RuH(CO)(PPh_3)_2$(AL-H), the structure of which we previously determined by X-ray crystallography. The ^1H NMR spectrum contains HO resonances at 15.55 and 8.04 ppm; the lower field signal is due the hydrogen-bonded 1- or 4-hydroxyl. The other signal is 1 ppm downfield of the chemical shift for the 2-OH moiety of $RuH(CO)(PCy_3)_2$(1,9-AL-H).[4] Because of the difference in chemical shifts for the free hydroxyl of $RuH(CO)(PCy_3)_2$(PUR-H) compared with $RuH(CO)(PCy_3)_2$-(1,9-AL-H) we favor the 4,10- isomer for the former. Two isomers due to the relative orientations of the cis-(H)(CO) ligands are expected but one predominates by 11.7:1.

The analogous reaction with anthragallol did not produce a significant yield of the corresponding AG-H complex.

Electrochemistry. The electrochemistry of these complexes was surveyed using cyclic voltammetry. All of the 1,2-catecholates exhibit a reversible to quasi-reversible 1-e oxidation, at potentials of −0.13 to +0.30 V, associated with catecholate/semiquinone couples, and reversible to quasi-reversible reductions associated with the 9,10-anthraquinone moiety at −1.70 to −2.1 V. The greatest number of reversible redox couples was found for Ru(CO)(dppe)(PBu_3)(QAL-2H) (Figure 3). We attribute the couple at +0.67 V to 1-e oxidation of the 5,8-

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(10) (a) Connelly, N. G.; Manners, I.; Protheroe, J. R. C.; Whiteley, M. W. *J. Chem. Soc., Dalton Trans.* **1984**, 2713. (b) Bohle, D. S.; Goodson, P. A. *J. Chem. Soc., Chem. Commun.* **1992**, 1205. (c) Bohle, D. S.; Carron, K. T.; Christensen, A. N.; Goodson, P. A.; Powell, A. K. *Organometallics* **1994**, *13*, 1355.

Table 3. Cyclic Voltammetric Data

complex	$(E_{p,a}+E_{p,c})/2$ $[E_{p,a1}]$ (V)	ΔE_p (mV)	i_{pc}/i_{pa}	$(E_{p,a}+E_{p,c})/2$ (V)	ΔE_p (mV)	i_{pc}/i_{pc}
$Ru(CO)_2(PBu_3)_2$(PUR-2H) (800 mV/s)	+0.22	88	0.84	[−1.92]		
Ru(CO)(dppe)(PBu_3)(PUR-2H) (400 mV/s)	0.0	84	0.45	[−2.1]		
$Ru(CO)_2(PCy_3)_2$(PUR-2H) (100 mV/s)	+0.18	66	0.81			
Ru(CO)(dppe)(PBu_3)(AG-2H) (800 mV/s)	−0.13	85	0.91	−1.81	60	0.82
$Ru(CO)_2(PBu_3)_2$(AG-2H) (400 mV/s)	+0.17	61	0.79	−1.70	72	0.92
				[−2.12]		
$Ru(CO)_2(PBu_3)_2$(QAL-2H) (1000 mV/s)	+0.30	87	0.82	−1.70	72	0.55
Ru(CO)(dppe)(PBu_3)(QAL-2H) (500 mV/s)	+0.67	102	0.66	−1.81	96	0.81
	+0.03	133	0.90			
RuH(CO)$(PCy_3)_2$(PUR-H) (400 mV/s)	+0.04	69	1.0	−1.61	62	1.0
	[+0.39]					
	[+0.82] (2e)					

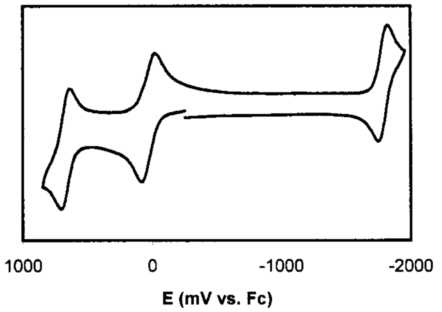

Figure 3. Cyclic voltammogram of Ru(CO)(dppe)(PBu_3)(QAL-2H) at 500 mV/s in dichloromethane (0.1 M NBu_4BF_4).

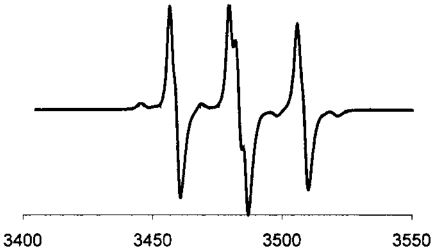

Figure 4. EPR spectrum for $[Ru(CO)(dppe)(PBu_3)(QAL\text{-}2H)]^{1+}$.

hydroquinone moiety, since no similar oxidation was present in the CVs of Ru(CO)(dppe)(PBu_3)(AG-2H) or Ru(CO)(dppe)(PBu_3)(PUR-2H). Electrochemical data are summarized in Table 3.

The CV of RuH(CO)$(PCy_3)_2$(PUR−H) displays a reversible 1-e oxidation at +0.04 V, irreversible oxidation waves at $E_{p,a}$ +0.39 (1-e) and +0.82 (2-e) V, and a reversible 1-e reduction at −1.61 V. For comparison, RuH(CO)$(PCy_3)_2$(1,9-AL-H) displays a single reversible 1-e oxidation at +0.076 V, which we assigned to a metal-centered couple, and two reductions at −1.40 and −1.67 V.[4] The two irreversible oxidations observed for RuH(CO)$(PCy_3)_2$(PUR-H) are likely associated with the PUR-H ligand.

Semi-quinone Complexes. Chemical oxidation, using ferrocinium hexafluorophosphate or tris(4-bromophenyl)ammoniumyl hexachloroantimonate (for those complexes with oxidation potentials more positive than that of ferrocene), was used to generate the semi-quinone complexes $[Ru(CO)(dppe)(PBu_3)(PHAQ\text{-}2H)]^{1+}$ (PHAQ = PUR, AG, and QAL) and $[Ru(CO)_2(PBu_3)_2(PHAQ\text{-}2H)]SbCl_6$, which were characterized in situ (dichloromethane solution). The IR spectra of the semi-quinone complexes show that the CO stretches are shifted to higher frequency by ca. 20−30 cm^{-1} versus the neutral precursor. In each case the EPR spectrum is a triplet near *g* 2.00, with hyperfine coupling to two ^{31}P nuclei in positions cis to the PHAQ ligand ($A(^{31}P)$ ca. 20−25 G) and to ^{99}Ru and ^{101}Ru (ca. 4 G for each). The spectrum of $[Ru(CO)_2(PBu_3)_2(QAL\text{-}2H)]^{1+}$ also shows resolvable coupling to an aromatic ring proton. Hyperfine coupling to the ^{31}P nucleus in the plane of the PHAQ ring, where present, is too small to resolve. A representative spectrum, for $[Ru(CO)(dppe)(PBu_3)(QAL\text{-}2H)]^{1+}$ is shown in Figure 4. The spectra are very similar to those of $[Ru(CO)_2(PPh_3)L(o\text{-}O_2C_6Cl_4)]^{1+}$, reported by previously by Connelly et al.[10a] and by Balch[11] (e.g., L = PPh_3, *g* 2.002 (t, $A(^{31}P)$ 25.2 G), and of analogous alizarinate complexes reported by our group.[4] The hexafluorophosphate complexes can be isolated and are stable to air for extended periods, but we did not obtain analytically pure compounds. The hexachloroantimonate salts decompose over a 24 h period, forming $Ru(CO)_2Cl_2(PBu_3)_2$.

Discussion

Transition metal complexes of catecholate ligands have received considerable attention because of their relationship to biologically important quinoids and catechols and because of their unique structural, magnetic, and electronic properties.[12] Although metal complexes of 1,2-dihydroxyanthracenediones have been used as dyes and indicators[2], except for alizarin[3] and purpurin,[3f] the chemistry of metal complexes of these catecholates has been unexplored. Although no complex was characterized, 5,10- and 8,9-chelation was proposed to account for the selective esterification of the 1- and 2-hydroxyl groups by reaction of a quinalizarin−Cu(II) complex with acyl halides.[13] No complexes of anthragallol appear to have been characterized previously.

We have shown that, as expected, catecholates and semiquinones can be prepared from anthragallol, purpurin, and quinalizarin, and additionally purpurin can act as a univalent acylphenolate ligand, and the preferred catecholate complex from anthragallol is the 2,3- isomer. Base-promoted functionalization of free hydroxyls is feasible. These ligand systems, therefore, provide for complexes with a variety of coordination modes, redox states, and photophysical properties which can be tuned via substitutuion on the metal and the anthraquinone ring. Although the catecholate/semiquinone redox couple is largely ligand based, the oxidation potential for $Ru(CO)_2$(dppe)(PBu_3)(PHAQ-2H) is 0.2−0.3 V lower than that of the corresponding $Ru(CO)_2(PBu_3)_2$(PHAQ-2H). The uncoordinated hydroxyls can be used to attach the complexes to supports or to linkers capable of selective binding of the complexes to biologically important targets. Finally, the solubilities of the

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complexes are easily adjustable by choice of appropriate phosphine ligands.

Since these ligands can coordinate via the 1,9- or 4(5),10-oxygens, the catecholate complexes of purpurin, anthragallol, and quinalizarin should be able to coordinate a second metal atom as acetylacetonate analogues. Homobimetallic complexes of 1,4-dihydoxoanthracenedione, in which both metals are chelated by the acylphenolate structure, have been characterized previously.[14] Bimetallic complexes of these catecholate-acylphenolate ligands should be accessible by base-promoted metathesis reactions with a second metal salt. The catecholate/semiquinone redox couple will allow redox-based switching of the ligands' donor properties toward the second metal atom. Attempts to prepare such bimetallic complexes are underway.

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Supporting Information Available: Listings of crystal data, crystallographic data collection information, solution and refinement information, atomic coordinates and equivalent isotropic displacement coefficients, bond lengths, bond angles, anisotropic displacement coefficients and hydrogen atom coordinates with their isotropic displacement coefficients (10 pages), diagram of packing of molecules within the unit cell (1 page). This material is available free of charge via the Internet at http://pubs.acs.org.

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