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Article

Paramagnetic Effects on the NMR Spectra of "Diamagnetic" Ruthenium (bis-phosphine)(bis-semiquinone) Complexes

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Ligand substitution on *cis*-$Ru(PPh_3)_2(1,2\text{-}O_2C_6H_4)_2$ gives *cis*-$RuL^1L^2(1,2\text{-}O_2C_6H_4)_2$ (L^1 = PPh_3, L^2 = $P(OPh)_3$, PBu_3; L^1 = L^2 = PBu_3, $P(OMe)_3$). Syntheses of *cis*-$Ru(PPh_3)_2(3,4\text{-}O_2C_6H_2(5\text{-}OH)CO_2Me)_2$ and *cis*-$Ru(PPh_3)_2(AGSQ)_2$ (AGSQ = the semiquinone derived from 1,2,3-trihydroxyanthracene-9,10-dione) are also reported. The upfield chemical shifts and line broadening of the semiquinone 4,5-proton resonances in the NMR spectra indicate that these complexes, while having no detectable magnetic moments, have a weak, temperature-, ligand- and solvent-variable residual paramagnetism, not previously recognized in this series. Density functional theory (DFT) calculations predict a low-lying triplet state, about 14 kJ/mol (0.15 eV) above the singlet ground state. The paramagnetic effects on the NMR spectra are attributed to singlet−triplet equilibria. Temperature dependence of the proton resonances of the semiquinone rings of *cis*-$Ru(PPh_3)_2(1,2\text{-}O_2C_6H_4)_2$ was used to calculate the singlet−triplet free energy difference as 17.5−18.0 kJ/mol in toluene.

Introduction

The electronic structures and redox states of metal complexes of o-quinone, semiquinone, and catecholate ligands have been of interest for over 30 years.[1] The variety of possible metal and ligand redox states and the resulting electrochemical and magnetic properties make these systems quite complicated. In complexes containing two or more semiquinone ligands spin exchange coupling between the ligands and with paramagnetic metal ions can result in highly variable magnetic behavior.

Complexes $Ru(PPh_3)_2(semiquinone)_2$ (Figure 1), where the semiquinone ligands are derived from catechol (SQ), 4-*t*-butylcatechol, 3,5-di-*t*-butylcatechol (DBSQ), and tetrachlorocatechol (Cl_4SQ), have been previously reported to be diamagnetic and have been characterized as $Ru^{II}(SQ)_2$ with strong electronic coupling between the semiquinone ligands.[2,3] These complexes have been prepared as both *cis* and *trans* isomers, but the factors determining which isomer is preferred have not been identified. Chakravorty et al. reported the crystal structure of *trans*-$Ru(PPh_3)(Cl_4SQ)_2\cdot 2H_2O$, prepared by reaction of $HRu(sal)(PPh_3)_3$ (sal = salicylate) with triethylamine and tetrachlorocatechol.[3] On the other hand Pierpont et al. reported the crystal structure of *cis*-$Ru(PPh_3)_2(Cl_4SQ)_2\cdot CH_2Cl_2$, prepared by reaction of triethylamine and tetrachlorocatechol with $RuCl_2(SQ)(PPh_3)_2$.[2]

We re-investigated the syntheses and properties of these bis(semiquinone) complexes, with the goal of preparing one-dimensional polymers based upon a repeat unit $RuL_2(RG\text{-}4H)$ where RG = rufigallol (1,2,3,5,6,7-hexahydroxyanthacene-9,10-dione). In the course of this investigation we observed unexpected NMR behavior which suggested a previously unrecognized paramagnetic component. These observations and the syntheses of phosphine ligand substitution products are reported here.

Experimental Section

$RuCl_2(PPh_3)_3$,[4] $Ru(PPh_3)_2(3,5\text{-}DBSQ)_2$,[2] $Ru(PPh_3)_2(SQ)_2$,[3] and anthragallol[5] were prepared by previously reported procedures. Catechol, 3,5-di-*t*-butylcatechol, and methyl 3,4,5-trihydroxybenzoate were obtained from Aldrich. $P(OMe)_3$, $P(OPh)_3$, and PBu_3 were obtained from Aldrich and were distilled under reduced pressure before use.

Physical Methods of Characterizations. ^1H and ^{13}C NMR spectra were obtained on Varian Associates Gemini 300 or Varian Associates VXR−400S instruments. Measurements of

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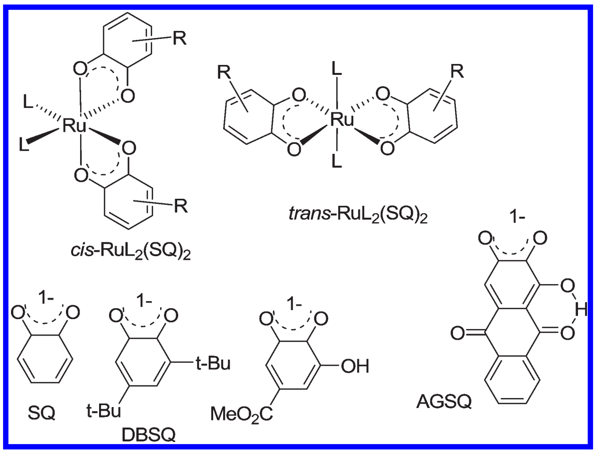

Figure 1. Structures of complexes and semiquinone ligands.

relaxation times, T_1, were done by the inversion recovery method. ^{31}P NMR spectra were recorded on the VXR−400S instrument, 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.

Electrochemistry. The electrochemical procedures were conducted as described previously.[6] All potentials are reported relative to the ferrocene/ferrocenium couple as 0 V.

***cis*-Ru(PPh$_3$)$_2$(SQ)$_2$.** This compound has been previously reported but was assumed to be the trans isomer.[3] The NMR data were not determined, and these indicate that only the cis isomer is present in solution. ^{1}H NMR (CDCl$_3$): 7.3−7.0 (m, 30 H), 6.54 (d, 2 H$_a$, J_{ad} 8 Hz, T_1 1.1 s), 6.49 (d, 2 H$_b$, J_{bc} 8 Hz, T_1 0.93 s), 5.49 ("t", 2 H$_c$, J_{bc} 8 Hz, J_{cd} 8 Hz, T_1 0.52 s), 4.91 (br t, 2 H$_d$, J_{ad} 8 Hz, J_{cd} 8 Hz, T_1 0.10 s) ppm. ^{31}P{^{1}H} NMR (CDCl$_3$): 23.53 ppm. ^{13}C{^{1}H} NMR (CDCl$_3$): 179.5, 165.0, 134.7 (*o*- or *m*-C and *i*-C, PPh$_3$), 132.9, 129.7 (*p*-C, PPh$_3$), 128.1 (*o*- or *m*-C, PPh$_3$), 121.9, 118.0, 114.4, 54.0 (CH$_2$Cl$_2$) ppm.

***cis*-Ru(PBu$_3$)$_2$(SQ)$_2$.** A solution of Ru(PPh$_3$)$_2$(SQ)$_2$ (31 mg, 0.037 mmol) and PBu$_3$ (20 μL) in 0.8 mL deuteriochloroform was monitored by ^{31}P NMR. After 3 days no starting material remained, and product mixture contained 42% Ru(PPh$_3$)(PBu$_3$)(SQ)$_2$ (^{31}P{^{1}H} NMR (CDCl$_3$): 22.8 (d), 8.0 (d) ppm, *J* 36 Hz) and 58% Ru(PBu$_3$)$_2$(SQ)$_2$. The latter was separated by thin layer chromatoraphy (TLC) on silica eluting with toluene.

Ru(PBu$_3$)$_2$(SQ)$_2$. Anal. Calcd for $C_{36}H_{62}O_4P_2Ru$: C, 59.90; H, 8.66. Found: C, 59.92; H, 8.41. ^{1}H NMR (CDCl$_3$): 6.88 (d, 2 H, *J* 7 Hz), 6.85 (d, 2 H, *J* 7 Hz), 6.37 (t, 2 H, *J* 7 Hz), 6.05 (br t, 2 H, *J* 7 Hz), 1.6 (m. 12 H), 1.35 (m, 24 H), 0.96 (m, 18 H) ppm. ^{31}P{^{1}H} NMR (CDCl$_3$): 8.23 ppm.

***cis*-Ru(P(OMe)$_3$)$_2$(SQ)$_2$.** A solution of Ru(PPh$_3$)$_2$(SQ)$_2$ (112 mg, 0.133 mmol) and P(OMe)$_3$ (80 μL, 0.68 mmol) in 25 mL dichloromethane was stirred for 4 days. The solution was evaporated to dryness, and the residue was separated by TLC on silica eluting with 8% ethyl acetate in toluene. Three blue bands eluted, in order: Ru(PPh$_3$)$_2$(SQ)$_2$ (2 mg, 2%), Ru(PPh$_3$)(P(OMe)$_3$)(SQ)$_2$ (1 mg, 1%), and Ru(P(OMe)$_3$)$_2$(SQ)$_2$ (37 mg, 49%). Anal. Calcd for $C_{18}H_{26}O_{10}P_2Ru$: C, 38.24; H, 4.64. Found: C, 38.79; H, 4.68. ^{1}H NMR (CDCl$_3$): 6.79 (d, 2 H, *J* 8 Hz), 6.59 (d, 2 H, *J* 8 Hz), 5.62 (br "t", *J* 8 Hz), 5.53 (br t, 2 H, *J* 8 Hz), 3.63 (br, 18 H) ppm. ^{31}P{^{1}H} NMR (CDCl$_3$): 130.26 ppm.

***cis*-Ru(PPh$_3$)(P(OPh)$_3$)(SQ)$_2$.** A solution of Ru(PPh$_3$)$_2$(SQ)$_2$ (52 mg, 0.062 mmol) and P(OPh)$_3$ (140 mg, 0.45 mmol) in 10 mL of dichloromethane was stirred under argon. After 4 days the solution was evaporated to dryness, and the residue was separated by TLC on silica eluting with 4% ethyl acetate in toluene. One blue band was extracted with ethyl acetate and evaporated to give 44.5 mg, 81%, of the product. Anal. Calcd for $C_{48}H_{38}O_7P_2Ru$: C, 64.79; H, 4.30. Found: C, 63.95; H, 4.36. ^{1}H NMR (CDCl$_3$): 7.4−6.6 (m, 30 H), 6.33 (d, 1 H, *J* 8 Hz), 6.21 (d, 1 H, *J* 8 Hz), 6.19 (d, 1 H, *J* 8 Hz), 5.98 (d, 1 H *J* 8 Hz), 5.52 (br, 1 H), 5.19 (br, 1 H), 4.88 (br, 1 H), 4.76 (br, 1 H) ppm. ^{31}P{^{1}H} NMR (CDCl$_3$): 111.57 (d, *J* 67 Hz), 37.44 (d, *J* 67 Hz) ppm.

***cis*-Ru(PPh$_3$)$_2$(3,5-DBSQ)$_2$.** This complex was prepared as reported previously.[2] NMR spectra were recorded for comparison.

^{1}H NMR (CDCl$_3$): 7.3−7.0 (m, ca. 30 H), symmetrical isomer - 6.83 (d, 2 H, *J* 8 Hz), 6.40 (d, *J* 2 Hz), 1.38 (s), 0.72 (s); unsymmetrical isomer - 6.77 (br), 6.63 (br), 1.44 (s), 1.43 (s), 1.20 (s), 0.86 (s) ppm. ^{31}P{^{1}H} NMR: symmetrical - 32.07 (s); unsymmetrical - 31.85 (br), 29.65 (br) ppm. Symmetrical/unsymmetrical ratio = 0.7.

***cis*-Ru(PPh$_3$)$_2$(3,4-O$_2$C$_6$H$_2$(5-OH)CO$_2$Me)$_2$.** A mixture of RuCl$_2$(PPh$_3$)$_3$ (214 mg, 0.223 mmol), methyl 3,4,5-trihydroxybenzoate (84 mg, 0.46 mmol), and acetone (10 mL) was placed in a 50 mL Schlenk flask, equipped with magnetic stir bar, under an argon atmosphere. Triethylamine (50 μL) was added, and the color of the solution immediately began to turn blue. The solution was stirred overnight. The next day solvent was removed by rotary evaporation. The residue was applied as a dichloromethane solution to a silica TLC plate. Elution with 10% ethyl acetate in toluene gave a black band, followed by two blue bands, which were extracted with ethyl acetate. The top blue band was one of the two symmetrical isomers. The second blue band was a mixture of the unsymmetrical isomer and the other symmetrical isomer. Band 1: 20 mg, 9.3% yield. ^{1}H NMR (CDCl$_3$): 7.3−7.0 (m, 30 H), 6.12 (s, 2 H, T_1 0.32 s), 5.27 (s, 2 H, T_1 0.58 s), 3.96 (s, 6 H, T_1 0.75 s) ppm. ^{31}P{^{1}H} NMR: 13.79 ppm. Anal. Calcd for $C_{52}H_{42}O_{10}P_2Ru$: C, 63.09; H, 4.28. Found: C, 62.86; H, 4.22. Band 2: 34 mg 15% yield. ^{1}H NMR (CDCl$_3$): 7.3−7.0 (m, 30 H), 6.61 (s), 6.58 (s), 6.15 (s), 5.99 (s), 5.35 (s), 4.00 (s), 3.98 (s), 3.92 (s) ppm. ^{31}P{^{1}H} NMR (CDCl$_3$): 29.21 (s, OPPh$_3$), 21.22 (s), 18.26 (d, *J* 31 Hz), 13.80 (d, *J* 31 Hz) ppm.

***cis*-Ru(PPh$_3$)$_2$(AGSQ)$_2$.** The same procedure but using anthragallol gave the product as a brown solid in 22% yield. The product was recrystallized from dichloromethane/methanol. UV/vis (dichloromethane): 298 (26000), 352 (15000), 422 (12400), 592 (4300) nm (ε, M^{-1} cm^{-1}). FAB MS (^{102}Ru): 1134 M + , 880 (M-AGSQ) + . Anal. Calcd for $RuP_2C_{64}H_{42}O_{10}$: C, 67.78; H, 3.73. Found: C, 67.26; H, 4.12. ^{1}H NMR (CDCl$_3$): 11.92 (s), 11.56 (s), 11.25 (s), 10.95 (s), 8.5−6.5 (m), 5.78 (s), 5.44 (s) ppm. ^{31}P{^{1}H} NMR (CDCl$_3$): −40.9 (br), −45.6 (br), −66.4 (br), −69.2 (br) ppm.

Carbonylation of *cis*-Ru(PPh$_3$)$_2$(AGSQ)$_2$. A solution of 20.0 mg of *cis*-Ru(PPh$_3$)$_2$(AGSQ)$_2$ in 10 mL THF was heated at 70−80 °C in a pressure bottle under 2 atm of carbon monoxide. After 3 h the solution was evaporated to dryness, and the residue was separated by preparative thin layer chromatography on silica, eluting with 4% ethyl acetate in dichloromethane. The bright green band was extracted with ethyl acetate, and the solvent was removed with vacuum. After transfer to a tared vial as a dichloromethane solution, evaporation yielded 12.3 mg (75%) Ru(CO)$_2$(PPh$_3$)$_2$(AG-2H) [19] (AG-2H refers to the catecholate dianion derived from anthragallol). The product was characterized by comparison of the IR and ^{1}H and ^{31}P NMR spectra to those of an authentic sample.

Computational Details

Density functional theory (DFT) computations were performed with the Amsterdam Density Functional program

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package (ADF).[7] All calculations employed the scalar relativistic zeroth-order regular approximation (ZORA) [8,9] and the revised Perdew-Burke-Ernzerhof (revPBE) functional.[10,11] Geometries were optimized using the valence triple-ζ polarized Slater-type basis TZP optimized for ZORA calculations (ZORA/TZP) from the ADF basis set database. Default settings were applied except for the geometry convergence (gradient convergence of 1×10^{-4}) and the numerical integration accuracy (parameters were set as 5.0 for "accint" and 6.0 for "accsph". The NMR computations were carried out with these integration grids, too). For the PH_3 model complex, the optimized closed shell ground state and the excited triplet state structure were confirmed by frequencies calculations. Apart from very low frequency imaginary modes (around 20 cm^{-1}) for the PH_3 rotations, all harmonic vibrations had real positive frequencies. The PH_3 hindered rotation wavenumber is within the accuracy of the numerical differentiation used to compute the normal modes and inconsequential for the results since these ligands would undergo quasi free rotations at the experimental temperatures. Singlet and triplet excitation energies were subsequently calculated by using time-dependent DFT (TDDFT) linear response theory,[12-14] as well as with a Δ-SCF approach.[15] Here, we have employed the doubly polarized ZORA basis TZ2P for Ru and the TZP basis for all other atoms. For the TDDFT computations an integration accuracy parameter of 8.0 was used which roughly corresponds to the number of significant figures for the integration of the electron density. In general, the results obtained from TDDFT and Δ-SCF to calculate excitation energies were in reasonable agreement with each other. To check for possible influence from the solvent, additional optimizations of the singlet ground state and the lowest triplet state were performed for the PH_3 model system, using the "COSMO" continuum solvation model with dielectric constants for toluene, chloroform, and acetone. A reduction of the singlet−triplet energy splitting from 0.163 to 0.135 eV when going from gas phase to the most polar solvent model, acetone, was calculated. However, this solvent model does not take into account specific hydrogen bonding effects which might be important to describe the overall effect from the solvent, and the solvent-polarity induced changes do not exceed the effects from changing the R-groups on the phosphine ligands nor do they exceed other remaining uncertainties in the excitation energies caused by the computational model. Therefore, the discussion is based on the gas phase calculations.

Results

Using a modification of procedures reported in the literature[2] we found that reaction of $RuCl_2(PPh_3)_3$ with 2 equiv of the appropriate catechol and excess NEt_3 in acetone gives the corresponding *cis*-$Ru(PPh_3)_2$(semiquinone)$_2$ in good yields.

The NMR characterizations of complexes previously prepared were not fully reported. Chakravorty et al. prepared $Ru(PPh_3)_2(SQ)_2$, among other semiquinone complexes, but did not report NMR data.[3] Bhattacharya and Pierpont noted that the NMR spectrum of $Ru(PPh_3)_2(DBSQ)_2$ contains three sets of *t*-Bu resonances, in a 2:1.3:1 ratio, characterized as cis-isomers, and did not comment on the other DBSQ resonances or the ^{31}P NMR data.[2]

The reactions of catechol, triethylamine, and either $RuCl_2(PPh_3)_3$ (Pierpont's conditions[2]) or HRu(salicylate)$(PPh_3)_3$ (Chakravorty's conditions[3]) in acetone give the same product, $Ru(PPh_3)_2(SQ)_2$. The NMR spectra for $Ru(PPh_3)_2(SQ)_2$ clearly indicate only the cis isomer in solution. The ^{31}P NMR spectrum displays a single resonance. The $^{13}C\{^1H\}$NMR spectrum displays six resonances for the semiquinone ligands, as expected for the C_2 symmetric *cis* geometry and inconsistent with the *trans* geometry. The ^1H NMR spectrum displays four resonances for the SQ ligands, as expected for the *cis* isomer. However, the appearance of the spectrum is unexpected. The 4,5-proton resonances are shifted upfield, and all four SQ proton resonances have different line-widths, with the 4- and 5-proton resonances broader than the 3- and 6-proton resonances. In deuteriochloroform the four SQ proton resonances appear at 6.54 (br d, T_1 1.1 s), 6.49 (d, T_1 0.93 s), 5.49 (t, T_1 0.52 s), and 4.91 (br t, T_1 0.10 s) ppm (Figure 2). Correlation spectroscopy (COSY) shows the coupling of the lowest field doublet to the highest field triplet. The T_1 measurements found a much shorter relaxation time for the most upfield resonance. This suggests that there is some residual paramagnetism associated with the complex.

Other phosphine complexes can be prepared by ligand substitution. We have found that *cis*-$Ru(PBu_3)_2(SQ)_2$ can be readily prepared by PBu_3 substitution on *cis*-$Ru(PPh_3)_2(SQ)_2$ at room temperature. The 4- and 5-proton resonances of this complex are not shifted as far upfield and are sharper than the corresponding resonances for *cis*-$Ru(PPh_3)_2(SQ)_2$. The $^{31}P\{^1H\}$ NMR spectrum of the intermediate $Ru(PPh_3)(PBu_3)(SQ)_2$ displays a pair of doublets with a coupling constant of 39 Hz. Ligand exchange was also used to prepare *cis*-$Ru(P(OMe)_3)_2(SQ)_2$ and *cis*-$Ru(PPh_3)(P(OPh)_3)(SQ)_2$.

The complex *cis*-$Ru(PPh_3)_2$(3,5-DBSQ)$_2$ (DBSQ = di-*t*-butylsemiquinone) has three possible isomers because of the orientations of the unsymmetrical DBSQ ligands. The NMR spectra are most consistent with the presence of two of the three isomers, one symmetrical (two *t*-butyl resonances and a single ^{31}P signal) and the other unsymmetrical (four *t*-butyl resonances and two broad doublet ^{31}P resonances); under these conditions the resonance for free PPh_3 is sharp, as expected since phosphine exchange occurs over a period of hours. Again the broadness of the ring proton resonances suggests a previously unrecognized paramagnetism.

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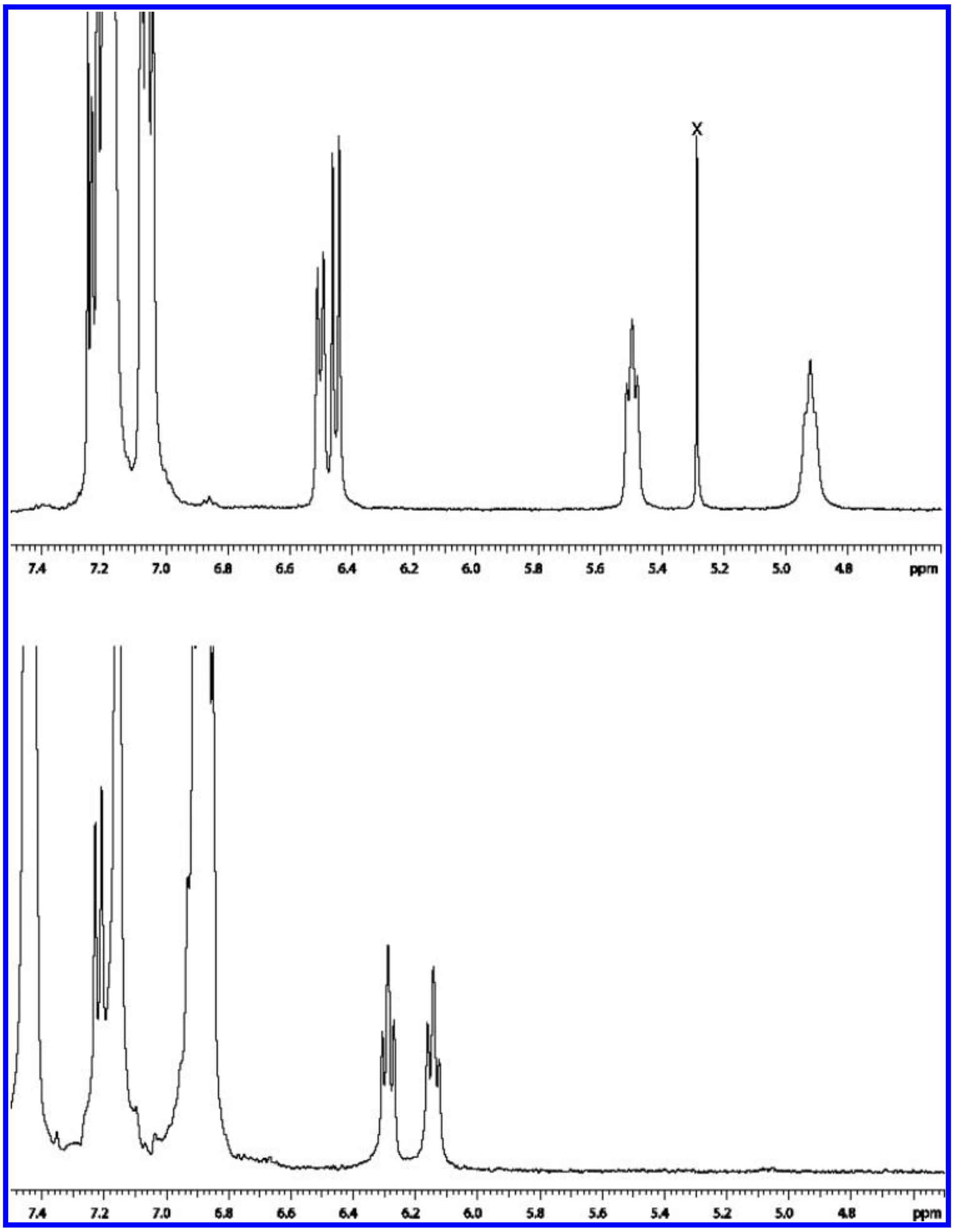

Figure 2. ^{1}H NMR spectra of Ru(PPh$_3$)$_2$(SQ)$_2$ in deuteriochloroform (upper, × marks co-crystallized dichoromethane) and d$_6$-benzene (lower).

Fox and Pierpont have reported a similar phenomenon for the ^{1}H NMR spectra of Pd(DBSQ)$_2$.[16] Temperature-dependent chemical shifts, larger for resonances associated with the 4,5-ring positions, were attributed to weak SQ-SQ exchange which results in low-level paramagnetism, even though the compound has no paramagnetism detectable by magnetic susceptibility measurements. A plot of the chemical shift of the 5-*t*-Bu group versus $1/T$ was termed “reasonably linear.” It was observed that SQ-SQ exchange was much greater for the analogous Pt complex, which does not display temperature-dependent spectra. Temperature-dependent spectra for diamagnetic Cr(DBSQ)$_3$ also suggested that this complex had low-level paramagnetism.

We therefore examined the temperature dependence of the ^{1}H NMR chemical shifts of the SQ protons of *cis*-Ru(PPh$_3$)$_2$(SQ)$_2$. Initial experiments in d$_8$-toluene solution found that the 4,5-ring proton resonances shift upfield by 0.73 and 0.95 ppm as the temperature is increased from −10 °C to +50 °C. This study also revealed a significant solvent effect on the chemical shifts and line-widths of the 4,5-ring proton resonances, with shifts for the highest field proton resonance at 6.14 ppm (sharp triplet) in d$_6$-benzene at 21°C (Figure 2) compared with 4.91 ppm (broad) in deuteriochloroform, 5.68 ppm in d$_2$-dichloromethane, 5.36 ppm in 5% d$_4$-methanol/95% d$_2$-dichloromethane, 5.06 ppm in 15% d$_4$-methanol/85% d$_2$-dichloromethane (the chemical shifts are the same in 30% d$_4$-methanol/70% d$_2$-dichloromethane), 5.88 ppm (sharp triplet) in carbon tetrachloride, and 5.83 ppm (sharp triplet) in d$_6$-acetone. The solvent shifts do not correlate with polarity (e.g., E values[17] for benzene (34.5), carbon tetrachloride (32.5),

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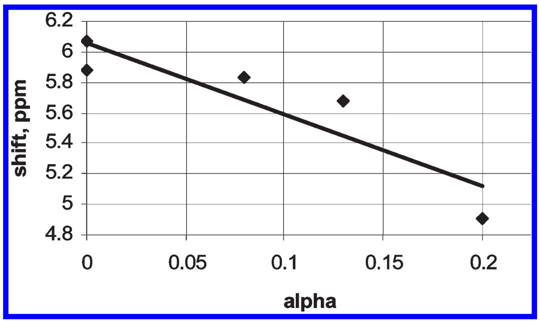

Figure 3. Plot of chemical shifts of highest field proton resonance of the SQ rings for $Ru(PPh_3)_2(SQ)_2$ versus the Kamlet–Taft solvent parameter α for the solvent (toluene (0), carbon tetrachloride (0), acetone (0.08), dichloromethane (0.13), chloroform (0.20)).

acetone (42.2), chloroform (39.1), and dichloromethane (41.1)), but do correlate reasonably well with the Kamlet–Taft solvent parameter α,[18] which is associated with the hydrogen bond donor ability of the solvent (Figure 3). The order of upfield shift of the 4,5-proton resonances for the $RuL_2(SQ)_2$ complexes, $L_2 = (PBu_3)_2 < (P(OMe)_3)_2 < (PPh_3)_2 < (PPh_3)(P(OPh)_3)$, does not correlate in any straightforward fashion with the sigma donor/pi acceptor properties of L. However, the broadness of the NMR resonances also depends on the semiquinone ligands, with the line width for the semiquinone aromatic proton resonances of *cis*-$Ru(PPh_3)_2(DBSQ)_2$ less than that for *cis*-$Ru(PPh_3)_2(SQ)_2$.

The reaction of anthragallol, $RuCl_2(PPh_3)_3$, and triethylamine produced a brown crystalline solid, characterized as *cis*-$Ru(PPh_3)_2(AGSQ)_2$, where AGSQ is the semiquinone derived from anthragallol (1,2,3-trihydroxyanthracene-9,10-dione). The FAB mass spectrum contains the molecular ion and a fragmentation pattern consistent with the composition $Ru(PPh_3)_2(AGSQ)_2$. The ^{1}H NMR spectrum contained unresolved aromatic proton resonances and four hydroxyl resonances suggesting a mixture of isomers. The AGSQ ligand most likely chelates through the 2- and 3-oxygens, as was shown previously for $Ru(PPh_3)_2(CO)_2(AG\text{-}2H)$ (AG-2H refers to the catecholate dianion derived from anthragallol).[19] In this coordination mode, as for *cis*-$Ru(PPh_3)_2(DBSQ)_2$, one would expect three possible isomers, two symmetrical with a single ^{31}P and hydroxyl proton resonance each and a single unsymmetrical isomer with two ^{31}P and two hydroxyl proton resonances. Consistent with this, the NMR spectrum displays very broad ^{31}P resonances at −40.9 (br), −45.6 (br), −66.4 (br), −69.2 (br) ppm, but these are far upfield from the resonances for *cis*-$Ru(PPh_3)_2(SQ)_2$, *cis*-$Ru(PPh_3)_2(3,4\text{-}O_2C_6H_2(5\text{-}OH)CO_2Me)_2$, and *cis*-$Ru(PPh_3)_2(DBSQ)_2$. This observation suggests a higher degree of residual paramagnetism for this complex. However, magnetic susceptibility measurements were unable to detect any paramagnetism at 300 K in the solid state. The Evans method was also unsuccessful for detecting paramagnetism of a saturated solution in dichloromethane, but the low solubility of the complex is problematic for this method.

The spectroscopic characterization of product as $Ru(PPh_3)_2(AGSQ)_2$ was ambiguous, particularly since the ^{31}P NMR resonances were unexpectedly broad and shifted upfield. To further support the identification of the product as $Ru(PPh_3)_2(AGSQ)_2$, a sample was heated at 70–80 °C in THF under 2 atm of carbon monoxide, yielding the known complex $Ru(PPh_3)_2(CO)_2(AG\text{-}2H)$[19] (74% yield after chromatography). This carbonylation product, in combination with the mass spectral data, supports the proposed ligand environment.

The cyclic voltammogram of $Ru(PPh_3)_2(AGSQ)_2$ displays two nearly reversible 1-e oxidations at +0.42 V (ΔE_p 60 mV) and −0.42 V (74 mV), a nearly reversible 1-e reduction at −1.15 V (ΔE_p 64 mV) and a nearly irreversible 1-e reduction at −1.8 V (ΔE_p 170 mV). This compares with two reversible oxidations (+0.41 and −0.045 V) and two reductions (−1.05 and −1.79 V) reported for $Ru(PPh_3)_2(DBSQ)_2$.

The unusual NMR behavior of these complexes prompted us to undertake a computational study to determine if a low-energy triplet state could account for the unexpected NMR behavior.

Our focus has been on the lowest triplet excitation energy to determine a trend among the series of complexes. Calculations were performed on *cis*-$Ru(PH_3)_2(SQ)_2$, *cis*-$Ru(PPh_3)_2(SQ)_2$, *cis*-$Ru(PMe_3)_2(SQ)_2$, *cis*-$Ru(P(OMe)_3)_2(SQ)_2$, and *cis*-$Ru(PMe_3)_2(DHAQ)_2$ (DHAQ = 2,3-oxo-1,4-dihydroxyanthracene-9,10-dione, chosen as a surrogate for $Ru(PPh_3)_2(AGSQ)_2$). For the vertical excitations, an analysis of the TDDFT density response vector showed that the lowest triplet excitation corresponds in all cases to a simple HOMO–LUMO transition (99% contribution to the transition density). We compared the TDDFT results to those obtained with a Δ-SCF approach to test for some potential shortcomings of the approximate exchange-correlation kernels applied[20] (in the present work we used the adiabatic local density approximation (ALDA)[21] kernel).

The calculations (both TDDFT and Δ-SCF) clearly demonstrate that the series of complexes has very low lying excited triplet states. Based on the C_2 point group of the complexes that was adopted in the computations, the calculated lowest triplet state is of B symmetry because of a HOMO (b-symmetry)-to-LUMO (a-symmetry) transition. The vertical triplet excited states (Table 1) are only 0.43 to 0.37 eV above the ground state (Δ-SCF data. For TDDFT we obtain 0.45 to 0.39 eV). The lowest singlet excited states are considerably higher, between 0.89 to 0.97 eV (Δ-SCF. In TDDFT: 0.95 to 1.25 eV). The agreement between Δ-SCF and TDDFT is quite reasonable, in particular for the triplet energies, which might be taken as an indication that the computations do not suffer substantial errors. Further details about the nature of the triplet states can be found in the Supporting Information. The molecular orbitals (MOs) indicate a significant interaction of the singly occupied semiquinone ligand orbitals with the metal center and with each other. The ground state is a closed shell singlet state in which the lower lying linear combination of the mainly ligand-centered singly occupied orbitals is doubly occupied. The lowest triplet state corresponds to the triplet diradical, with some involvement of the metal center, while the open shell singlet diradical electronic

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Table 1. Δ-SCF Vertical Triplet Excitation Energies for Model Complexes, and Some Experimental NMR Characteristics of the Full Systems

complex	calcd $E_T - E_G$ (eV) (vertical)	complex	δ for highest field 4,5-proton resonance ($CDCl_3$)
$Ru(PH_3)_2(SQ)_2$	0.430		
$Ru(PMe_3)_2(SQ)_2$	0.423	$Ru(PBu_3)_2(SQ)_2$	6.05, sharp ^{31}P resonances
$Ru(P(OMe)_3)_2(SQ)_2$	0.413	$Ru(P(OMe)_3)_2(SQ)_2$	5.53, sharp ^{31}P resonances
$Ru(PPh_3)_2(SQ)_2$	0.403	$Ru(PPh_3)_2(SQ)_2$	4.91, sharp ^{31}P resonances
$Ru(PMe_3)_2(DHAQ)_2$	0.369	$Ru(PPh_3)_2(AGSQ)_2$	NA − very broad ^{31}P resonances

structure as described by the lowest TDDFT and Δ-SCF excitations is significantly higher in energy.

The vertical singlet−triplet energy gap (Table 1) varies in a way consistent with the observed NMR behavior. The singlet−triplet gap decreases as $Ru(PH_3)_2(SQ)_2$ > $Ru(PMe_3)_2(SQ)_2$ > $Ru(P(OMe)_3)_2(SQ)_2$ > $Ru(PPh_3)_2(SQ)_2$ > $Ru(PMe_3)_2(DHAQ)_2$, and the NMR spectra suggest increasing paramagnetic effects as $Ru(PBu_3)_2(SQ)_2$ < $Ru(P(OMe)_3)_2(SQ)_2$ < $Ru(PPh_3)_2(SQ)_2$ < $Ru(PPh_3)_2(AGSQ)_2$.

We have subsequently optimized the geometries of the Δ-SCF triplet states and obtained considerable stabilization (Table 2). The optimized triplet states are now less than 0.2 eV above the ground state.

Discussion

Complexes containing two or more semiquinone ligands can display different magnetic properties, depending on the degree of electronic coupling between the ligands and between the ligands and unpaired electrons of the metal center.[22] For example, $Cr(Cl_4SQ)_3$ is paramagnetic at room temperature and the magnetic moment drops to near-zero at low temperature,[35] whereas $Cr(DBSQ)_3$ appears to be diamagnetic at room temperature but with residual paramagnetism causing broadening of the NMR resonances.[16]

Neutral complexes *cis*- and *trans*-$RuL_2(SQ)_2$, where L = nitrogen donor, phosphine, or CO, have been studied by several research groups. All complexes have been reported to be diamagnetic. The complexes $Ru(bpy)(SQ)_2$, and *trans*-$RuL_2(SQ)_2$, where L = nitrogen donor, were proposed to have a fully delocalized mixed-valence state best described as $Ru^{III}L_2$(catecholate)(semiquinone).[23−25] On the other hand *cis*-$Ru(CO)_2(3,6\text{-}DBSQ)_2$ and *cis*-$Ru(CO)_2(PhenoxSQ)_2$ were characterized as Ru^{II}(semiquinone)$_2$ redox states with antiferromagnetic coupling giving rise to diamagnetism and sharp NMR resonances.[26] The complexes $Ru(PPh_3)_2(SQ)_2$ were described as diamagnetic with redox states best regarded as Ru^{II}(semiquinone)$_2$.[2,3]

We propose that the unusual NMR spectral behavior of *cis*-RuL_2(semiquinone)$_2$ complexes is due to thermally accessible triplet states. The diamagnetism of the ground state arises from antiferromagnetic coupling of the semiquinone ligands, which are ferromagnetically coupled in the triplet state. The upfield shifts of the proton resonances as the temperature increases are explained by the greater triplet population at higher temperatures.

The magnetic and NMR spectral properties of Ni(II) complexes have previously been analyzed in terms of equilibria between diamagnetic, square planar and paramagnetic, tetrahedral species.[27] The temperature dependence of the chemical shifts was used to determine $\Delta G°$ for the singlet−triplet equilibrium and the hyperfine coupling constants in the paramagnetic complexes.

Table 2. Calculated Adiabatic Triplet Excitation Energies (eV)

	E(optimized triplet) − *E*(optimized singlet) (eV)
$Ru(PH_3)_2(SQ)_2$	0.163
$Ru(PMe_3)_2(SQ)_2$	0.132
$Ru(PPh_3)_2(SQ)_2$	0.147
$Ru(POMe_3)_2(SQ)_2$	0.170
$Ru(PMe_3)_2(DHAQ)_2$	0.159

In the triplet state the NMR resonances will be strongly affected by the electron spin, mainly because of the contact shift. If we consider only the contact hyperfine interaction, the contact shift δ^C is given by eq 1 below, where a is the isotropic hyperfine coupling constant, β and β_N are the Bohr and nuclear magnetons, respectively, g and g_N are the electronic and nuclear g-values, respectively, and $(2S+1)$ is the electronic spin multiplicity:[28,29]

$$\delta^{C} = \frac{g\beta}{g_N\beta_N}\frac{aS(S+1)}{3kT} \qquad (1)$$

The hyperfine coupling constants in semiquinone radical anions have been reported.[30,31] Although the values are somewhat dependent on the cation and solvent, typical values are about −0.5 G for the 3,6-hydrogens and −4 G for the 4,5-hydrogens. Since the unpaired electron spin density in the semiquinone radical is greater at the 4- and 5-positions than at the 3- and 6-positions, this accounts for the shorter T_1's for the 4- and 5-protons of the semiquinone ligands. The calculated contact shift the 4,5-H resonance of the triplet would be upfield by about 300 ppm at 300 K, assuming a hyper-fine coupling constant a of −4 G and S = 1/2 for a semiquinone radical anion. The observed shift for $Ru(PPh_3)_2(SQ)_2$ is upfield on the order of 1 ppm or less. If the observed shift is due to the population-weighted, exchange averaged shift of singlet and triplet, one can estimate that the

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equilibrium constant is about 3.3×10^{-3}, or the triplet state is about 14 kJ/mol higher in energy than the singlet state. This estimate is in good agreement with the optimized singlet-optimized triplet energy gap of 14.2 kJ/mol (0.147 eV).

The temperature dependence of the chemical shifts is thus due to both the temperature dependence of the contact shift (eq 1), which decreases with increasing temperature, and the equilibrium population of the triplet ($S = 1$, triply degenerate), which increases with temperature. Combining the two, the chemical shift is given by eq 2:[27,32]

$$\delta(\text{ppm}) = \delta_{\text{singlet}} + 10^6 \frac{g\beta_e}{g_N\beta_N}\frac{aS(S+1)}{kT}\{3+\exp((E_{\text{triplet}}-E_{\text{singlet}})/RT)\}^{-1} \quad (2)$$

where g is the electronic g value for the triplet (assumed to be 2), δ_{singlet} is the chemical shift (ppm) of the resonance in the singlet state, a is the hyperfine coupling constant (negative sign) for the unpaired electron with the proton in the triplet state, and ($E_{\text{triplet}} - E_{\text{singlet}}$) is the optimized singlet-optimized triplet energy gap (approximately equal to $\Delta G°$ since $\Delta V°$ and $\Delta S°$ should be small). The result is not linear with either temperature^{-1} or ln(temperature).

The theoretical calculations allow us to predict the chemical shifts for singlet states as 6.7−7.0 ppm for H_4 and H_5. Plots [1] and [2] in Figure 4 display the experimentally determined (in d_8-toluene) chemical shifts of the H_4 and H_5 proton resonances of *cis*-$Ru(PPh_3)_2(SQ)_2$, with the curves representing the best fits to eq 2, with a, ($E_{\text{triplet}} - E_{\text{singlet}}$), and the value of the singlet chemical shift as adjustable parameters. The best fits give $\delta_{\text{singlet}} = 6.94(0.02)$ and 6.90(0.02) ppm, ($E_{\text{triplet}} - E_{\text{singlet}}$) = 17.5(0.3) and 18.0(0.5) kJ/mol and $a = -1.7(0.2)$ and $-1.5(0.2)$ G (error limits are one standard deviation). Additional calculations were performed which estimated the hyperfine coupling constants for the 4- and 5-H nuclei in the triplet states of the complexes as −0.8 to −1.3 G (−2.2 to −3.6 MHz). The calculated curves are clearly consistent with the observed data, and the best-fit parameters for ($E_{\text{triplet}} - E_{\text{singlet}}$) and a are in good agreement with the theoretically calculated values. Of course, chemical shifts in clearly diamagnetic species are subject to solvent and temperature variations, but the NMR behavior observed for these complexes is best explained by exchange between diamagnetic and paramagnetic complexes.[33] The singlet−triplet energy gap appears to be affected by the phosphine ligand, by the semiquinone ring substituents, and by hydrogen bond donor solvents.

The solvent effects suggest that the triplet state is stabilized relative to the ground state by hydrogen bonding.[34] Hydrogen bonding between the solvent and the oxygen atoms of the semiquinone ligands might shift electron density away from the metal onto the semiquinone rings, stabilizing the triplet state which may have greater electron localization in the semiquinone rings, compared to the singlet state. The fact that the chemical shift of the most upfield ring proton resonance is about the same in 15% d_4-methanol/85% d_2-dichloromethane and in 30% d_4-methanol/70% d_2-dichloromethane suggests that saturation of the hydrogen bonding is achieved in the former solvent mixture and perhaps in deuteriochloroform since the chemical shift in that solvent is almost the same.

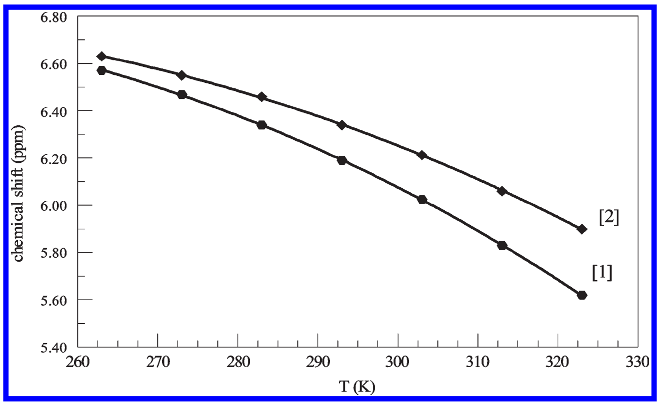

Figure 4. Temperature dependence of chemical shifts of protons at 4- and 5-positions (curves [1] and [2]) of the SQ rings for $Ru(PPh_3)_2(SQ)_2$ in d_8-toluene.

The degree of antiferromagnetic coupling also depends on the semiquinone ligands. Qualitatively, the NMR spectra suggest that the contribution of the triplet state increases in the series DBSQ < SQ < AGSQ. This observation is consistent with the semiquinone ligand dependence of the magnetic properties of $Fe(SQ)_3$ complexes.[35] Strong antiferromagnetic exchange interaction between the SQ-based unpaired electrons and the Fe^{III} unpaired d electrons would create a triplet ground state with two unpaired electrons. Weak exchange interaction gives rise to thermally accessible excited states of higher spin multiplicity. Thus, the magnetic moments of these complexes are temperature- and ligand dependent. A study of the magnetic susceptibility of Fe (semiquinone)$_3$ found the relative degree of intramolecular antiferromagnetic coupling to decrease as 3,5-DBSQ > Cl_4SQ > phenSQ; this trend was attributed to reduction of unpaired electron density on the oxygens (because of electron withdrawing ring substituents or increased delocalization in a larger aromatic ring), causing reduced antiferromagnetic interaction between the ligands through the metal bridge. The same argument can be made for $Ru(PPh_3)_2$(semiquinone)$_2$.

Finally, the singlet−triplet equilibrium also depends on the phosphine ligands. The order of upfield shift of the 4,5-proton resonances for the *cis*-$RuL_2(SQ)_2$ complexes, L_2 = $(PBu_3)_2$ < $(P(OMe)_3)_2$ < $(PPh_3)_2$ < $(PPh_3)(P(OPh)_3)$ does not correlate in any straightforward fashion with the sigma donor/pi acceptor properties of L since the order of sigma donor/pi capability decreases in the series PBu_3 > PPh_3 > $P(OMe)_3$. However, the calculated vertical singlet−triplet energy gap decreases slightly as $Ru(PMe_3)_2(SQ)_2$ > $Ru(P(OMe)_3)_2(SQ)_2$ > $Ru(PPh_3)_2(SQ)_2$; the optimized singlet-optimized triplet gaps are all small, and the small differences in energies for the various complexes may already

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(32) Some previous analyses (ref 27) of NMR shifts due to diamagnetic-paramagnetic equilibria replace the isotropic hyperfine coupling constant a with a/2S. Equation (2) is as used in ref 27(g).

(33) Indeed, analysis of the published[16] temperature dependence of chemical shift data for $Pd(DBSQ)_2$ according to eq 2 gives a much superior fit to the data (see Supporting Information) than does a fit to inverse temperature.

(34) Hyperfine coupling constants are also affected by solvent but the variations are not large.

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be exceeding the accuracy limits of the calculations. Differential solvation may be a factor accounting for the differences among these complexes.

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Supporting Information Available: Computational results. Variable temperature ^{1}H NMR spectra of *cis*-Ru(PPh_3)$_2$(SQ)$_2$ in d_8-toluene between −10 and +50 °C. Details for fitting the temperature dependence of the chemical shifts to eq 2 and analysis of the published[16] temperature dependence of chemical shift data for Pd(DBSQ)$_2$. This material is available free of charge via the Internet at http://pubs.acs.org.