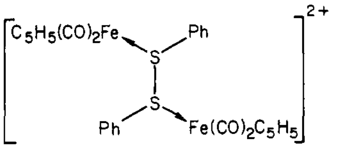

This complex, as a BF_4^- salt, can be made independently in the reaction of $[Fe(C_5H_5)(CO)_2(THF)]BF_4$ and diphenyl disulfide in CH_2Cl_2, using a 2:1 ratio of these reactants. Facile displacement of THF from the precursor is well-known.[5] This compound is soluble in CH_3CN but decomposes slowly to $[Fe(C_5H_5)(CO)_2(PhSSPh)]BF_4$[4] and known $[Fe(C_5H_5)(CO)_2(CH_3CN)]BF_4$. The former compound is also formed from $[Fe(C_5H_5)(CO)_2(THF)]BF_4$ and diphenyl disulfide when these species are reacted in a 1:1 molar ratio. This compound is believed to have a monodentate disulfide ligand.[6] The structure of this compound and its formation from $[Fe(C_5H_5)(CO)_2\text{-}\mu\text{-PhSSPh-}Fe(CO)_2(C_5H_5)]^+$ under mild conditions argue strongly for the proposed structure of the disulfide-bridged dinuclear complexes.[7]

Oxidations of the related compounds $Fe(C_5H_5)(CO)(L)SPh$[4,8] ($L = P(OPh)_3, P(OEt)_3, PPh_2Me, PPhMe_2, PMe_3$) were carried out with $AgPF_6$ (for the phosphine complexes) or $NOPF_6$ (for the phosphite complexes). Dark colored products were obtained from each reaction, for which analyses also confirm a stoichiometry $[Fe(C_5H_5)(CO)(L)SPh]X$ ($X = PF_6$ or BF_4).[4] Magnetic moments between 0.5 and 1.0 μ_B were measured for these species at ambient temperatures. Concentrated solutions of the phosphite complexes are red, but dilution caused a color change to blue. The phosphine complexes are blue at room temperature. A reversible blue-red color change can be induced by temperature variation; the higher temperature color is blue while cooling causes the solution to become red. These data suggest an equilibrium between blue 17e monomer and red 18e dimer, viz.,

$$2[Fe(C_5H_5)(CO)(L)SPh]^+ \rightleftharpoons [Fe(C_5H_5)(CO)(L)\text{-}\mu\text{-PhSSPh-}Fe(C_5H_5)(CO)(L)]^{2+}$$

We have maintained that the facile oxidation of electron-rich complexes is a consequence of the destabilization accorded to HOMO orbitals of primarily metal character by the donation of electronic charge from good donor ligands.[1] The removal of an electron from this orbital would leave an unpaired electron to reside in an orbital which is primarily of metal character. In 17e, d^5 octahedral complexes (such as the $[Fe(C_5H_5)(L)_2SPh]^+$ complexes mentioned above) there usually is no chemical reactivity associated with the unpaired electron. Radical reactions at a metal site are encountered with other types of 17e complexes such as $Mn(CO)_5$, a d^7 five-coordinate species. Our observation of what is apparently a ligand-based radical reaction in these 17e mercaptide species is of some interest in this frame of reference. Only a few other examples of ligand-centered radical reactions have come to our attention.[9]

We suspect that the HOMO in $Fe(C_5H_5)(CO)_2SPh$ is not a metal orbital at all but is in fact a sulfur lone-pair orbital. We base this assumption on PES data and theoretical calculations for $Mn(CO)_5X$ species (X = Cl, Br, I) which indicate that the HOMO is a halogen lone pair.[10] The extrapolation to metal thiolate complexes seems a reasonable one. If so, the oxidation of $Fe(C_5H_5)(CO)(L)SPh$ species ($L = CO, P(OR)_3, PR_3$) might be assumed to occur by loss of an electron from a sulfur orbital, giving a radical site located at sulfur. This then reacts in typical radical fashion to give the dimeric product.

A few complexes containing an organic disulfide ligand bridging two metals are known; this includes three organometallic species[11] and several other coordination compounds.[12] A potential bioinorganic interest in related complexes involving metals complexed to the sulfur containing amino acids is noted.

It is our belief that these results are most significant in directing attention to the possibility of a range of radical reactions at ligands not anticipated previously. We are currently investigating this problem in this broader context.

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(6) The synthesis of this compound under mild conditions argues strongly for this structure. Infrared data [ν(CO) at 2068 s and 2025 s cm^{-1}] similar to data on many other $[Fe(C_5H_5)(CO)_2L]^+$ complexes support this formulation. NMR data only confirm the stoichiometry. However, the NMR spectrum of an analogous compound, $Fe(C_5H_5)(CO)_2(CH_3SSCH_3)]BF_4$, shows proton resonances at δ 5.76, 2.98, and 2.80, intensities 5:3:3, confirming the different methyl proton environments expected for such a structure.

(7) Raman data might have provided further evidence for this structure, since disulfide groups show characteristic strong absorptions. However, attempts to obtain Raman data were frustrated by the decomposition of the sample under laser irradiation. A crystal structure study is under way which should verify the proposed structure.

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First Authentic Example of a Difference in the Structural Organometallic Chemistry of Zirconium and Hafnium: Crystal and Molecular Structure of $(\eta^5\text{-}C_5H_5)_2Hf(\eta^1\text{-}C_5H_5)_2$

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Received October 20, 1980

The road to understanding the structures of $(C_5H_5)_4M$, M = Ti, Zr, and Hf, has been long and filled with crystallographic pitfalls. All three structures were determined initially in the early 1970s. An accurate determination showed that $(C_5H_5)_4Ti$ has two σ- and two π-bonded ligands.[1] Poor quality X-ray studies indicated that $(C_5H_5)_4Zr$ has one σ- and three π-bonded groups,[2] while $(C_5H_5)_4Hf$ was formulated with two σ- and two π-cyclopentadienyl units.[3] In retrospect this was most unusual because (1) zirconium and hafnium differ only slightly (but significantly) in chemical behavior and never in the structure of organometallic derivatives[4] and (2) the crystallography of $(C_5H_5)_4Zr$ and $(C_5H_5)_4Hf$ suggested some serious problems. In particular, that of $(C_5H_5)_4Zr$ was questioned.[1] However, our group showed in 1978 that the one σ three π mode was correct even though the initial X-ray work was faulty.[5] It was supposed that $(C_5H_5)_4Hf$, when properly determined, would likewise prove to be of one σ three π formulation. However, we now report the results of an accurate study of $(C_5H_5)_4Hf$: the compound is correctly viewed as $(\eta^5\text{-}C_5H_5)_2Hf(\eta^1\text{-}C_5H_5)_2$. The original work was in error in that the c axis was given only half its true value. The apparent disorder in the space group $P\bar{4}2_1m$ does not exist in the proper choice of $P\bar{4}2_1c$. The molecule is shown in Figure 1.

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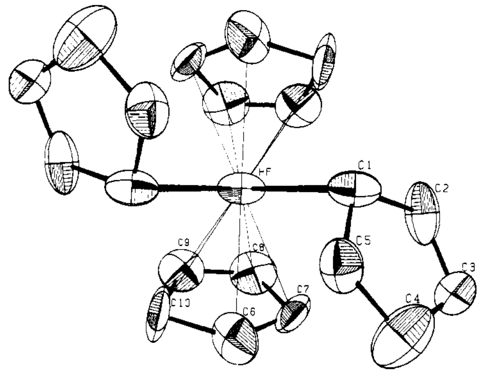

Figure 1. Molecular structure of $(\eta^5\text{-}C_5H_5)_2Hf(\eta^1\text{-}C_5H_5)_2$ with the atoms represented by their 50% probability ellipsoids for thermal motion. The hafnium atom resides on a crystallographic twofold axis.

Tetracyclopentadienylhafnium was prepared by the reaction of $(\eta^5\text{-}C_5H_5)_2HfCl_2$ with NaC_5H_5 in diethyl ether. Crystals appropriate for the X-ray diffraction study were grown by the slow cooling of a toluene solution. A yellow crystal of the compound was sealed under a N_2 atmosphere in a thin-walled capillary, and contrary to a previous report no decomposition in the X-ray beam was observed.[6]

The Hf–C(σ) bond length, 2.38 (2) Å, is considerably larger than the 2.24 (1) Å value found for the sp³ carbon in $(\eta^5\text{-}C_5H_5)_2Hf(CH_3)_2$.[7] It is, however, significantly shorter than that found in $(\eta^5\text{-}C_5H_5)_3Zr(\eta^1\text{-}C_5H_5)$: 2.447 (6) Å. The contraction can be ascribed either to steric considerations or to the 16- vs. 18-electron configurations in $(C_5H_5)_4Hf$ and $(C_5H_5)_4Zr$, respectively.[8] The Hf–C bond vector makes an angle of 66° with the plane of the $\eta^1\text{-}C_5H_5$ ring.

The Hf–C(π) distances range from 2.48 (3) to 2.57 (3) Å. The 2.50 (4) Å average is slightly larger than normal but is of no consequence because of the high esd's. More important, the ligand is planar to within 0.02 Å. (The σ-bonded cyclopentadienyl ligand is planar to 0.03 Å.)

Bond angles which involve the ring centroids and the σ-bonded carbon atoms agree rather well with those found in $(\eta^5\text{-}C_5H_5)_2Ti(\eta^1\text{-}C_5H_5)_2$: centroid–Hf–centroid′ = 130° (129.9° for the Ti analogue), centroid–Hf–C(1)′ = 108° average (108°), and C(1)–Hf–C(1)′ = 88 (1)° (86.3°).

Acknowledgment. We are grateful to the National Science Foundation for support of this research program.

Supplementary Material Available: Tables of bond distances, angles, final fractional coordinates, thermal parameters, and observed and calculated structure factors (6 pages). Ordering information is given on any current masthead page.

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(6) The unit cell parameters are a = 9.790 (5), c = 16.211 (8) Å; D_c = 1.88 g cm^{-3} for Z = 4. Least-squares refinement based on 531 observed reflections led to a final R value of 0.040. Hydrogen atoms were included with fixed contributions, and all nonhydrogen atoms were refined with anisotropic thermal parameters.

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Manifestations of Sulfur to Sulfur Through-Bond Interactions in Complex Ion Spectra

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Received August 25, 1980

In a previous communication,[1] through-space electronic delocalization in mixed-valence complexes of ruthenium ammines with 1,5-dithiocane as bridging ligand was demonstrated. We now report results for a ligand in which the character of the molecular orbitals is exclusively σ, but in which the sulfur lone pairs do not overlap directly.

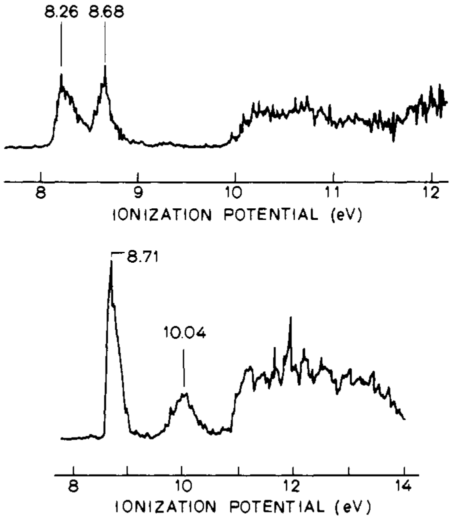
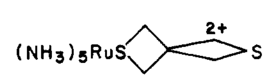


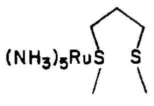
Figure 1. He I photoelectron spectra of 1,5-dithiocane (top) and 2,6-dithiaspiro[3.3]heptane.

2,6-Dithiospiro[3·3]heptane was synthesized by the method of Backer:[2] mp 31–32 °C (lit;[2] 31.5 °C); ¹H NMR (CCl_4) δ 3.3 (s, 8 H), ¹³C NMR ($CDCl_3$) δ 52.32 (s), 40.54, 39.77, 39.00 (t) (Me_4Si = 0 ppm). (The triplet was obtained by irradiation near 0 ppm in the ¹H spectrum and corresponds to the disubstituted carbon. The singlet corresponds to the tetrasubstituted carbon.)[3]

Pentaammine(2,6-dithiaspiro[3·3]heptane)ruthenium(II), I, and pentaammine(2,6-dithiaheptane)ruthenium(II), II (included for purposes of comparison), were synthesized by reaction of a 10-fold excess of ligand with 200 mg of $[(NH_3)_5RuH_2O](PF_6)_2$[4] in 5 mL of deaerated acetone and were worked up as previously described.[1]



I



II

The binuclear species were produced by the reaction of the mononuclear species with a 5% excess of $[(NH_3)_5RuH_2O](PF_6)_2$ in the minimum volume of acetone needed to provide for a homogeneous reaction system. μ-(2,6-Dithiaspiro[3·3]heptane)-bis-[*trans*-(isonicotinamide)tetraammineruthenium(II)], III, was synthesized by combining 200 mg of *trans*-$[isn(NH_3)_4RuSO_4]Cl$[5] and 200 mg of the ligand in a minimum of argon-deaerated 0.10 M HCl and adding acetone dropwise until the cloud point. A few pieces of Zn/Hg amalgam were then added, and after 3 h in the dark under continuous argon flow, the mixture was filtered and solid NH_4PF_6 added. The orange solid was collected by filtration, washed with ethanol and ether, and purified by reprecipitation from a minimum of 0.10 M HCl. A single product with the elution characteristics of a tetrapositive ion was found on chromatography on Dowex 50W-X2 ion exchange resin. The overall yield was ~20%.

Analyses were performed on the hexafluorophosphate salts containing ruthenium(II). Anal. Calcd for $[(NH_3)_5Ru(C_5H_8S_2)(PF_6)_2$: C, 9.87; H, 3.81; H, 11.51; S, 10.54; Ru, 16.62; F, 37.47. Found: C, 9.54; H, 3.77; N, 11.17; S, 10.28; Ru, 16.4; F, 36.9. Calcd for $[(NH_3)_5Ru(C_5H_{12}S_2)](PF_6)_2$: C, 9.81; H, 4.44; N, 11.44; S, 10.47; Ru, 16.51; F, 37.22. Found: C, 8.58; H, 4.26; N, 11.58; 10.89; Ru, 16.6; F, 37.6. Calcd for $[((NH_3)_5Ru)_2$-

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