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Preliminary Note

Metal atom reactions with fluorocarbons.
IV.* Nickel(0) and other transition metal zero-valent complexes with hexafluorobenzene and benzene†

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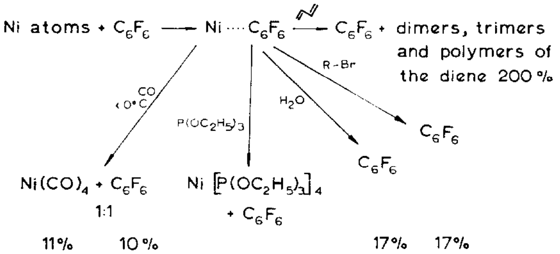
The production and some chemistry of a highly reactive hexafluorobenzene–nickel(0) [HFB–Ni^0] complex together with preliminary investigations of other HFB–M^0 and benzene–M^0 complexes are reported.

Although aryl C–Br and C–I bonds have been found to be susceptible to oxidative insertion by nickel and palladium atoms[1], C–F bonds are not. Thus when nickel atoms react with hexafluorobenzene (HFB), insertion into the C–F bond does not take place, but instead a highly reactive and explosive complex is formed which we have shown to be a Ni^0 compound. Thus the co-condensation of nickel atoms with a high excess of HFB at −196 °C produces a green-black matrix which turns black on warming. If the excess HFB is pumped off, the material left in the reactor has been found to decompose explosively with the slightest provocation (flakes falling to the bottom of the reactor, static charge or uneven warming). On careful even warming, the complex decomposes at *ca.* 70 °C. At room temperature, the matrix reacts explosively with air and most compounds including hydrogen, carbon monoxide, allyl bromide and trifluoromethyl iodide, but the complex did not decompose upon the addition of argon.

The compound has been found to react smoothly with a secondary substrate if it is re-cooled to −196 °C before the substrate is added and then allowed to slowly warm. Some of these reactions are shown below.



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* Reported in part: K. J. KLABUNDE, H. EFNER AND J. Y. F. LOW, *164th National Meeting of Amer. Chem. Soc., Symposium on Fluoroaromatic Chemistry, New York, N.Y.*, August 1972. For Part III see ref. 1.

† For general technique *cf.* P. L. TIMMS, *Advan. Inorg. Chem. Radiochem.*, *14* (1972) 121.

Water and alkyl halides cause decomposition of the complex with the release of HFB. Butadiene is telomerized under very mild conditions (< 40 °C). Both triethylphosphite and carbon monoxide react with the complex to yield HFB and the nickel(0) products shown. Numerous control experiments showed only a very slight reaction of carbon monoxide or triethylphosphite with freshly deposited nickel films under the conditions employed. The percentage yields (*cf.* Table 1, footnote c) shown are quite low due to partial decomposition of the complex on initial warm-up and pump off of excess HFB. If the reactions are carried out on the complex without allowing it to warm above —40 °C, much higher yields result. Thus, $Ni(CO)_4$ and $Ni[P(OC_2H_5)_3]_4$ can be obtained in > 40% yields.

TABLE 1

DECOMPOSITION TEMPERATURES (°C) OF METAL COMPOUNDS WITH HFB AND BENZENE[a,b]

	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
C_6F_6	—50	100	40	—	—40	10	70	*	—
C_6H_6	—50	>300[c]	>300[c]	—	—50	—	—	—	—

[a] (—) indicates no complex formed, or decomposition occurred at very low temperature (< —80 °C).
[b] (*) indicates a red charge-transfer complex formed at low temperature. On pyrolysis a little decafluorobiphenyl was formed.
[c] In these cases the known compounds $(C_6H_6)_2Cr^0$ and $(C_6H_6)_2V^0$ were isolated in *ca.* 60% yields based on metal vaporized. The percentage yields are always corrected for the fact that only about 60 % of the metal vapor reaches the reaction zone.

The isolation and purification of the complex has not been successful due to its insolubility and/or reactivity with organic solvents and its sensitive nature. The Ni–HFB complex is similar to other M–HFB complexes formed by the co-deposition of metal atoms and HFB. In a preliminary study, HFB and benzene have been allowed to react with the metals shown in Table 1 and their approximate thermal stabilities are indicated*.

There is an interesting trend shown in the table. The early transition metals such as chromium and vanadium form more stable complexes with benzene and the stability of these bis-arene complexes are increased by electron-donating substituents such as methyl groups[2]. On the other hand, HFB complexes with the later transition metals are more stable than the benzene complexes. This stability trend might be explained in the following way. In the metals with low d-electron populations (vanadium and chromium), added stability is gained by the increased donation of electron density from the populated π-bonding orbitals of the aromatic systems into the unoccupied orbitals of the metal. In the later transition metals

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* It is possible for these decompositions to occur at lower temperatures, especially if large amounts of complexes are present (personal discussions with P. L. Timms).

with high d-electron populations (cobalt and nickel), complex stability is increased by back-donation into the π^* antibonding orbitals, and the π^* orbitals of HFB would be expected to be better acceptors than the π^* orbitals of benzene[3].

Decomposition of the HFB–M complexes always occurs extremely violently with an explosive flash. This must be due to the very exothermic formation of M–F bonds on decomposition. The benzene–M complexes decompose rapidly in some cases but without such violent explosions.

Timms has previously reported that the metal-atom technique can be used to synthesize $(C_6H_6)_2Cr$ in good yields[4] and Skell and co-workers have also been able to carry out the same synthesis along with some substituted benzene Cr^0 derivatives[5]. However, our work shows the first example of using the technique for synthesizing benzene complexes of V as well as Cr. Thus, we have produced and isolated complexes of these metals with C_6H_6, C_6H_5F, C_6H_5Cl, $C_6H_5CF_3$ and others. Details of these syntheses will be reported at a later date.

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