radicals are present.[4] One explanation for the negative results is that the OH radical is extremely reactive and the concentration at any time is too small to observe. This explanation would reaffirm the steady state approximation in the kinetic treatment of this system. Another explanation, presented by Dixon,[23] is that the hydrogen atoms in water exchange rapidly and the signal from OH is broadened.

$$\mathrm{HOH} + \mathrm{OH} \rightleftharpoons \mathrm{HOH}^* + \mathrm{OH} \qquad (10)$$

In the Fe(II)-H_2O_2 system, there was some indirect evidence for radical formation. When 1,4-butenediol was added to the Fe(II) solution, organic radicals were observed.[22] Thus, butenediol was used as a substrate in the copper–histidine system also. Initial concentrations of reactants were the same as concentrations used for radical production in the Fe(II)-H_2O_2 system (0.5 *M* butenediol, 0.1 *M* H_2O_2, 0.1 *M* Cu–histidine chelate). In separate runs, the diol was reduced to 0.2 *M*, and then the peroxide to 0.1 *M*. No substrate radicals were observed in any case.

The involvement of a cupric–cuprous couple in the reaction mechanism of hydrogen peroxide decomposition by copper chelates was indicated by the biquinoline test,[20] which is far more sensitive than the esr analysis.

Conclusions

The main conclusions of the present investigation are (1) the active species in the decomposition of hydrogen peroxide by copper–histidine chelates are the 1:1 copper–histidine complex and peroxide anion; (2) the splitting of the peroxide bond, O–O, is presumably brought about by the change in the stereochemistry of the complex due to reduction of the Cu(II) complexes to cuprous complexes; (3) the reaction is favored by an increase in pH; (4) the presence of an anionic group, COO^-, on the chelate reduces its catalytic activity toward hydrogen peroxide decomposition; (5) the esr studies do not provide evidence for the presence of free radicals or a radical intermediate in the H_2O_2–Cu–histidine system, and the kinetic data can be explained by a reaction mechanism that does not involve free radicals.

Acknowledgment. This work was supported by a grant from the Environmental Control Administration, CPEHS, U. S. Public Health Service, EC00098, and The Robert A. Welch Foundation, Grant A-177.

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The Cyclopentadienyls of Titanium, Zirconium, and Hafnium

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Abstract: The first synthesis of bis(cyclopentadienyl)hafnium is reported; numerous physical and chemical properties of this species are considered in relation to those of the titanium and zirconium analogs and the bis-cyclopentadienyls of other transitional metals.

In earlier publications the synthesis and certain chemical and physical properties of bis(cyclopentadienyl)titanium were described[1] and the first synthesis of the zirconium analog was announced.[2] Here the synthesis of the hitherto unreported bis(cyclopentadienyl)hafnium, its behavior upon oxidation, adduct formation with diphenylacetylene, and a comparison of its properties with those of certain other transitional metals are described.

In addition to prior work in this general area cited earlier,[1,2] the authors became aware belatedly of a reported synthesis of $(C_5H_5)_2Ti$ by Shikata *et al.*,[3] *via* the reduction of $(C_5H_5)_2TiCl_2$ with NaHg. They reported a carbon content 5% below the calculated value, and a very poorly resolved infrared spectrum. They did, however, find molecular weights indicative of $[(C_5H_5)_2Ti]_2$ in agreement with earlier results from this laboratory.[1] It seems likely that they did indeed produce $[(C_5H_5)_2Ti]_2$ but in rather low purity.

Experimental Section

Unless otherwise indicated, analytical methods and procedures for physical measurements were essentially the same as those reported previously.[1,2]

Synthesis of $(C_5H_5)_2Hf$. In an oxygen-free dry helium atmosphere, 3.6 g (9.46 mmol) of $(C_5H_5)_2HfCl_2$, 0.44 g (18.96 mg-atom) of Na, 3 g of $C_{10}H_8$ (*ca.* 15% molar excess), and a magnetic stirring bar were placed in a 250-ml flask. The pressure was reduced and

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[2] G. W. Watt and F. O. Drummond, Jr., *ibid.*, 88, 5926 (1966).

[3] K. Shikata, K. Yokogawa, S. Nakao, and K. Azuma, *Kogyo Kagaku Zasshi*, 68 (7), 1248 (1965).

125 ml of tetrahydrofuran (THF) was distilled into the flask. Pure dry nitrogen was introduced at 25° to provide a small positive pressure, and the reaction mixture was stirred for 6 days. The THF was removed under reduced pressure and the solid residue was leached with 200 ml of dry benzene (without exposure to the atmosphere) to provide a dark purple solution. By means of an X-ray diffraction pattern, NaCl was identified as a component of the benzene-insoluble residue.

Benzene was removed from the purple solution by distillation under reduced pressure and naphthalene was largely removed by sublimation for 24 hr at 100° and 10^{-2} mm to afford *ca.* 2 g of purple crystals, mp >300° dec. X-Ray diffraction data for this product (corrected for lines attributable to residual $C_{10}H_8$) are compared with similar data for the Ti and Hf analogs in Table I.

Table I. X-Ray Diffraction Data

$(C_5H_5)_2Ti$		$(C_5H_5)_2Zr$		$(C_5H_5)_2Hf$	
d, Å	I/I_0	*d*, Å	I/I_0	*d*, Å	I/I_0
5.6	0.9	5.8	0.8	5.8	0.3
5.3	0.9	5.2	0.4	5.2	0.1
4.6	1.0	4.5	1.0	4.5	1.0
3.6	0.5	3.5	0.2	3.5	0.2
2.6	0.2	2.5	0.2	2.5	0.1
2.0	0.2	1.9	0.3	1.9	0.1

Further removal of $C_{10}H_8$ was effected by sublimation for 10 hr at 100° and 10^{-3} mm. *Anal.* Calcd for $(C_5H_5)_2Hf$: Hf, 57.8; C, 38.9; H, 3.27. Found: Hf, 56.7; C, 38.7; H, 3.42. The molecular weight could not be determined owing to too limited solubility of $(C_5H_5)_2Hf$ in benzene, THF, methanol, N,N-dimethylformamide, chloroform, etc. The product was diamagnetic at 25°; this was confirmed by an esr spectrum. In an effort to sublime $(C_5H_5)_2Hf$, a sample was heated to 345° at 10^{-3} mm; it decomposed to a black solid without sublimation. The infrared spectrum of $(C_5H_5)_2Hf$ is compared with those of the Ti and Zr analogs in Figure 1.

Synthesis of $(C_5H_5)_2Ti$. The following alternative routes to $(C_5H_5)_2Ti$ were investigated.

The synthesis described earlier[1] employed a 10% molar excess of naphthalene. This synthesis was repeated using 0.96 g of $(C_5H_5)_2TiCl_2$, 0.17 g of Na, but *only 3 mg* of $C_{10}H_8$. The formation of $(C_5H_5)_2Ti$ proceeded to completion as in the earlier experiments.

Several attempts to produce $(C_5H_5)_2Ti$ by the method of Clauss and Bestain,[4] *i.e.*, the reduction of $(C_5H_5)_2Ti(CH_3)_2$ with H_2 in hexane, failed to provide the desired product.

Diphenylacetylene Adducts. These substances were prepared directly by a procedure different from that of Vol'pin, *et al.*[5]

In a dry oxygen-free helium atmosphere, 4.14 g (0.017 mol) of $(C_5H_5)_2TiCl_2$, 5.91 g (0.034 mol) of $C_6H_5C{\equiv}CC_6H_5$, 0.76 g (0.034 g-atom) of Na, and *ca.* 5 g of $C_{10}H_8$ were placed in a flask, and 150 ml of dry THF was distilled into the flask under reduced pressure. This mixture was refluxed in an atmosphere of dry N_2 for 3 hr and stirred overnight. The THF was removed under reduced pressure and the solid residue was extracted with 35 ml of dry benzene. The solution was separated by centrifugation and treated with 1.75 ml of dry heptane, whereupon a finely divided brown-yellow solid separated. Over 2 days at 10° dark green crystals formed on the bottom and walls of the flask. The solution and brown-yellow solid were decanted from the green crystals, which were washed with dry petroleum ether and dried *in vacuo* for 24 hr; yield 0.5 g; mp 150°. *Anal.* Calcd for $(C_5H_5)_2Ti(C_6H_5C{\equiv}CC_6H_5)_2$: Ti, 9.0; C, 85.4; H, 5.66; mol wt, 535. Found: Ti, 9.1; C, 85.4; H, 5.93; mol wt, 492. X-Ray diffraction data (*d* spacings in Å; relative intensities in parentheses): 9.2 (0.3), 7.8 (1.0), 5.5 (0.3), 5.1 (0.2), 4.9 (0.4), 4.2 (0.2).

Starting with 6.47 g of $(C_5H_5)_2ZrCl_2$, the corresponding adduct was formed by essentially the same procedure. The purified product, however, consisted of only 200 mg of orange-colored crystals, mp 140°. *Anal.* Calcd for $(C_5H_5)_2Zr(C_6H_5C{\equiv}CC_6H_5)_2$: Zr, 15.8; C, 79.0; H, 5.21; mol wt, 578. Found: Zr, 16.4; C, 77.3; H, 5.34; mol wt, 650. X-Ray diffraction data: 9.4 (0.4), 7.9 (1.0), 5.6 (0.4), 5.2 (0.3), 5.0 (0.2), 4.2 (0.1).

Similar attempts to form the diphenylacetylene adduct of $(C_5H_5)_2Hf$ led to a dark orange-colored product, but in quantities too small to permit further examination.

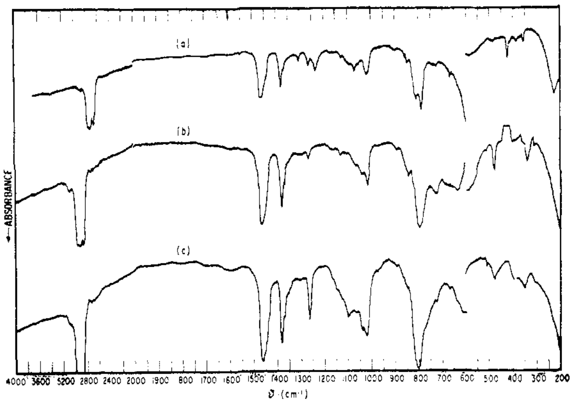

Figure 1. The infrared spectra of: (a) $(C_5H_5)_2Ti$, (b) $(C_5H_5)_2Zr$, and (c) $(C_5H_5)_2Hf$.

Oxidation of $(C_5H_5)_2Hf$. Exposure of the solid to atmospheric oxygen generated yellow-orange products having properties substantially the same as those reported previously[1,2] for the Ti and Zr analogs.

Discussion

The biscyclopentadienyls of the first member of each of the three d series have now been synthesized by a common procedure in which the role of naphthalene has been shown to be truly catalytic. The generality of application of this procedure, however, remains in doubt; efforts to produce the analogous compounds of Mo and W have been unsuccessful thus far.[6]

For the three species of the type $(C_5H_5)_2M$, the following properties decrease in the order Ti > Zr > Hf: (1) yield in synthesis, (2) solubility in solvents such as THF and benzene, (3) reactivity toward H_2O and O_2, and (4) volatility. Intensity of color, however, varies as, $(C_5H_5)_2Ti$, dark green; $(C_5H_5)_2Zr$, dark purple; and $(C_5H_5)_2Hf$, very dark purple.

Otherwise, these compounds exhibit the expected similarities. The X-ray diffraction data in Table I show that they are isomorphous; the same is true of the precursor species of the type $(C_5H_5)_2MX_2$.[6] All three are pyrophoric, of comparable thermal stability, and are oxidized (under necessarily very carefully controlled conditions) to apparently polymeric species of nonreproducible composition. Magnetic susceptibility and esr data show that all three are diamagnetic. The titanium compound is dimeric; the Zr and Hf analogs were not sufficiently soluble to permit molecular weight determinations. The carbenoid character[7,8] of these species is demonstrated by their formation of adducts with diphenylacet-

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[5] M. E. Vol'pin, V. A. Dubovitsker, O. V. Nogina, and D. N. Kurnasov, *Dokl. Akad. Nauk SSSR*, **151**, 623 (1963).

[6] F. O. Drummond, Jr., Dissertation, The University of Texas at Austin, 1968.

[7] M. E. Vol'pin and D. N. Kursanov, *J. Gen. Chem. U.S.S.R.*, **32**, 1188, 1443 (1962).

[8] M. E. Vol'pin and Y. D. Koreshkov, *Tetrahedron*, **18**, 107 (1962).

ylene, although the adduct was not isolated in the case of Hf.

The infrared spectra of the three metallocenes are compared in Figure 1; these data rule out species of the types $(C_5H_5)_2MH$ and $(C_5H_5)_2MH_2$. These spectra are closely similar to those of the metallocenes of Fe, Ru, and Ni,[9] in that all six spectra include five intense bands: C–H stretch at 3100 cm^{-1}, two C–H bends at 810 and 1000 cm^{-1}, an antisymmetrical ring breathing mode at 1100–1110 cm^{-1}, and an antisymmetrical C–C stretch at 1410–1430 cm^{-1}. The most noteworthy difference in these six spectra is in the vicinity of 1700 cm^{-1}. The metallocenes of Fe, Ru, and Ni exhibit five bands in this general region, in which the Ti, Zr, and Hf compounds do not absorb. In the latter three, however, a system of three bands (at 1232, 1262, and 1302 cm^{-1} for $(C_5H_5)_2Ti$) suggests a shift of all five bands in each of these spectra to lower energies, two being obscured by absorption attributable to Nujol.

Finally, the pyrophoric nature of the metallocenes of Ti, Zr, and Hf and their extreme reactivity toward a wide variety of reagents cannot be overemphasized.

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