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SIGMA-BONDED ORGANIC DERIVATIVES OF HAFNIUM

M. D. RAUSCH, H. B. GORDON, and E. SAMUEL†

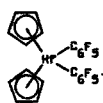
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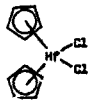
The formation and properties of bis-(π -cyclopentadienyl)-bis-(σ -pentafluorophenyl) hafnium and 5,5-bis-(π -cyclopentadienyl)octafluorodibenzohafnol are discussed

Organotitanium compounds have been widely studied in recent years, primarily in connection with catalytic processes, and an appreciable number of organozirconium compounds have also been described in the literature. In contrast, the organometallic chemistry of hafnium is presently limited to a few π -cyclopentadienyl derivatives of this metal.¹⁻⁸ In this paper, we describe the first organometallic compound containing a carbon-hafnium σ -bond, and the first example of a hafnium-containing metallocycle.

Bis-(π -cyclopentadienyl)-bis-(σ -pentafluorophenyl)hafnium (**1**) was prepared in 16% yield from a reaction between bis-(π -cyclopentadienyl)hafnium dichloride (hafnocene dichloride) (**2**) and pentafluorophenyllithium in ethyl ether, followed by sublimation of the product in high vacuum. As might be expected by analogy to the properties of bis(π -cyclopentadienyl)-bis-(σ -pentafluorophenyl)-zirconium,⁹ **1** appears to be sensitive to moisture. In contrast, the thermal stabilities of both **1** and its zirconium analog are relatively high, since when



1



2

each compound was sealed in a capillary *in vacuo* and heated at 125° for 48 hours, no apparent changes in the color or the melting point of either organometallic compound could be detected.

The mass spectrum of **1** was consistent with the proposed structure, since it exhibited a strong

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molecular ion peak at m/e 643, as well as peaks assignable to $[(C_5H_5)_2Hf(C_6F_5)]^+$ (476), $[(C_5H_5)Hf(C_6F_5)]^+$ (411), and $[(C_5H_5)_2Hf]^+$ (309). Evidence for the moisture sensitivity and partial hydrolysis of **1** prior to the mass spectral determination was also indicated by minor peaks at m/e 493 $[(C_5H_5)_2Hf(C_6F_5)OH]^+$ and 342 $[(C_5H_5)_2Hf(OH)_2]^+$.

The proton NMR spectra of **1**, **2**, and their respective titanium and zirconium analogs are summarized in Table I.

TABLE I

Proton NMR spectra of bis-(π -cyclopentadienyl) derivatives of titanium, zirconium and hafnium

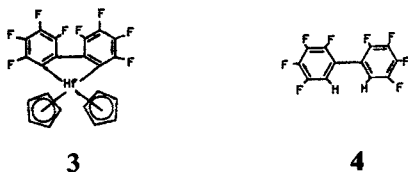
Compound	π -C ₅ H ₅ , Chemical shift and multiplicity*
$(\pi$ -C ₅ H ₅) ₂ TiCl ₂	3.43 (s)
$(\pi$ -C ₅ H ₅) ₂ ZrCl ₂	3.53 (s)
$(\pi$ -C ₅ H ₅) ₂ HfCl ₂	3.63 (s)
$(\pi$ -C ₅ H ₅) ₂ Ti(σ -C ₆ F ₅) ₂	3.50 (t)
$(\pi$ -C ₅ H ₅) ₂ Zr(σ -C ₆ F ₅) ₂	3.56 (s)
$(\pi$ -C ₅ H ₅) ₂ Hf(σ -C ₆ F ₅) ₂	3.63 (s)

* Given in τ p.p.m. units (s = singlet, t = triplet) in CDCl₃ solution relative to tetramethylsilane as internal standard. All spectra were calibrated by imposing side bands of known frequency on tetramethylsilane with an external audio-oscillator.

In contrast to the trends found for the Iron-group metallocenes,¹⁰ the effect of changing the metal from titanium to zirconium to hafnium in each series results in a progressive upfield shift of the π -cyclopentadienyl ring proton resonance. Long-range ¹⁹F-¹H spin-spin coupling, which was noted in the spectra of various (π -cyclopentadienyl)-(σ -pentafluorophenyl)titanium derivatives,¹¹ was

not detected in the present studies (at 60 MHz) on zirconium and hafnium analogs.

A reaction between 2,2'-dilithiooctafluorobiphenyl¹² and **2** afforded the hafnium metallocycle 5,5-bis(π -cyclopentadienyl)octafluorodibenzohafnol (**3**) in 23% yield. Massey and co-workers have synthesized the titanium analog of **3** in a similar manner,¹² and we have likewise been able to extend the reaction to produce the zirconium analog of **3**.¹³



Compared to the σ -bonded organohafnium compound **1** and the zirconium analog of **3**,¹³ metallocycle **3** exhibits enhanced stability towards hydrolysis. It is insoluble in and unreactive to water, even at elevated temperatures. It is stable in air for several weeks, but decomposes slowly to give 2,2'-dihydrooctafluorobiphenyl (**4**) and inorganic materials. The hydrolysis of **3** proceeded more rapidly by dissolving the metallocycle in acetone containing a few drops of water, and then refluxing the mixture for several minutes. Hydrolysis product **4** was identified by its melting point and gas chromatographic retention time compared to an authentic sample.¹²

The infrared spectrum of **4** is identical to that of the titanium and zirconium analogs, and is different from that of **2**. Strong sharp bands attributable to the perfluoroaryl ligand are observed near 1000, 900, 760, and 680 cm^{-1} . Two bands of medium intensity are also present at 1590 and 1610 cm^{-1} .

EXPERIMENTAL SECTION

Hafnium tetrachloride was generously donated by The Carborundum Company, and also purchased from Research Organics/Inorganics Chemicals Corporation. Both samples were over 99% pure on a metal-metal basis. Ethyl ether was predried over sodium wire and distilled from lithium aluminium hydride under nitrogen immediately before use. Tetrahydrofuran was predried over potassium hydroxide and distilled under nitrogen from lithium aluminum hydride immediately be-

fore use. Titanocene and zirconocene dichlorides were obtained from the Arapahoe Chemical Company. Bis-(π -cyclopentadienyl)-bis-(σ -pentafluorophenyl)-titanium and -zirconium were prepared by literature procedures.^{9, 14} All melting points are uncorrected. Elemental analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, New York, and by Mr. Charles Meade of the Microanalytical Laboratory, Office of Research Services, University of Massachusetts.

Bis-(π -cyclopentadienyl)hafnium dichloride

A 250-ml 3-necked flask was equipped with a reflux condenser, addition funnel, nitrogen inlet and outlet, and a mercury check valve. An atmosphere of dry nitrogen was provided throughout the reaction. Freshly distilled cyclopentadiene (10.2 ml, 8.24 g, 125 mmol), dry tetrahydrofuran (150 ml) and a magnetic stirring bar were placed in the flask and were cooled to 0°. *n*-Butyllithium (54.8 ml, 125 mmol) in hexane solution was added over a period of 30 min to the stirred solution. The reaction mixture was then heated to reflux and maintained at this temperature until the evolution of butane had ceased (ca. 45 min). The reaction mixture was again cooled to 0°, hafnium tetrachloride (17.8 g, 55.7 mmol) was added, and the mixture was refluxed overnight. The solvent was removed under reduced pressure to yield a black residue. The use of the protective atmosphere of nitrogen was discontinued at this point. The black residue was air-dried, and subsequently dried under vacuum at room temperature. Sublimation (160–170°, 0.01 mm) produced 10.5 g (50%) of white crystals, mp 230–232°. An analytical sample was prepared by recrystallization of the sublimate from benzene-hexane to produce white needles, mp 231.5–232.5° (lit.¹ 236°).

Anal. Calcd for $\text{C}_{10}\text{H}_{10}\text{Cl}_2\text{Hf}$: C, 31.65; H, 2.65; Cl, 18.68; Hf, 47.02. Found: C, 31.71; H, 2.38; Cl, 18.86; Hf, 46.79.

Bis-(π -cyclopentadienyl)-bis-(σ -pentafluorophenyl)hafnium Pentafluorophenyl-lithium was prepared by the slow addition (ca. 20 min) of *n*-butyllithium (9.0 ml, 20.2 mmol) in hexane to bromopentafluorobenzene (5.0 g, 20.2 mmol) in ethyl ether (25 ml) at -78° . The lithium reagent was transferred to a cooled (-78°) jacketed addition funnel connected to a 250-ml, 3-necked flask containing a magnetic stirring bar. The usual nitrogen inlet-outlet system provided protection from atmos-

pheric oxygen and moisture. The lithium reagent was added over a period of 30 min to a suspension of bis-(π -cyclopentadienyl)-hafnium dichloride (3.80 g, 10.0 mmol) in 100 ml of ethyl ether at 0°. The cooling bath was removed and the reaction mixture allowed to warm to room temperature overnight. The mixture was filtered under nitrogen and the solvent removed under reduced pressure. The white residue was transferred to a sublimator (previously flushed with nitrogen) and dried *in vacuo* at room temperature. Subsequent sublimation of the product at 135° (0.013 mm) produced 0.994 g (16%) of white microcrystals, mp 221–223°.

Anal. Calcd for C₂₂H₁₀F₁₀Hf: C, 41.11; H, 1.57. Found: C, 41.30; H, 1.63.

5,5-Bis-(π -cyclopentadienyl)octafluorodibenzohafnol 2,2'-Dibromooctafluorobiphenyl (2.25 g, 5.0 mmol) in 25 ml of ethyl ether was introduced into a 3-necked flask. The system was purged with nitrogen and cooled in a dry-ice bath. *n*-Butyllithium in hexane (4.5 ml, 10 mmol) was then slowly added through an addition funnel with stirring. The temperature was maintained at -78° during this operation (addition time = 2 h). Bis-(π -cyclopentadienyl)-hafnium dichloride (1.9 g, 5.0 mmol) was dissolved in 15 ml of tetrahydrofuran, the solution placed in the addition funnel, and then very slowly added to the dilithium reagent at -78° (addition time = 2 h). The color turned slowly to gray, then to dark green with separation of a white precipitate. The mixture was stirred overnight at room temperature. The solvent was removed under vacuum and the residue was extracted in a Soxhlet extractor with benzene for several hours. The benzene extracts were concentrated to produce 700 mg (23%) of the product as cream-colored crystals, melting at 325°.

Anal. Calcd. for C₂₂H₁₀F₈Hf: C, 43.68; H, 1.67; F, 25.13. Found: C, 43.54; H, 1.73; F, 24.97.

Mass spectrometry indicated a parent molecular ion of 605 (calcd. 605). The product showed a sharp singlet for the π -cyclopentadienyl protons at τ 3.62 (CDCl₃ solution).

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REFERENCES

1. M. A. Lynch, Jr., and J. C. Brantley, British Patent 785, 760, 1957; *Chem. Abstr.* **52**, 11126e (1958).
2. M. Kh. Minacheva, E. M. Brainina, and R. Kh. Freidlina, *Dokl. Akad. Nauk S.S.S.R.* **173**, 581 (1967).
3. E. M. Brainina, M. Kh. Minacheva, and B. V. Lokshin, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 817 (1968).
4. E. M. Brainina, M. Kh. Minacheva, B. V. Lokshin, E. I. Fedin, and P. V. Petrovskii, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 2492 (1969).
5. M. Kh. Minacheva, E. M. Brainina, and L. A. Fedorov, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 1104 (1969).
6. A. N. Nesmeyanov, R. B. Materikova, E. M. Brainina, and N. S. Kochetkova, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, 1323 (1969).
7. G. W. Watt and F. O. Drummond, *J. Am. Chem. Soc.* **92**, 826 (1970).
8. P. M. Druce, B. M. Kingston, M. F. Lappert, T. R. Spaulding, and R. C. Srivastava, *J. Chem. Soc. (A)* 2106 (1969).
9. M. A. Chaudhari and F. G. A. Stone, *J. Chem. Soc.* 838 (1966).
10. M. D. Rausch and V. Mark, *J. Org. Chem.* **28**, 3225 (1963).
11. M. D. Rausch, *Inorg. Chem.* **3**, 300 (1964).
12. A. G. Massey, S. C. Cohen, D. E. Fenton, and A. J. Tomlinson, *J. Organometal. Chem.* **6**, 301 (1966).
13. M. D. Rausch, H. B. Gordon, and E. Samuel, unpublished studies.
14. P. M. Treichel, M. A. Chaudhari, and F. G. A. Stone, *J. Organometal. Chem.* **1**, 98 (1963); **2**, 206 (1964).