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Schiff Base Complexes of Rhodium Containing Alkyl, Hydride, and Formyl Ligands

D. Joe Anderson and Richard Eisenberg*

Department of Chemistry, University of Rochester, Rochester, New York 14627

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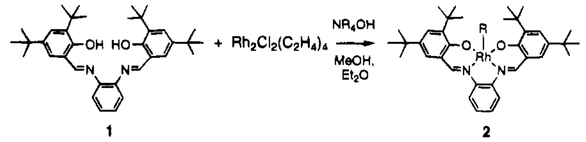
Studies by Wayland and co-workers on the chemistry of rhodium(II) porphyrin systems over the past decade have shown that these systems react readily with a variety of substrates including CO, H_2, olefins, isocyanides, methane and alkylarenes.[1,2] The key to the reactivity of these systems lies in their "metalloradical" character.[3−5] The chemistry of the d^7 Rh(II) porphyrin systems, including the activation of methane,[6,7] has stimulated us to examine the behavior of other Rh(II) complexes with different chelating ligands. While organometallic rhodium complexes with tetradentate Schiff bases are known,[8−11] relatively little has been published of their reactivity. In the present study, we describe the reaction chemistry of Rh Schiff base complexes based on the Bu_4salophen ligand (**1**) including the formation of square pyramidal Rh(III) alkyl and hydride complexes, and conversion of the latter via Rh(II) into the corresponding formyl complex upon reaction with CO.

Reaction of the free ligand Bu_4salophenH_2 (155 mg, 0.4 mmol)[12,13] with di-μ-chlorotetrakis(ethylene)dirhodium (436 mg, 0.8 mmol) in the presence of $(NR_4)OH$ (4 mL of 1.0 M methanol solution, 4 mmol) in refluxing methanol (4 h) produces a dark purple precipitate, **2**, which varies slightly with the tetraalkylammonium hydroxide employed as shown in eq 1 (for R = *n*-Bu: 191 mg, 0.27 mmol, 34% yield). For **2a** (R = Et), the ^{1}H NMR spectrum exhibits a quartet of doublets and a triplet of doublets, consistent with a rhodium-bound ethyl group, as well as the resonances characteristic of coordinated Bu_4-salophen.[14] For **2b** (R = *n*-Bu), analytically pure compound is obtained as dark purple crystals suitable for X-ray study.[15] The structure of **2b** is shown in Figure 1 and establishes that **2** is a square pyramidal Rh(III) alkyl complex with an essentially planar Bu_4salophen ligand occupying the basal sites and the *n*-butyl group in the apical position.[16] The Rh−C(butyl) distance of 2.04 (1) Å is slightly but significantly shorter than other Rh−alkyl C distances reported due in part to the absence of a trans ligand.[17]



1 **2**

(1)

Benzene solutions of **2** are stable for days in the dark. However, upon photolysis with $\lambda > 475$ nm, a red-brown solution is generated that exhibits a broad NMR spectrum and an ESR signal at ambient temperature.[18] The ESR signal diminishes upon addition of H_2. When photolysis is carried out under H_2, the solution turns bright red and exhibits a doublet at δ −25.77 ppm (J_{Rh-H} = 51 Hz) indicative of a rhodium hydride species.[19] For **2a** (R = Et), the photolysis under H_2 also leads to NMR observation of the singlet characteristic of C_2H_6 (δ 0.798 ppm), while for **2b** (R = *n*-Bu), butane is detected by GC/mass spectrometry of the volatiles of the reaction. The hydride species may also be produced by subsequent addition of H_2 to the red-brown solution produced by photolyzing **2**. Application of vacuum to the bright red hydride solution leads to regeneration of the darker red-brown color, the broad NMR spectrum and the ESR signal. Addition of H_2 returns the solution to that of the diamagnetic hydride species. Alternatively, the hydride species can be produced by heating a photolyzed sample of **2** with excess triethylsilane in THF-d_8. When a benzene solution of the hydride species is placed under D_2, the only observed spectral changes are disappearance of the hydride resonance and emergence of a 1:1:1 triplet at δ 4.42 ppm (J_{H-D} = 43 Hz) characteristic of HD. These results are consistent with the photolysis of RhR(Bu_4salophen), **2**, leading to Rh−alkyl bond homolysis and generation of d^7 Rh^{II}(Bu_4-

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(14) Selected ^{1}H NMR data for **2a**: 8.35 (d, J_{Rh-H} = 1.9 Hz, 2H, -N=C*H*-); 7.87, 7.32 (d, 4H, -$C_6H_2(C(CH_3)_3)_2$-); 7.10, 6.85 (dd, $^3J_{H-H}$ = 6.2 Hz, $^4J_{H-H}$ = 3.3 Hz 2H, -NC_6H_4N-); 2.37 (qd, 2H, $RhCH_2$-CH_3, $^2J_{Rh-H}$ = 3.2 Hz,$^3J_{H-H}$ = 7.4 Hz); 1.98, 1.46 (s, 36H, -$C(CH_3)_3$); 0.23 (td, 3H, $RhCH_2CH_3$, $^3J_{Rh-H}$ = 1.1 Hz,$^3J_{H-H}$ = 7.4 Hz).

(15) Anal. Calcd for $C_{40}H_{55}N_2O_2Rh$: C, 68.75; H, 7.93; N, 4.01. Found: C, 68.28; H, 7.80; N, 3.80. Selected ^{1}H NMR data for **2b**: 8.40 (d, J_{Rh-H} = 1.9 Hz, 2H, -N=C*H*-); 7.86, 7.33 (d, J_{H-H} = 2.4 Hz, 4H, -$C_6H_2(C(CH_3)_3)_2$); 6.86 (dd, $^3J_{H-H}$ = 6.2 Hz, $^4J_{H-H}$ = 3.2 Hz, 2H, -NC_6H_4N-); 2.36 (m, 2H, $RhCH_2CH_2CH_2CH_3$); 1.99, 1.45 (s, 36H, -$C(CH_3)_3$); 0.90 (m, 2H, $RhCH_2CH_2CH_2CH_3$); 0.44 (t, J_{H-H} = 7.0 Hz, 2H, $RhCH_2CH_2CH_2CH_3$).

(16) Crystal data: ($RhC_{40}H_{55}N_2O_2$), dark purple, dimensions (0.16 × 0.4 × 0.5 mm^3), M = 698.79, monoclinic, space group $P2_1/a$ (No. 14); a = 12.031(8), b = 25.540(5), c = 12.78(1) Å, β = 97.05(3)°, V = 3896(4) $Å^3$, T = 268 K, Z = 4, D_c = 1.191 g cm^{-1}, μ(Mo Kα) = 4.62 cm^{-1}, $F(000)$ = 1480. Disorder in the methylene carbon atoms β and γ (C38 and C39) to the rhodium atom was modeled over two sites. All non-hydrogen atoms were refined anisotropically, except for the *n*-butyl carbon atoms. Of 4873 ($4° < 2\theta < 44°$) unique data collected on an Enraf-Nonius CAD4, 2604 independent reflections ($F > 3\sigma(F)$) were used for least-squares refinement to R = 0.0624, R_w = 0.0754, and GOF = 2.091.

(17) This comparison is based on a survey of $Rh-CH_2-CH_2$- distances from the Cambridge Crystallographic Database. Seven relevant structures were identified, yielding nine Rh−C(sp^3) distances averaging 2.105 Å. Allen, F. H.; Davies, J. E.; Galloy, J. J.; Johnson, O.; Kennard, O.; Macrae, C. F.; Mitchell, E. M.; Mitchell, G. F.; Smith, J. M.; Watson, D. G. *J. Chem. Inf. Comp. Sci.* **1991**, *31*, 187−204.

(18) Benzene (108 K): g_{11} = 2.862, g_{22} = 2.030, g_{33} = 1.993; g_{iso} = 2.037 (294 K).

(19) Selected ^{1}H NMR data for **3**: 8.26 (bs, 2H, -N=C*H*-); 7.85, 7.20 (bs, 4H, -$C_6H_2(C(CH_3)_3)_2$-); 7.02, 6.81 (dd, 4H, -NC_6H_4N-); 1.98, 1.48 (s, 36H, -$C(CH_3)_3$); −25.77 (bd, $^1J_{Rh-H}$ = 51 Hz, 1H, Rh*H*). Yield of **3** by ^{1}H NMR, 76%.

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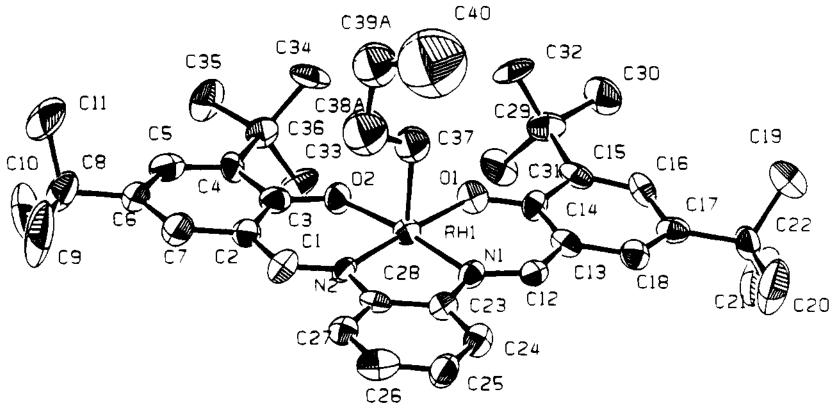
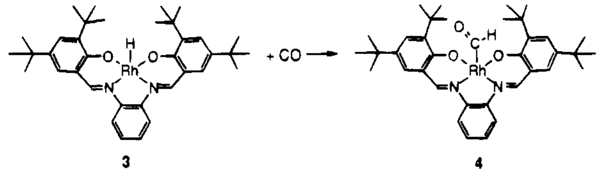


Figure 1. Perspective drawing (ORTEP) of Rh(*n*-Bu)(Bu$_4$salophen) (**2a**). Selected distances (Å): Rh1−O1, 2.009(8); Rh1−O2, 2.009(8); Rh1−N1, 1.98(1); Rh1−N2, 1.96(1); Rh1−C37, 2.04(1).

salophen), which under H_2 is in equilibrium with RhH(Bu$_4$salophen), **3**. The fact that the reaction of d^7 Rh^{II}(Bu$_4$salophen) with triethylsilane requires heating is consistent with the notion that the d^7 metalloradicals associate as metal−metal bonded dimers, though no other evidence yet exists to support the presence of dimers. However, the existence of the dimer in solution may be extrapolated from previously reported studies of Rh(II) porphyrins and related systems.[20,21]

Exposure of a benzene solution of the hydride complex **3** to low pressures of CO (p_{CO} < 200 Torr) generates within minutes an orange solution which shows a ^{1}H NMR doublet at δ 11.05 ppm (J_{Rh-H} = 3.4 Hz).[22] Removal of benzene from a frozen sample of this solution yields an air-stable orange solid that exhibits a weak IR (KBr) band at 1734 cm^{-1} indicative of the formation of a formyl group as well as strong bands at 1604, 1578 and 1519, and 1167 cm^{-1} consistent with the imino C=N, phenyl C=C, and phenolate C−O stretches of the Bu$_4$salophen ligand, respectively. When ^{13}CO is employed in the reaction system, the ^{1}H NMR resonance at 11.05 ppm for the formyl proton changes to a doublet of doublets with J_{C-H} = 198 Hz and the weak IR band shifts to 1702 cm^{-1}. The ^{13}C{^{1}H} NMR spectrum of the labelled sample exhibits a doublet at δ 210 ppm with coupling to ^{103}Rh (J = 34 Hz). The results are consistent with the insertion reaction of eq 2 to generate the formyl species Rh(CHO)(Bu$_4$salophen) (**4**) analogous to that found with the corresponding rhodium porphyrin systems.[5,23−25] For reactions of **3** with CO at pressures greater than 200 Torr, or for such reactions in THF or cyclohexane solution, products in addition to **4** are seen that may correspond to Rh(I) carbonyl complexes with partially dissociated Bu$_4$salophen ligands.[26]

The intermediacy of radicals in eq 2 is strongly supported by the fact that **4** can also be generated *in situ* by photolysis at 0 °C of **2b** in toluene-d_8 solution, followed by exposure to CO and the well-known H-atom transfer agent Bu$_3$SnH. For prolonged periods at room temperature, the solution turns deep green and a new diamagnetic product forms. Photolysis of a



3 **4** (2)

toluene-d_8 solution of **2b** in the presence of Bu$_3$SnH only yields the green diamagnetic product as well. The ^{13}C NMR spectrum of this compound includes a doublet at δ 11.49 (J_{Rh-C} = 2 Hz) that also exhibits ^{117}Sn and ^{119}Sn satellites ($J_{^{117}Sn-C}$ = 247, $J_{^{119}Sn-C}$ = 258 Hz). This resonance is assignable to the *n*-butyl carbon atoms adjacent to Sn in the tributyltin adduct Rh(SnBu$_3$)(Bu$_4$salophen) (**5**).[27,28]

The observed chemistry clearly indicates that Rh Schiff base complexes having N_2O_2 donor sets behave similarly to the well studied Rh porphyrin systems through involvement of metalloradical species. In a parallel study using a different rhodium Schiff base complex, Wayland has observed analogous Rh(II) and formyl species.[21] The synthetic flexibility that Schiff base ligands offer, coupled with the unusual reactivity of Rh complexes based on them, make the study of these systems attractive for substrate activation and catalytic chemistry.

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Supplementary Material Available: Tables giving crystal data and details of the structure determination, bond lengths, bond angles, anisotropic thermal parameters, and positional parameters including hydrogen atom locations and equivalent isotropic temperature factors for **2b** (11 pages). Ordering information is given on any current masthead page.

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(22) Selected ^{1}H NMR data for **4**: 11.05 (d,1H, Rh−*H*, J_{Rh-H} = 3.4 Hz); 8.19 (d, 2H, -N=C*H*-); 7.86, 7.20 (d, 4H, -C$_6$*H*$_2$(C(CH$_3$)$_3$)$_2$-); 7.01, 6.86 (dd, 4H, -NC$_6$*H*$_4$N-); 1.93, 1.44 (s, 36H, -C(C*H*$_3$)$_3$). The ^{1}H NMR spectrum of **4** synthesized with ^{13}CO shows $^2J_{Rh-H}$ of 3.4 Hz and $^1J_{C-H}$ of 197.9 Hz, while the ^{13}C NMR shows $^1J_{Rh-C}$ coupling of 34 Hz. Yield of **4** (NMR), 72%. The ^{1}H NMR resonance of **4** and **4** obtained using ^{13}CO is shown in a figure in supplementary material.

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(26) ^{1}H NMR (benzene-d_6): 13.66 ppm, s; IR (CH$_2$Cl$_2$): 2076, 2004 cm^{-1}).

(27) Selected ^{1}H NMR data for **5**: 8.52 (d, J_{Rh-H} = 1.5 Hz, 2H, -N=C*H*-); 7.82, 7.34 (d, J_{H-H} = 2.5 Hz, 4H, -C$_6$*H*$_2$(C(CH$_3$)$_3$)$_2$-); 7.21, 6.87 (dd, $^3J_{H-H}$ = 6.2 Hz, $^4J_{H-H}$ = 3.4 Hz, 4H, -NC$_6$*H*$_4$N-); 1.93, 1.45 (s, 36H, -C(C*H*$_3$)$_3$), 1.06−0.95 (m, Sn(CH$_2$C*H*$_2$C*H*$_2$CH$_3$)$_3$, 12H); 0.68 (t, $^3J_{H-H}$ = 7.1 Hz, Sn(CH$_2$CH$_2$CH$_2$C*H*$_3$)$_3$, 9H); 0.64 (m, Sn(C*H*$_2$CH$_2$CH$_2$CH$_3$)$_3$, 6H). Selected ^{13}C NMR data for **5**: 168.29, 151.66, 145.32, 142.72, 136.39, 129.87, 128.58, 125.19, 114.36, 121.26 (d, J_{Rh-C} = 2 Hz), 36.69, 34.23 (-*C*(CH$_3$)$_3$), 31.55, 30.34 (-C(*C*H$_3$)$_3$), 29.36 (s, with satellites, J_{Sn-C} = 20, Sn(CH$_2$CH$_2$*C*H$_2$CH$_3$)$_3$), 27.45 (s, with satellites, $J_{^{117}Sn-C}$ = 66, $J_{^{119}Sn-C}$ = 69 Hz, Sn(CH$_2$*C*H$_2$CH$_2$CH$_3$)$_3$) 13.65 (s, Sn(CH$_2$CH$_2$CH$_2$*C*H$_3$)$_3$) 11.49 (d, with satellites, J_{Rh-C} = 2 Hz, $J_{^{117}Sn-C}$ = 247, $J_{^{119}Sn-C}$ = 258, Sn(*C*H$_2$CH$_2$CH$_2$CH$_3$)$_3$).

(28) A crystal structure determination for **5** confirms this assignment and will be published separately along with a luminescence study of this system.