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FORMATION OF A HAFNIUM—TRANSITION METAL BOND; SYNTHESES OF (η^5-C_5H_5)$_2$HfFe(CO)$_4$ VIA NUCLEOPHILIC DISPLACEMENT

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Summary

Reaction of (η^5-C_5H_5)$_2$HfX_2, (X = Cl, I), and Na_2Fe(CO)$_4$ in THF yields (η^5-C_5H_5)$_2$HfFe(CO)$_4$, a dimer containing Hf—Fe bonding. An isocarbonyl is formed as a minor product in the synthesis and also following dissolution of (η^5-C_5H_5)$_2$HfFe(CO)$_4$ in THF. The synthesis, spectra and properties of (η^5-C_5H_5)$_2$HfFe(CO)$_4$ are reported.

Metal—metal bonding has been studied actively for some time now, and most of the transition elements have been shown to form metal—metal bonds. The Group IVB metals are a notable exception; no hafnium to transition metal-bonding compound is known. In fact, no IVB-metal to transition metal compounds have been synthesized via nucleophilic substitution, a common route to metal—metal bonded compounds, and only three have been reported to date; Cp_3MoTi(OR)$_3$ [1], Cp(CO)$_3$MoTiCp_2 [2], and Cp_2CH_3ZrMo(CO)$_3$Cp [3]. Each of these was obtained by a gas elimination reaction typified by that between Cp_2Zr(CH_3)$_2$ and HMo(CO)$_3$Cp, in which CH_4 is eliminated.

In this work the first Hf—transition metal and first iron to IVB metal compound was obtained via reaction 1.

$$n\,Cp_2HfCl_2 + n\,Na_2Fe(CO)_4 \rightarrow [Cp_2HfFe(CO)_4]_n + 2n\,NaCl \qquad (1)$$

As detailed in the Experimental section, reaction of equimolar quantities of Cp_2HfCl_2 and Na_2Fe(CO)$_4$ in THF for three days affords a dark brown, air-sensitive compound (I) in 95% yield. It does not melt, but decomposes at ca. 190°C, producing an orange solid (FeCp_2, also a principal mass spectral product), a black solid (presumably HfC_2), and the gases CO and CO_2. Compound I dissolves in THF, with solvolysis, but is only slightly soluble in diethyl

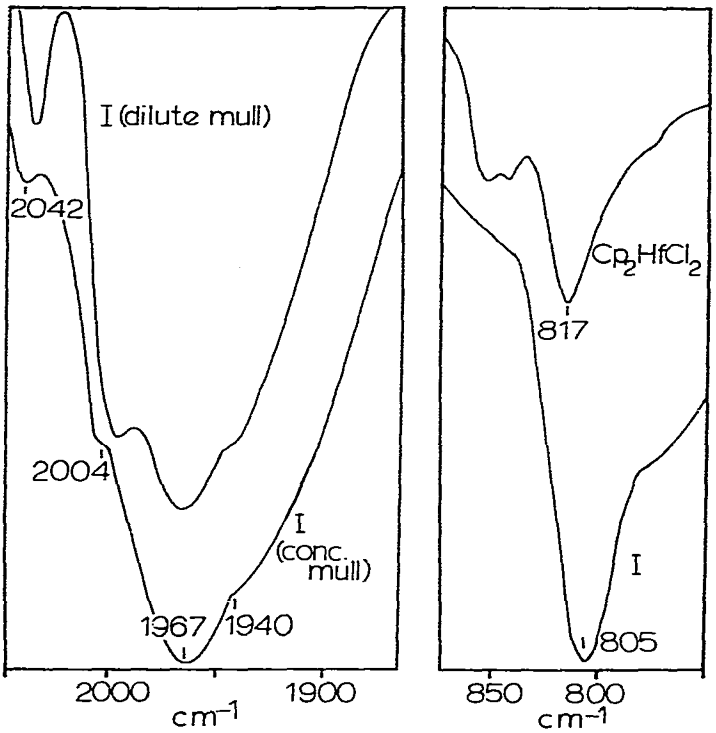


Fig. 1. The infrared spectrum of $[(\eta^5\text{-}C_5H_5)_2HfFe(CO)_4]_2$ (structure I), measured as Nujol mulls in the 1850—2050 cm^{-1} and 750—875 cm^{-1} regions, and (inset) the spectrum of $(\eta^5\text{-}C_5H_5)_2HfCl_2$ in the 750—875 cm^{-1} region.

ether, Et_2O. A minor product (II) was isolated by extracting the reaction products with Et_2O. If pure I is taken up in THF, additional small amounts of II are found in the solid obtained when the solvent is removed.

The elemental analysis shows that I has the empirical formula $Hf_{1.0}Fe_{0.99}C_{13.5}H_{9.6}$, in agreement with that of the postulated product $[(\eta^5\text{-}C_5H_5)_2HfFe(CO)_4]_n$.

The IR spectrum of solid I in Nujol (Fig. 1) clearly indicates the presence of both a metal carbonyl moiety with only terminal CO groups and of an MCp_2 moiety. The Raman spectrum contains intense peaks at 184 and 138 cm^{-1}, which are characteristic of metal—metal bond vibrations and assigned to ν(Hf—Fe) modes.

The four IR bands in the 5-μ region are consistent with a locally C_{2v} $M(CO)_4$ moiety having $(2A_1 + B_1 + B_2)$ ν(CO) modes. Three ν(CO) bands would be expected for a C_{3v} $M(CO)_4$ moiety. No bands for bridging-CO or isocarbonyl-CO stretches are observed for I. The shifts of the IR bands from reactants to product I are consistent with formation of an essentially neutral $Fe(CO)_4$ group covalently bound to $HfCp_2$. Thus, the ν(CO) shift from 1788 cm^{-1} ($Fe(CO)_4{}^{2-}$) to the 1940—2040 cm^{-1} range, indicates removal of electron density from the Fe atom, as expected for a neutral, metal—metal bonded complex. The δ_S(C—H) band of the $(\eta^5\text{-}C_5H_5)$ group, whose frequency is quite sensitive to the charge on the attached metal atom as shown by Fritz [4] and Wailes et al. [5], shifts from 817 to 805 cm^{-1}. This indicates that the positive charge at the Hf atom has decreased from that in Cp_2HfCl_2, and reflects the covalency expected from metal—metal bond formation.

All spectral features indicate that in I $Fe(CO)_4$ moieties (C_{2v}) are metal—metal bonded to $HfCp_2$, but do not directly determine whether I is monomeric or oligomeric. The fact that I is solvolyzed in THF and insoluble in nonpolar solvents suggests that it is oligomeric, but its molecular weight (MW) cannot be determined independently of the solution equilibria in which it participates. Even then, a MW measurement in solution would aid only in finding its base-associated MW.

The spectral properties of I do indicate indirectly that it is oligomeric, and probably dimeric. Thus, an ionic complex, $Cp_2Hf^{2+}\ Fe(CO)_4{}^{2-}$, is ruled out because the ν(CO) bands are much higher than ν(CO) of $Fe(CO)_4{}^{2-}$. A monomeric compound, with bonding analogous to the $B_3M^+\ {}^-Fe(CO)_4$ type discussed by Marks et al. [6], is eliminated because it probably would have only 3 ν(CO) bands resulting from C_{3v} symmetry around Fe. The dark color of I indicates extensive electron-delocalization or low energy charge-transfer. This is consistent with an oligomeric structure, as found in $[CdFe(CO)_4]_4$, for example [7]. However, the ν(CO) IR spectrum of I is much simpler than that of $[CdFe(CO)_4]_4$; it is much more similar to that of $[R_2MFe(CO)_4]_2$ (M = Ge, Sn) [6]. The Raman observation of the two ν(Fe—Hf) bands is consistent with a dimeric structure. On the basis of this and the fact that Hf has a tendency toward tetrahedral bonding, as do Ge and Sn, the dimeric structure shown in Fig. 2 for I is proposed.

The chemistry of I also supports the proposed Hf—Fe bond formation. As in the case of $Cp_2(CH_3)ZrMo(CO)_3Cp$ [3], I reacts rapidly with anhydrous HCl and with BrC_2H_4Br. The reaction with HCl, for instance, yields Cp_2HfCl_2 and $Fe_3(CO)_{12}$, with the $Fe_3(CO)_{12}$ presumed to result from the formation and thermal decomposition of $H_2Fe(CO)_4$.

As noted above, a minor product II forms during the synthesis and in the solid that is obtained after I is dissolved in THF and the THF subsequently removed. Four ν(CO) bands for terminal CO stretches appear in the spectrum of solid II (2073,2039,2003, and 1939 cm^{-1}) as does a sharp band at 1683 cm^{-1}, which is interpreted as being due to formation of an isocarbonyl. Although II has not been fully characterized, its existence and relationship to I is understandable in light of the base (solvent)-induced metal—metal cleavage

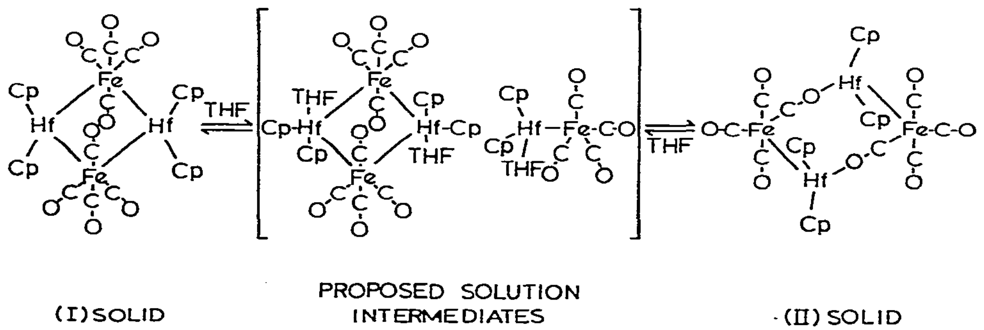
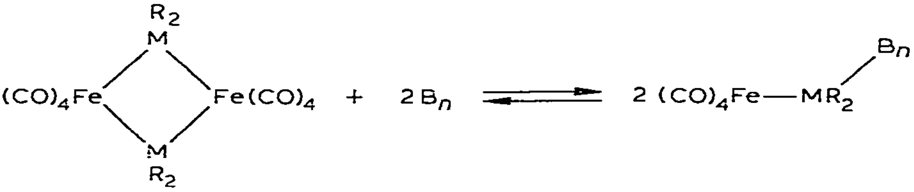


Fig. 2. The proposed structure of $[(\eta^5\text{-}C_5H_5)_2HfFe(CO)_4]_2$ (I), Product II, and the solution species through which they are interconverted.



(2)

reaction of $[R_2MFe(CO)_4]_2$ compounds described by Ernst et al. [6] (eq. 2); and the formation of isocarbonyls with strong Lewis acid centers, shown by Shriver [8,9], for the $AlEt_3$ adduct $Cp_2Fe_2(CO)_4 \cdot 2AlEt_3$, Kotz [10] for $CpMo(CO)_3 \cdot AlMe_3$, and Burlitch et al. [11] $Al[W(CO)_3Cp]_3 \cdot 3THF$. Combining these phenomena in the present case, it is seen that a product with the essential features of II could be obtained via the reaction in Fig. 2.

The isocarbonyl drawn in Fig. 2 not only has the essential ν(CO) features of II, but the δ_S(CH) region of the IR spectrum of II and the presence of a ν(Hf—OC) band are consistent with this structure. The solution spectrum of II does not contain the isocarbonyl band but is consistent with a solvated Hf—Fe bonded complex such as those represented as solution intermediates. Since the CO—Hf bond in II is weaker and more susceptible to solvation than the Fe—Hf bond, it is understandable that I can be placed in THF and removed quickly without extensive formation of II, and that II is an Et_2O and THF-soluble minor product.

In summary, the compound $[Cp_2HfFe(CO)_4]_n$, with a transition metal to Hf bond has been synthesized, and shown to undergo solvolysis and exist in slowly established equilibrium with a compound in which the $Fe(CO)_4$ moiety is joined to Hf through an isocarbonyl linkage. The analogous Zr and Ti compounds also are afforded by this synthetic route and are under study.

Experimental

All procedures were carried out under Ar or in vacuo using dried, degassed solvents. The $Na_2Fe(CO)_4 \cdot 1.5$ dioxane was obtained from Alfa Inorganics, and the Cp_2HfCl_2 was obtained from Aldrich Chemicals. In a typical reaction, 0.393 g of Cp_2HfCl_2 was dissolved in 0.150 l THF to form a colorless solution. To it, a 0.350 l solution of 0.242 g $Na_2Fe(CO)_4 \cdot 1.5$ dioxane in THF was added dropwise with stirring. This produced an immediate color change, and later the solution took on a dark brown-purple color. The reaction was allowed to proceed 3 days. The reaction mixture was filtered, yielding a white solid (NaCl as identified by X-ray diffraction) and a brown-purple solution. The solvent was removed on a rotary evaporator at 25° C and the resulting solid was dried at 45° C in vacuo. This solid was dissolved in 0.03—0.05 l THF and filtered to remove residual NaCl, and the solvent was again removed. The resulting solid was purified by continuous extraction with diethyl ether until the extracting solvent ran colorless. The resulting dark brown compound I obtained in 95% yield, was dried at 45° C in vacuo, recrystallized quickly from a minimum of THF, and dried. The elemental analysis, performed by Dornis and Kolbe (W. Germany), shows I to have the empirical formula $Hf_{1.0}Fe_{0.99}C_{13.5}H_{9.6}$, in agreement with the formula $Hf_1Fe_1C_{14}H_{10}$ expected for (η^5-C_5H_5)$_2$HfFe(CO)$_4$. The minor product II was obtained as the purple solid extracted by Et_2O from the reaction products mixture.

The IR spectra were measured as Nujol and fluorolube mulls and KBr pellets on a Digilab FTS-15B interferometer, and the Raman spectra were measured on a Jarrell-Ash 25-300 spectrometer employing 488.0 nm and 632.8 nm radiation from Spectra Physics 164 Ar^+ and 125 He—Ne lasers. The X-ray powder patterns were measured using a Debye—Scherer camera with Ni-filtered Cu-K_α X-rays.

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References

1 D.J. Cardin, S.A. Keppie, and M.F. Lappert, J. Chem. Soc. A, (1970) 2594.
2 M.F. Lappert and A.R. Sanger, J. Chem. Soc. A, (1971) 1314.
3 P. Renaut, G. Tainturier, and B. Gautheron, J. Organometal. Chem., 150 (1978) C9.
4 H.P. Fritz, Advan. Organometal. Chem., 1 (1964) 240.
5 P.C. Wailes, R.S.P. Coutts, and H. Weingold, Organometallic Chemistry of Ti, Zr, and Hf, Academic Press, New York, NY, 1974.
6 R.D. Ernst and T.J. Marks, Inorg. Chem., 17 (1978) 1477.
7 R.D. Ernst, T.J. Marks, and J.A. Ibers, J. Amer. Chem. Soc., 99 (1977) 2090.
8 N.J. Nelson, N.E. Kime, and D.F. Shriver, J. Amer. Chem. Soc., 91 (1969) 5173.
9 J.S. Kristoff and D.F. Shriver, Inorg. Chem., 12 (1973) 1788.
10 J.C. Kotz and C.D. Turnipseed, Chem. Commun., (1970) 41.
11 R.B. Petersen, J.J. Stezowski, C. Wan, J.M. Burlitch, and R.E. Hughes, J. Amer. Chem. Soc., 93 (1971) 3532.