Dimerization of a 17-Electron Cation Radical by Formation of a Rhodium-Rhodium Bond

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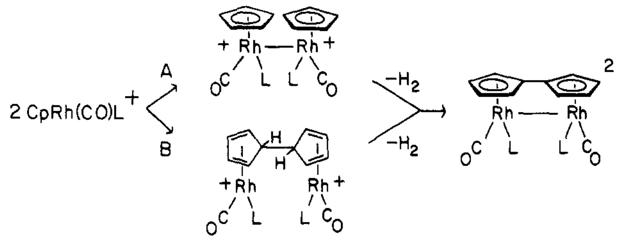
Received November 30, 1987

Summary: CpRh(CO)L, L = PMe_3 or $P(OPh)_3$, oxidize by one electron to form dinuclear dications of the type $[CpRh(CO)L]_2^{2+}$. In contrast to the previously studied L = PPh_3 system, which oxidizes to a fulvalene complex, the PMe_3 and $P(OPh)_3$ derivatives dimerize through the metals. X-ray crystallography of $[CpRh(CO)P(OPh)_3]_2^{2+}$ confirms this rare example of a strong unsupported Rh-Rh bond (2.814 Å). The metal-metal coupling reaction was unexpected since dimerizations of 17-electron organometallic cations usually occur at a ligand site.

The oxidation of complexes of the type $CpML_2$ (M = Co, Rh; L = carbonyl or phosphine) is generally agreed to involve formation of a 17-electron cation.[1-3] In some cases the cation radical has proved to be sufficiently stable to isolate or study by ESR spectroscopy.[1b,c,2b,c] In two cases, namely, $CpRhL(PPh_3)$, L = CO or PPh_3, the major oxidation product is the dication of a fulvalene complex.[1a,2a,4] This reaction involves formal coupling of two cation radicals and loss of H_2. Formation of the dinuclear complexes by ring-ring coupling (route B in Scheme I) has been considered to be more feasible than the route (A) of direct coupling between the positively charged metal centers, owing to the increased Coulombic repulsions inherent to the latter pathway. Indeed, previous reports of dimerization of 17-electron cations have generally shown that coupling occurs through ligands rather than through the metals.[5]

We now demonstrate that 17-electron cations of the type $CpRh(CO)L^+$ may form the metal-metal bonded dications $[CpRh(CO)L]_2^{2+}$ when L is either trimethylphosphine or triphenyl phosphite. This is a rare, if not unique, example of dimerization of positively charged paramagnetic metal centers.

Scheme I



Oxidation of $CpRh(CO)[P(OPh)_3]$ (1) is an irreversible one-electron process at a Pt electrode. The anodic peak potential is about +0.70V.[6] No return wave for the reoxidation of 1^+ is observed even at cyclic voltammetry scan rates in excess of 10^3 V/s, implying a lifetime of less than a millisecond for the 17-electron cation. Electrolytic oxidation of 1 in dichloromethane[7] at 243 K released 1.1 F and gave an orange solution displaying a reduction wave in at least 70% yield with a peak potential of about 0 V. Re-reduction of this product gave a high yield of 1, the starting material, showing that the oxidation-reduction process is chemically reversible. This immediately set apart 1 from $CpRh(CO)[PPh_3]$, which is not re-formed by reduction of the fulvalene dication $[(C_{10}H_8)Rh_2(CO)_2(PPh_3)_2]^{2+}$.[2a] The oxidation product was isolated from the electrolysis solution[8] as an orange solid which analyzed for $\{CpRh(CO)[P(OPh)_3][PF_6]\}_n$[9] and showed a field desorption mass spectrum consistent with $n = 2$.[10] NMR and IR data also agreed with a dimeric formulation.[11] Chemical oxidation of 1 using equimolar ferrocenium was also successful, the dimer being isolated in 65% purified yield. Since the standard potential of ferrocene is about 200 mV negative of 1, the rapid dimerization of 1^+ apparently provides the driving force for the reaction.

Crystals of the dication were grown from acetone/ether at 293 K under nitrogen and analyzed by X-ray crystallography.[12] The dication consists of two CpRh(CO)[P-

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(6) Potentials are referenced to the aqueous saturated calomel electrode. The potential of the $Cp_2Fe^{+/0}$ couple was +0.46 V.

(7) The supporting electrolyte was 0.1 M Bu_4NPF_6.

(8) The solution was evaporated and the residue redissolved in 1:1 ether/dichloromethane, after which the solution was cooled and filtered to remove supporting electrolyte. The filtrate was concentrated, and the orange dication was filtered off. Washing this powder several times with small amounts of cold CH_2Cl_2 gave a sample suitable for elemental analysis.[9]

(9) Calcd for $C_{24}H_{20}F_6O_4P_2Rh$: C, 44.3; H, 3.1. Found: C, 43.8 H, 3.5 (Robertson Laboratories).

(10) The FDMS base peak was at *m/e* 1157, corresponding to the monohexafluorophosphate salt of the dimeric dication. We thank Dr. Catherine Costello at MIT for this measurement.

(11) NMR in acetone-d_6, δ scale: 6.58 (d, Cp), 7.2-7.6 (m, Ph). IR (KBr): carbonyl bands at 2106 and 2060 cm^{-1}.

(12) Crystallographic data for $[CpRh(CO)P(OPh)_3]_2[PF_6]_2$: $C_{48}H_{40}F_{12}O_8P_4Rh_2$; orthorhombic; *Pbca*; $a = 15.965$ (4), $b = 19.683$ (4), $c = 35.706$ (8) Å; $V = 11\,220$ Å^3; $Z = 8$; D(calcd) = 1.542 g cm^{-3}; μ(Mo Kα) = 7.65 cm^{-1}. The large brick-shaped, deep orange crystal (0.3 × 0.4 × 0.6 mm) selected for data collection was the best of seven screened, but diffracted diffusely. Corrections were applied for a linear 5% decay in reflection intensity, but none for absorption was needed. Of 8450 reflections collected (Nicolet R3m, Mo Kα, 293 K, $\lambda_{max} = 46°$), 3926 were observed at the $5\sigma(F_o)$ level. Direct methods provided the Rh atom positions. The PF_6 anions were constrained to rigid octahedral geometry with a single refined P-F distance (1.467 (2) Å) and the phenyl rings to rigid, planar hexagons with a fixed C-C distance (1.395 Å). Difference maps revealed a cluster of peaks in a region distant from the ions with maximum contours in the range of fractionally occupied C, N, or O atoms, but no assignment of molecular identity was possible. These peaks were refined as CW, CX, CY, and CZ with a refined occupancy of 0.67 (2); D(calcd) does not include these contributions. At convergence with all non-hydrogen atoms anisotropic (except for the phenyl ring carbon atoms and the partial occupancy solvent molecule) and hydrogen atoms idealized: $R(F) = 7.17\%$, $R(wF) = 7.68\%$, GOF = 1.484, $\Delta/\sigma = 0.05$; $\Delta(\rho) = 0.83$ e Å^{-3}, and $N_o/N_v = 8.90$. All computations used the SHELXTL (5.1) program library (Nicolet Corp., Madison, WI).

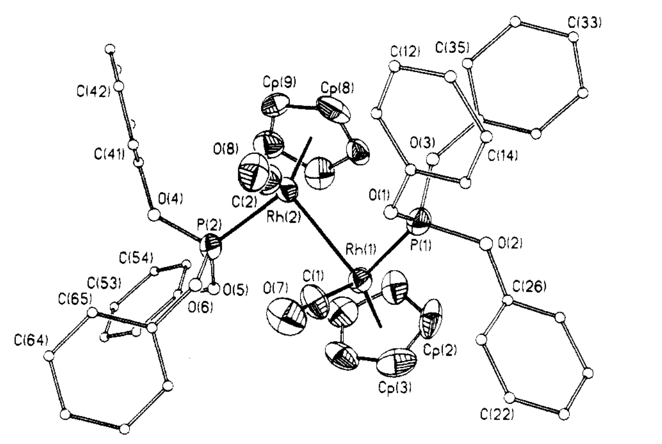

Figure 1. Cation structure and labeling scheme for $[CpRh(CO)P(OPh)_3]_2^{2+}$. Thermal ellipsoids are shown at the 50% probability level. Bond distances (Å): Rh(1)–Rh(2), 2.814 (1); P(1)–Rh(1), 2.258 (4); P(2)–Rh(2), 2.252 (4); Rh(1)–C(1), 1.88 (1); Rh(2)–C(2), 1.86 (1); Rh(1)–CENT(1), 1.873 (6); Rh(2)–CENT(2), 1.876 (7). Bond angles (deg): P(1)–Rh(1)–C(1), 89.8 (4); P(1)–Rh(1)–CENT(1), 128.6 (3); CENT(1)–Rh(1)–C(1), 126.8 (6); P-(2)–Rh(2)–C(2), 90.4 (4); P(2)–Rh(2)–CENT(2), 125.5 (4); CENT(2)–Rh(2)–C(2), 128.6 (7); CENT(1)–Rh(1)–Rh(2)–CENT(2), –62.2 (6).

$(OPh)_3]$ cations joined by a Rh–Rh bond (Figure 1). The phosphite groups occupy essentially transoid positions, the P(1)–Rh(1)–Rh(2)–P(2) dihedral angle being 150.5°. The carbonyls are therefore rotated by 29.6° from an eclipsed position. The Rh–Rh bond length of 2.814 Å is somewhat longer than that of Rh metal[13] but is still consistent with the presence of a single metal–metal bond. There are very few compounds known with Rh–Rh bonds unsupported by bridging ligands.[14] Two binuclear isocyanide structures appear to have the greatest relevance to the present structure. The Rh(I) complex $(CNPh)_8Rh_2^{2+}$ has a very long Rh–Rh bond (3.193 Å),[15] but a much shorter distance (2.785 Å) is found in the formal Rh(II) analogue $(CNR)_8Rh_2I_2^{2+}$.[16]

The trimethylphosphine complex $CpRh(CO)PMe_3$ (**2**) also forms a metal–metal bonded dication, $\mathbf{2}_2^{2+}$, upon oxidation. The peak potentials for the oxidation of **2** and the reduction of $\mathbf{2}_2^{2+}$ are +0.32 and –0.23 V, respectively. The dication was poorly soluble, leading to voltammetric difficulties (e.g., electrode passivation) but easy isolation of $\mathbf{2}_2^{2+}$ from coulometric experiments. When millimolar solutions of **2** in CH_2Cl_2 were electrolyzed, pure red microcrystals of $[CpRh(CO)PMe_3]_2[PF_6]_2$ were obtained.[17]

Two aspects of these results deserve some comment at this stage of our investigations. First, it has now been demonstrated that cationic 17-electron complexes differing only in the coordinated phosphine can undergo metal–metal as well as ligand–ligand coupling. On the subject of the unsupported M–M bond, two recent reports are relevant. The osmocenium dimer $[Cp_2Os]_2^{2+}$ is formed when osmocene is treated with the two-electron oxidant Ce(IV).[18] This reaction most likely involves comproportionation of Cp_2Os^{2+} and Cp_2Os, with dimer formation proceeding through the coupling of two Cp_2Os^+ radicals. Comproportionation of $Ni(CNMe)_4{}^n$ (n = 0, 2+), leads to the Ni–Ni bonded dication $[Ni_2(CNMe)_8]^{2+}$ also through the likely intermediacy of the Ni(I) monocation $Ni(CNMe)_4{}^+$.[19] It appears that one-electron oxidation should be considered as a general strategy for the synthesis of charged complexes with unsupported metal–metal bonds. Second, it is not yet clear why the $P(OPh)_3$ and PMe_3 derivatives **1** and **2** behave differently than the PPh_3 derivative, which forms the fulvalene complex. Molecular orbital calculations[20,21] and photoelectron spectroscopy data[22] have shown that the HOMO in CpRh(CO)L complexes is $1b_1$, an admixture of the cyclopentadienyl $e_1{}^+$ and metal d_{xz}. The latter is oriented in the right direction to account for the observed M–M coupling. Experiments on the oxidation of other complexes with bulky phosphines are proceeding to see if steric effects are the reason for the lack of a stable metal–metal bonded dimer arising from the oxidation of $CpRh(CO)PPh_3$.

Acknowledgment. We gratefully acknowledge the support of the National Science Foundation (NSF CHE86-03728) and Research Corp. NSF also provided funds to the University of Delaware for purchase of its diffractometer.

Supplementary Material Available: Tables of atomic coordinates and isotropic thermal parameters, bond lengths and bond angles, anisotropic thermal parameters, and H-atom coordinates (7 pages); a listing of observed and calculated structure factors (24 pages). Ordering information is given on any current masthead page.

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Dynamics of Hydrogen Migrations in $(H)Fe_2(ethene)^+$ and $(H)Fe_2(propene)^+$ in the Gas Phase

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Received September 21, 1987

Summary: The dynamics of hydrogen migration in $(H)Fe_2(ethene)^+$ and $(H)Fe_2(propene)^+$ systems are investigated in the gas phase by using Fourier transform mass spectrometry along with specific isotopic labeling. The results suggest small barriers for reversible insertion into allylic C–H bonds for $(H)Fe_2(propene)^+$ with substantially larger barriers for either reversible vinylic C–H bond insertion or reversible olefin insertion/β-elimination processes.

Studying the dynamics of fundamental hydrogen migrations of organometallic species is of paramount im-

