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Reduction of Carbon Monoxide by $[(TMTAA)Rh]_2$ To Form a Dimetal Ketone Complex

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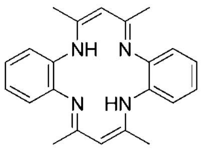
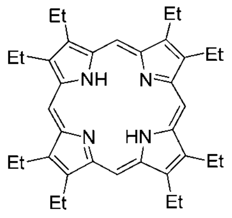
Supporting Information

ABSTRACT: Benzene solutions of $[(TMTAA)Rh]_2$ (**1**) react with CO (P_{CO} = 0.8−20 atm; T = 298 K) by cleaving the $Rh^{II}-Rh^{II}$ bond to form dirhodium(III) ketone (TMTAA)Rh−C(O)−Rh(TMTAA) [**2**; ν_{CO} = 1726 cm^{-1}; $^1J^{103}Rh^{13}C(O)^{103}Rh$ = 45 Hz]. Thermodynamic values for the reaction of **1** with CO to form **2** were evaluated from equilibrium constant measurements [K_1(298 K) = 5.0(0.6) × 10^3, $\Delta G_1°$(298 K) = −5.0(0.1) kcal mol^{-1}, $\Delta H_1°$ = −14(1) kcal mol^{-1}, and $\Delta S_1°$ = −30(3) cal K^{-1} mol^{-1}].

The resurgence of interest in the activation and transformation of carbon monoxide (CO)[1−5] is motivated by the inevitable transition to the utilization of synthesis gas (CO/H_2) from coal and biomass to replace petroleum for chemical feedstocks and liquid fuels.[6−10] The formation of dimetal ketone species [M−C(O)−M][11,12] by two one-electron reductions of CO at metal centers is an unusual form of CO activation that is an underinvestigated pathway for CO activation. The bridging CO unit in dimetal ketone species is clearly distinguished from the type of bridging carbonyl group that is supported by metal−metal bonds that occur in complexes such as $Co_2(CO)_8$ and $[CpFe(CO)_2]_2$.[13] Transition-metal complexes that contain a ketone-like bridging CO unit are unusual, but examples are known for second and third transition series "A-frame" complexes[14−20] and tetradentate N_4 and N_2O_2 ligand complexes of rhodium,[21−26] and are implicated in the all-iron hydrogenases.[27] The best known examples of dimetal ketones that are unsupported by either M−M bonds or bridging ligands are formed by rhodium porphyrins such as octaethylporphyrin [(OEP)Rh−C(O)−Rh(OEP)].[21] This article reports on the use of the smaller and more flexible TMTAA (dibenzotetramethylaza[14]annulene)[28−30] macrocycle as an alternative to porphyrins in forming a dirhodium ketone complex.



dibenzotetramethylaza[14]annulene
TMTAA



octaethylporphyrin
OEP

Benzene solutions of $[(TMTAA)Rh]_2$ (**1**)[30,31] when water is rigorously excluded react with CO (P_{CO} = 0.8−20 atm; T = 298 K) in vacuum-adapted thick-walled NMR tubes by cleaving the Rh−Rh bond to form a dimetal ketone (TMTAA)Rh−C(O)−Rh(TMTAA) (**2**) as the exclusive product detected by ^{1}H NMR (eq 1).

$$[(TMTAA)Rh]_2 + CO \rightleftharpoons (TMTAA)Rh{-}C(O){-}Rh(TMTAA) \qquad (1)$$

The dirhodium ketone is observed to be highly sensitive to photolysis in laboratory light, and all studies of **2** were carried out with exclusion of visible and UV light. Solution IR spectra for **2** show a CO stretching frequency similar to that of organic ketones at 1726 cm^{-1}, which disappears when CO is removed under vacuum. Compound **2** is thus viewed as a dirhodium(III) complex of a doubly reduced bridging CO unit in analogy with organic ketones.

The reaction of the emerald green $Rh^{II}-Rh^{II}$-bonded dimer **1** with CO to form the dirhodium(III) carbonyl **2** results in a striking color change to burgundy red. The green color of **1** results from the band centered in the red region at 650 nm that is assigned to transitions from the M−M bond and ligand molecular orbitals that terminate in the M−M σ^*. The reaction of **1** with CO results in the disappearance of this band, which signals cleavage of the $Rh^{II}-Rh^{II}$ bond (Figure 1a,b). ^{13}C NMR for the ^{13}CO derivative of **2** in benzene has a triplet resonance at δ = 159.2 ppm (Figure 1c). The 1:2:1 triplet arises from coupling of the ^{13}CO with 2 equiv of ^{103}Rh ($^1J^{103}{}_{Rh-}{}^{13}{}_{C}$ = 45 Hz), which clearly identifies the dirhodium ketone **2** (Figure 1c, inset). A $^1J^{103}{}_{Rh-}{}^{13}{}_{C}$ coupling constant of 45 Hz in **2** is consistent with an sp^2-hybridized carbonyl carbon based on a $^1J^{103}{}_{Rh-}{}^{13}{}_{C}$ of 35 Hz for the sp^3-hybridized CH_3 complex $(TMTAA)Rh{-}^{13}CH_3$.

The distribution of **1**, **2**, and CO in solution is accurately fitted to the 1:1 equilibrium described by eq 1. Thermodynamic values to form the dirhodium ketone **2** by reaction (1) were evaluated from equilibrium constant measurements at a series of temperatures [T = 290−320 K; K_1(298 K) = 5.0(0.6) × 10^3, $\Delta G_1°$(298 K) = −5.0(0.1) kcal mol^{-1}, $\Delta H_1°$ = −14(1) kcal mol^{-1}, and $\Delta S_1°$ = −30(3) cal K^{-1} mol^{-1}; Figure 2).

TMTAA and porphyrins are related as ligands through coordination with metals as tetradentate dianions (N_4^{-2}). Porphyrins are near-planar aromatic 18π-electron rings, but

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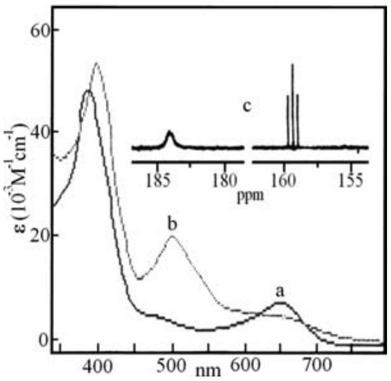

Figure 1. Electronic spectra in benzene for (a) 5×10^{-5} M **1** and (b) $[(TMTAA)Rh]_2$ + CO (P_{CO} = 0.9 atm). (c) ^{13}C NMR of $[(TMTAA)Rh]_2$ with 0.8 atm of ^{13}CO in C_6D_6 [$\delta(^{13}CO)$ = 184 ppm; $\delta(^{13}CRh-^{13}C(O)-Rh)$ = 159.2 ppm; $^1J(^{103}Rh^{13}C(O)^{103}Rh)$ = 45 Hz].

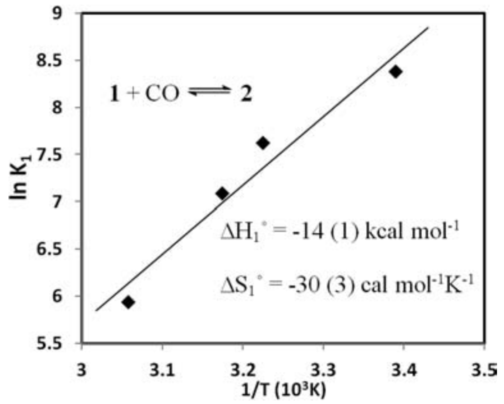

Figure 2. van't Hoff plot for reaction (1). P_{CO}(295 K) = 152 Torr, K_1(298 K) = 5.0×10^3, $\Delta G_1°$ = −5.0 kcal mol^{-1}, $\Delta H_1°$ = −14(1) kcal mol^{-1}, and $\Delta S_1°$ = −30(3) cal K^{-1} mol^{-1}.

TMTAA is a 16π-electron antiaromatic macrocycle with a structure that is more flexible. The structural flexibility lowers the steric demands of TMTAA compared to the more rigid porphyrins, which is reflected by the shorter $Rh^{II}-Rh^{II}$ distance of 2.62 Å in **1**[30] compared to 2.81 Å in the rhodium octaethylporphyrin dimer ($[(OEP)Rh]_2$).[32] A stronger Rh−Rh bond in **1** compared to $[(OEP)Rh]_2$ is indicated by the absence of ^1H NMR line broadening from bond homolysis up to 370 K and the inability to observe a reaction with H_2 (P_{H_2} = 1 atm) in benzene, which are prominent features of $[(OEP)Rh]_2$ chemistry.[33,34] These observations place a lower limit of 20 kcal mol^{-1} on the Rh−Rh bond dissociation energy (BDE) in **1** compared to ∼17 kcal mol^{-1} in $[(OEP)Rh]_2$. The $\Delta G_1°$ value of −5.0 kcal mol^{-1} for insertion of CO into the Rh−Rh bond of **1** is more favorable than the corresponding reaction for $[(OEP)Rh]_2$ (−2.8 kcal mol^{-1}),[21] even though the Rh−Rh bond is stronger in **1**, which indicates that (TMTAA)Rh−C(O) bonding is stronger than that for the (OEP)Rh−C(O) unit. The enthalpy change for the general reaction of a M−M-bonded dimer with CO to form a dimetal ketone (eq 2) is given by eq 3. Evaluating eq 3 for reaction (1) using $\Delta H_1°$ = −14 kcal mol^{-1}, (C≡O)−(C═O)[21] = 70 kcal mol^{-1}, and a lower limit of 20 kcal mol^{-1} for the Rh−Rh BDE in **1** gives a lower limit for the (TMTAA)Rh−C(O) BDE of 54 kcal mol^{-1}, which is substantially larger than the (OEP)Rh−C(O) value of 49 kcal mol^{-1}.[21] 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 Rh−C(O)−Rh angle needed to maximize the (OEP)Rh−C(O) BDE.[21] The smaller more flexible TMTAA ligand allows structural adjustments for **2** that allow one to approach closer to the optimum Rh−C(O) BDE in **2**.

$$\mathrm{M{-}M + CO \rightleftharpoons M{-}C(O){-}M} \tag{2}$$

$$\Delta H_5° = (\mathrm{M{-}M}) + (\mathrm{C{\equiv}O}) - (\mathrm{C{=}O}) \\ - 2(\mathrm{M{-}C(O)-}) \tag{3}$$

The reaction of $[(OEP)Rh]_2$ with CO produces an equilibrium distribution of dimetal ketone (OEP)Rh−C(O)−Rh(OEP) similar to that of **1** but also forms a 1,2-ethanedionyl complex (OEP)Rh−C(O)−C(O)−Rh(OEP). Thermodynamically favorable CO reductive coupling is driven by relief of the steric strain in the dimetal ketone, and porphyrins with steric demands larger than those of OEP thermodynamically favor the 1,2-ethanedionyl-bridged complexes, (por)Rh−C(O)−C(O)−Rh(por).[21,22] Exclusive formation of the dirhodium ketone in the (TMTAA)Rh system results from the smaller TMTAA steric demands and the associated higher stability of the dimetal ketone. These results are fully consistent with the expectations of the thermodynamic analysis for CO reduction and coupling observed for rhodium porphyrins.[21] The 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.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Solution spectra and equilibrium measurements. 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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