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Evaluation of the $Rh^{(II)}-Rh^{(II)}$ Bond Dissociation Enthalpy for $[(TMTAA)Rh]_2$ by ^1H NMR T_2 Measurements: Application in Determining the Rh–C(O)– BDE in $[(TMTAA)Rh]_2C{=}O$

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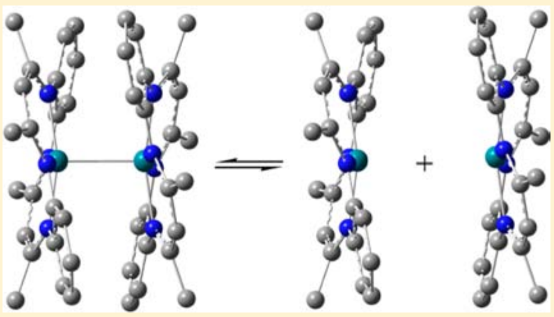
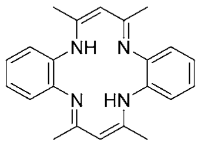
Supporting Information

ABSTRACT: Toluene solutions of the rhodium(II) dimer of dibenzotetramethylaza[14]annulene ($[(TMTAA)Rh]_2$; (**1**)) manifest an increase in the line widths for the singlet methine and methyl ^1H NMR resonances with increasing temperature that result from the rate of dissociation of the diamagnetic $Rh^{II}-Rh^{II}$ bonded dimer (**1**) dissociating into paramagnetic Rh^{II} monomers (TMTAA) Rh (**2**). Temperature dependence of the rates of $Rh^{II}-Rh^{II}$ dissociation give the activation parameters for bond homolysis $\Delta H^{\ddagger}_{app}$ = 24(1) kcal mol^{-1} and $\Delta S^{\ddagger}_{app}$ = 10 (1) cal K^{-1} mol^{-1} and an estimate for the $Rh^{II}-Rh^{II}$ bond dissociation enthalpy (BDE) of 22 kcal mol^{-1}. Thermodynamic values for reaction of **1** with CO to form (TMTAA)Rh–C(O)–Rh(TMTAA) (**3**) $\Delta H_1°$ = −14 (1) kcal mol^{-1}, $\Delta S_1°$= −30(3) cal K^{-1} mol^{-1}) were used in deriving a (TMTAA)Rh–C(O)– BDE of 53 kcal mol^{-1}.

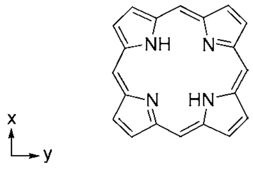


INTRODUCTION

The macrocyclic ligand dibenzotetramethylaza[14] annulene (TMTAA)[1−4] is an easily prepared low cost macrocycle that coordinates as a dianion (N_4^{-2}) that may provide a substitute for porphyrin ligands for applications that require relatively large quantities of materials. The wide scope of small molecule reactions and thermodynamic measurements available for rhodium porphyrin derivatives[5−19] make the rhodium complexes particularly useful for detailed comparative studies with the (TMTAA)Rh system.



dibenzotetramethylaza[14]annulene
(TMTAA)



Porphyrin
(POR)

The rhodium(II) derivative of TMTAA occurs as a $Rh^{(II)}$-$Rh^{(II)}$ bonded dimer ($[(TMTAA)Rh]_2$)[20] (**1**) which parallels rhodium(II) complexes of low steric demand porphyrins like octaethyl porphyrin that forms $[(OEP)Rh^{(II)}]_2$.[21] Evaluation of (TMTAA)Rh-X bond energies from equilibria for substrate reaction of **1** require knowledge of the $Rh^{(II)}$-$Rh^{(II)}$ bond dissociation enthalpy (BDE) to form the paramagnetic $(TMTAA)Rh^{(II)}$ (**2**) (eq 1). Compound **1** has been observed to react in benzene, toluene, and tetrahydrofuran (THF) with small molecule substrates including H_2, CO, and $CH_2{=}CH_2$ to produce hydride, formyl, and alkyl complexes,[22,23] but equilibrium thermodynamics have at present only been evaluated for the net insertion of CO into the Rh–Rh bond of **1** (eq 2) to form an unsupported dimetal ketone complex $[(TMTAA)Rh]_2C{=}O$ (**3**) ($\Delta H_2°_{(app)}$ = −14(1) kcal mol^{-1} and $\Delta S_2°_{(app)}$ = −30(2) cal K^{-1} mol^{-1}).[23] Compound **3** is very unusual because carbon monoxide is reduced to a carbonyl (C═O) unit by Rh–C σ bonding with two $(TMTAA)Rh^{(II)}$ units to give an organometallic analogue of an organic ketone.[24−29]

$$[(TMTAA)Rh]_2 \rightleftharpoons 2(TMTAA)Rh\cdot \qquad (1)$$

$$[(TMTAA)Rh]_2 + CO \rightleftharpoons (TMTAA)Rh{-}C(O){-}Rh(TMTAA) \qquad (2)$$

This article reports on evaluation of the $Rh^{(II)}$-$Rh^{(II)}$ bond dissociation energetics of **1** by analysis of the ^1H NMR line broadening for $[(TMTAA)Rh]_2$ and on using the $\Delta H_2°_{(app)}$ to derive the average (TMTAA)Rh–C(O)– BDE in $[(TMTAA)Rh]_2C{=}O$ (**3**).

RESULTS AND DISCUSSION

Activation parameters for the homolytic dissociation of $[(TMTAA)Rh]_2$ into paramagnetic monomers ($(TMTAA)Rh^{\bullet}$) were determined in toluene from the temperature dependence of the ^1H NMR line broadening which depends on the proton nuclear magnetic lifetime of the diamagnetic dimer (**1**). The ^1H NMR spectra for the singlet methine (C–H) and methyl (CH_3) groups of $[(TMTAA)Rh]_2$ in toluene-d_8

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solutions exhibit substantial broadening of the resonances as the temperature is elevated from 290 to 385 K (Figure 1, Supporting Information, Figure S1). Plots of the observed line width at half-maximum intensity ($\Delta\nu_{1/2\ (obs)}$; $T_2^{-1}{}_{(obs)} = \pi\Delta\nu_{1/2(obs)}$) for the methine and methyl hydrogen resonances of **1** as a function of temperature are illustrated in Figure 1 and Supporting Information, Figure S1. Measurement of rate constants for transverse nuclear relaxation ($k = T_2^{-1}{}_{(obs)} = \pi\Delta\nu_{1/2(obs)}$) for nuclei in a diamagnetic compound M-X that is exchanging with paramagnetic components M· and X· has been applied as an effective method to determine activation parameters for M-X bond homolysis[30−34] including the $\mathrm{Rh^{(II)}}$-$\mathrm{Rh^{(II)}}$ bond dissociation energetics for $[(\mathrm{OEP})\mathrm{Rh^{(II)}}]_2$.[35]

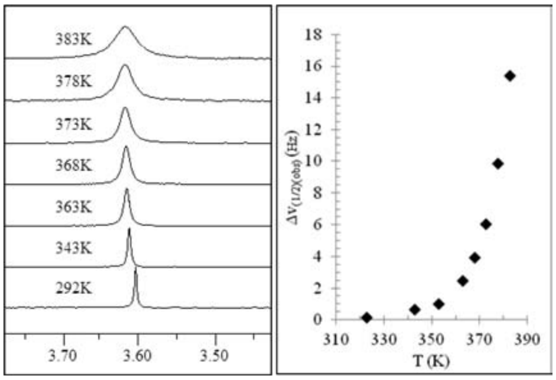

Figure 1. Temperature dependence of line width for methine proton in $[\mathrm{Rh(TMTAA)}]_2$.

The observed increase in the methine and methyl ^{1}H NMR line widths of **1** as the temperature is elevated is ascribed to the lifetime broadening that results from dissociation of diamagnetic $[(\mathrm{TMTAA})\mathrm{Rh}]_2$ to the paramagnetic ($S = 1/2$) $(\mathrm{TMTAA})\mathrm{Rh^{(II)\bullet}}$ monomers in the slow exchange regime and where the extent of dissociation is vanishingly small. The line width observed for this exchange situation is given as a sum of the natural line width and the line width from exchange ($\Delta\nu_{1/2\ (obs)} = \Delta\nu_{1/2(nat)} + \Delta\nu_{1/2(ex)}$). The full expression that describes this exchange case is given by eq 3 which reduces to $T_2^{-1} = \tau_d^{-1} = k_{(ex)(app)}$ for nuclei in paramagnetic species where the mean lifetime (τ_p) is relatively long and the electron−nuclear coupling constant (A) is sufficiently large such that $(A\tau_p/2)^2 \gg 1$.

$$\pi\Delta\nu_{1/2(ex)} = T_2^{-1} = \tau_d^{-1}[(A\tau_p/2)^2][1 + (A\tau_p/2)^2]^{-1} \tag{3}$$

When this condition is fulfilled each dissociation event that produces the paramagnetic monomer results in nuclear magnetic relaxation.[36−40] The apparent mean lifetime for the diamagnetic species (τ_d) that results from the observed T_2^{-1} yields the apparent rate constant ($\tau_d^{-1} = k_{app}$) for bond homolysis events that produce paramagnetic species with efficient nuclear relaxation ($(A\tau_p/2)^2 \gg 1$).

Bond homolysis that produces freely diffusing radicals in solution occurs through the intermediacy of solvent caged radical pairs (M-M ⇌ M··M ⇌ M·). The activation parameters to produce freely diffusing radicals are said to be apparent values ($\Delta H^\ddagger{}_{app}$, $\Delta S^\ddagger{}_{app}$) because they are composites of activation values for the fundamental steps of radical pair formation and separation.[41−43] The predominant contribution to $\Delta H^\ddagger{}_{app}$ is from the bond homolysis step that produces the radical pair. Apparent activation parameters for dissociation of $[(\mathrm{TMTAA})\mathrm{Rh}]_2$ (**1**) were obtained by application of transition state theory ($K^\ddagger = k_{app}(h/kT)$; $-RT \ln K^\ddagger{}_{app} = \Delta G^\ddagger{}_{app} = \Delta H^\ddagger{}_{app} - T\Delta S^\ddagger{}_{app}$)[14,15,35,41−43] Using a $\Delta\nu_{1/2\ (nat)}$ of 1.9 Hz for the methine hydrogen of **1** yields the apparent activation parameters of $\Delta H^\ddagger{}_{app} = 24(1)$ kcal mol^{-1} and $\Delta S^\ddagger{}_{app} = 10\ (1)$ cal K^{-1} mol^{-1} for homolytic dissociation of $[(\mathrm{TMTAA})\mathrm{Rh}]_2$ (**1**) (Figure 2). The corresponding analysis for the methyl resonance give comparable dissociation activation parameters (SI) ($\Delta H^\ddagger{}_{app}$) = 23(1) kcal mol^{-1}; $\Delta S^\ddagger{}_{app} = 8\ (1)$ cal K^{-1} mol^{-1}) (Supporting Information, Figure S2). Activation enthalpies for homolytic bond dissociation ($\Delta H^\ddagger{}_{app}$) in a low viscosity medium like toluene are about 2 kcal mol^{-1} larger than the BDEs ($\Delta H^\circ{}_{app}$)[41,42,44,45] which places the $\mathrm{Rh^{(II)}}$-$\mathrm{Rh^{(II)}}$ BDE in $[(\mathrm{TMTAA})\mathrm{Rh}]_2$ at ~22 kcal mol^{-1}. The observed positive activation entropy ($\Delta S^\ddagger{}_{app}$) is appropriate for a bond dissociation process, but $\Delta S^\ddagger{}_{app}$ (10 cal K^{-1} mol^{-1}) is substantially smaller than the expected $\Delta S^\circ{}_{app}$ which should be in the range of about 25−35 cal K^{-1} mol^{-1}. Activation entropies ($\Delta S^\ddagger{}_{app}$) are invariably less than the bond dissociation entropies ($\Delta S^\circ{}_{app}$)[30,33] and are not used in estimating thermodynamic $\Delta S^\circ{}_{app}$ values because the dissociating components can have highly variable freedom of motion in the transition state.

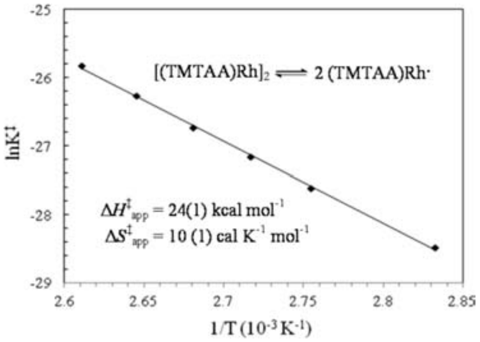

Figure 2. Determination of activation parameters for homolytic dissociation of $[\mathrm{Rh(TMTAA)}]_2$ in d_8-toluene by NMR line width measurements of the methine hydrogens.

Close agreement between activation parameters obtained from two independent ^{1}H NMR peaks in **1** provides confidence that the observed line broadening is associated with the homolytic dissociation of **1** into $(\mathrm{TMTAA})\mathrm{Rh^{(II)\bullet}}$ and that the limiting condition of $(A\tau_p/2)^2 \gg 1$ is fulfilled for both the methine and methyl hydrogens in $(\mathrm{TMTAA})\mathrm{Rh^{(II)\bullet}}$. The derived value of 22 kcal mol^{-1} for Rh−Rh BDE in $[(\mathrm{TMTAA})\mathrm{Rh}]_2$ is ~5 kcal mol^{-1} larger than the ~17 kcal mol^{-1} Rh−Rh BDE obtained by the same line broadening method for $[(\mathrm{OEP})\mathrm{Rh^{(II)}}]_2$.[35]

The structure of **1** was first reported by Cotton,[20] and a new high quality crystal structure detemination of this compound with a different lattice solvate has been obtained and shown in Figure 3. TMTAA metal complexes have a pronounced nonplanar saddle shape for the macrocyclic ligand that predominantly arises from steric interactions between the methyl groups and the benzenoid rings.[3,4] The $\mathrm{Rh^{(II)}}$-$\mathrm{Rh^{(II)}}$ (2.612 Å) and mean Rh−N (1.993 Å) internuclear distances along with the displacements of the Rh atoms from the least-squares-fitted $\mathrm{N_4}$ planes of the ligands by 0.2204 ± 0.0011 Å for Rh(1) and 0.2125 ± 0.0011 Å for Rh 2 are the most defining structural features. The distinct nonplanarity of TMTAA

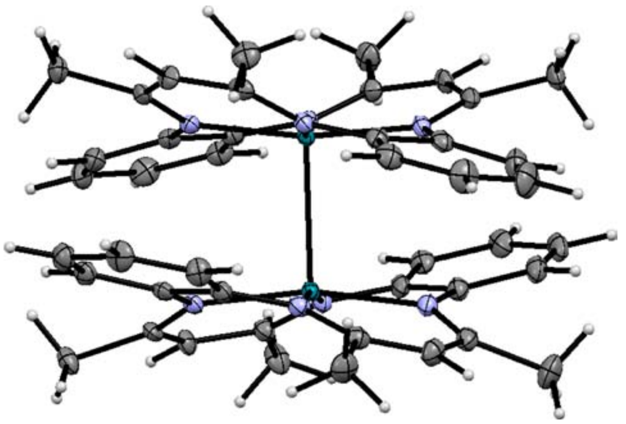

Figure 3. Structure of $[\text{Rh(TMTAA)}]_2$ with thermal ellipsoids shown on non-hydrogen atoms (50% probability level) and hydrogen atoms shown as open circles.[46].

contrasts with the near planar stuctures observed for porphyrin macrocycles and is a major contribution to reducing the importance of dπ to pπ interactions in TMTAA complexes relative to porphyrins.[4] Flexibility of the antiaromatic 16 π-electron macrocycle can also function to reduce unfavorable ligand steric effects.

Density functional theory (DFT) calculations (B3LYP, 3-21G)[47] were carried out for the $S = 1/2$ (TMTAA)Rh$^{(II)\bullet}$ and (POR)Rh$^{(II)\bullet}$ metallo radicals, and the computed atomic spin density (ρ) contours are illustrated in Figure 4. The DFT calculation (B3LYP, 3-21G) for (POR)Rh$^{(II)\bullet}$ places the unpaired electron in a relatively localized dz^2 molecular orbital (mo) which is in agreement with electron paramagnetic resonance (EPR)[48] of rhodium(II) porphyrin complexes where ligand steric demands prohibit Rh$^{(II)}$-Rh$^{(II)}$ bonding. Small positive spin density on the porphyrin methine and pyrrole hydrogens from direct participation in the dz^2 σ mo is consistent with the observed downfield contact shifts.[49,50] DFT calculations[47] for the (TMTAA)Rh$^{(II)\bullet}$ metallo radical in contrast with (POR)Rh$^{(II)\bullet}$ place the unpaired electron in a dπ (dxz) mo directed at the center of the 2,4-pentane diiminato chelate rings (Figure 4A). Reduced dπ to pπ interactions in (TMTAA)Rh$^{(II)}$ have a major influence on the relatively higher energy position of the dxz mo relative to that for rhodium(II) porphyrins.

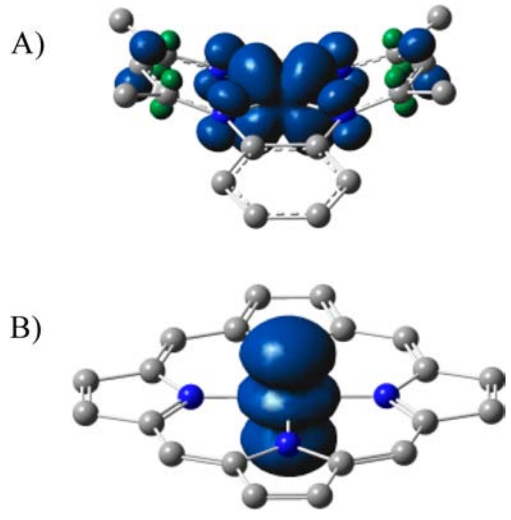

Figure 4. Atomic spin density (ρ) distributions from DFT calculations for ($S = 1/2$) (A) (TMTAA)Rh$^\bullet$ and B) (POR)Rh$^\bullet$ (Positive ρ is blue and negative ρ is green).

The unpaired electron in the dxz mo of (TMTAA)Rh$^{(II)\bullet}$ is much more highly delocalized on to the ligand 2,4-pentane diiminato units than the dz^2 σ of (POR)Rh$^{(II)\bullet}$. Placement of the unpaired electron in the dxz molecular orbital of (TMTAA)Rh$^{(II)\bullet}$ is supported by the observation that both the methine and methyl hydrogens have large enough hydrogen coupling constants (A_H) to fulfill the$(A_H \tau_p/2)^2 \gg 1$ criterion. The DFT calculated methine carbon pπ spin density of +0.048 corresponds to an A_H (C−H) = −3.1 MHz and the C−CH$_3$ pπ spin density of −0.024 gives an A_H(C−CH$_3$) = −2.05 MHz from the McConnell carbon pπ spin density relationships.[51−53] The calculated proton coupling constants from DFT calculations are large enough to fullfil the observation that $(A_H\tau_p/2)^2 \gg 1$ for both the methine and the methyl hydrogens of (TMTAA)Rh$^{(II)\bullet}$. The expectation that the unpaired electron ($S = 1/2$) for (TMTAA)Rh$^{(II)}$ is in the dxz rhodium-centered mo provides the clear prediction that upfield contact shifts from negative proton spin densities will be observed for both the methine and the methyl hydrogens if sterics from substituents on the tetraaza[14] annulene macrocycle framework can be used to produce stable rhodium(II) metallo radical derivatives.

Evaluating the Average Rh−C(O)− BDE in (TMTAA)-Rh−C(O)−Rh(TMTAA). Solutions of [(TMTAA)Rh]$_2$ (**1**) (1 × 10^{-3} M) in rigorously dried and degassed toluene-d$_8$ in vacuum adapted NMR tubes were pressurized with CO (0.1−0.7 atm) resulting in formation of a dirhodium ketone (TMTAA)Rh−C(O)−Rh(TMTAA) (**3**) (eq 2) in equilibrium with **1** and CO. Integration of the ^{1}H NMR for **1** and **3** in conjunction with the pressure and temperature dependencies of the CO concentration[23] allowed evaluation of equilibrium constants for reaction 2. The thermodynamic values for reaction 2 in toluene ($K(298) = 6.1 \times 10^3$; $\Delta G^\circ_2 = -5.2$ kcal mol^{-1}; $\Delta H^\circ_2 = -14(1)$ kcal mol^{-1}) are close to the values previously reported in reaction 2 in benzene ($\Delta G^\circ = -5.0$ kcal mol^{-1}; $\Delta H^\circ = -14(1)$ kcal mol^{-1}).[23]

The enthalpy change for reaction 2 can be expressed as a set of BDEs (eq 4). Evaluating eq 4 with ΔH°_2 (−14(1) kcal mol^{-1}), (Rh−Rh) (22 kcal mol^{-1}) and (C≡O − C=O) (+70 kcal mol^{-1})[14] permits deriving a a value of 53 kcal mol^{-1} for the average Rh−C(O)− BDE in the dimetal ketone (**3**).

$$\Delta H^\circ_2 = (\text{Rh–Rh}) + (\text{C}{\equiv}\text{O–C}{=}\text{O}) - 2(\text{Rh–C(O)–}) \tag{4}$$

The (TMTAA)Rh−C(O)− BDE of 53 kcal mol^{-1} compares to a (OEP)Rh−C(O)− value of 49 kcal mol^{-1}.[14] The bent (L)Rh−C(O)−Rh(L) unit is sensitive to the steric demands of the ligands (L), and interporphyrin repulsions for the rigid macrocycle prohibit achieving the maximum Rh−C(O)− bond energy. The smaller and more flexible antiaromatic TMTAA ligand permits structural changes for **3** that reduce interligand repulsions and increase the Rh−C(O)− BDE in **3** relative to aromatic porphyrin derivatives. Enhanced reactivity of transition metal TMTAA complexes compared to porphyrin derivatives may be a general consequence of the smaller size and higher flexibility of the antiaromatic TMTAA macrocycle compared to the more rigidly planar aromatic porphyrins.

[(OEP)Rh]$_2$ and other (POR)Rh$^{(II)}$ derivatives react with CO to produce equilibrium distributions of both dirhodium ketone (POR)Rh−C(O)−Rh(POR) and CO reductively coupled 1,2 ethanedionyl species (POR)Rh−C(O)−C(O)−Rh(POR).[14,54−57] Thermodynamically favorable CO reductive coupling is driven by relief of steric strain in the bent Rh−C(O)−Rh unit of the dimetal ketone which is relieved in the Rh−C(O)−C(O)−Rh unit.[14] Porphyrins with steric demands larger than OEP thermodynamically favor the 1,2 ethanedionyl bridged complexes, (POR)Rh−C(O)−C(O)−Rh(POR)[21,22] even at low CO pressures. Exclusive observation of the dirhodium ketone in the (TMTAA)Rh system at one atmosphere of CO pressure is a consequence of the relatively small steric demands of TMTAA and the associated higher relative stability of the dimetal ketone. Introduction of more sterically demanding groups on the dibenzoaza[14]annulene macrocycle ring can be expected to destabilize the bent dirhodium ketone and produce the CO reductively coupled dirhodium diketone complex (L)Rh−C(O)−C(O)−Rh(L). Design and preparation of sterically encumbered dibenzoaza[14] annulene macrocycle rings are in progress to determine experimentally the ground electron configuration of the Rh(II) derivatives and to test the anticipated capability to achieve CO reductive coupling.

ASSOCIATED CONTENT

Supporting Information

Crystallographic data in CIF format. Further details on $[(TMTAA)Rh]_2$ are given in Figures S1−S4 and Tables 1 to 6. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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