

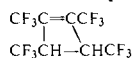
Table I. Spectroscopic Data for M-HFB and M₄(CO)₄(HFB)₃ Complexes

complex	$\nu_{C\equiv C}$, cm ⁻¹	$\nu_{C=O}$, cm ⁻¹	¹⁹ F NMR (up- field from CFCl ₃)	IR, cm ⁻¹
Ni ₄ (CO) ₄ - (HFB) ₃	1570 1552	2120 2110	cf. ref 6, 7	2120 (vs), 2110 (vs), 1570 (s), 1552 (s), 1263 (m), 1240 (s), 1225 (s), 1207 (vs), 1170 (vs), 1155 (vs), 925 (w), 813 (w), 673 (m), 650 (w) (hexane solution)
Pd ₄ (CO) ₄ - (HFB) ₃	1600	2138 2122	(acetone) multiplet 56.2 ppm	2138 (vs), 2122 (vs), 1600 (s), 1232 (s), 1203 (vs), 1180 (s), 1170 (sh), 920 (w), 645 (m) (hexane solution)
Ni-HFB	1695		(acetone) broad singlet 57.0 ppm, singlet 52.1 ppm [(CF ₃) ₆ C ₆]	1695 (s), 1260 (m), 1223 (vs), 1195 (vs, broad), 1020 (sh), 800 (m) (Nujol)
Pd ₂ (HFB) ₂	1675		(acetone) multiplet 56.2 ppm, singlet 51.5 ppm [(CF ₃) ₆ C ₆]	1675 (s), 1190 (s, broad), 802 (w) (Nujol)
Pt _x (HFB) _y	1735			1735 (s), 1352 (s), 1330 (s), 1290 (m), 1246 (s), 1120 (m), 800 (m) (Nujol)
(Au) _x (HFB) _y	1725			1725 (s), 1460 (w), 1260 (vs), 1138 (vs), 1030 (s), 854 (m), 795 (s) (neat)
(Ge) _x (HFB telomer)	1715	(acetone) broad s, 55.7 ppm, area 8 s, 63.0 ppm, area 1		1715 (s), 1450 (w); 1275 (vs), 1190 (vs), 1010 (w), 900 (m), 710 (w), 617 (w) (KBr pellet)

Table II. Product Yields from HCl Decompositions of Ni-HFB and Pd-HFB Complexes

metal	MCl ₂ ^b	products ^a		
		<i>cis</i> - CF ₃ CH= CHCF ₃ ^c	<i>trans</i> - CF ₃ CH= CHCF ₃ ^c	C ₈ F ₁₂ H ₂ ^{c,d}
Ni	19	11	1.3	7.6
Pd	31	6.2	8.3	8.4

^a % yields based on metal vaporized. ^b Determined by addition of PEt₃, extraction, and recrystallization of MCl₂(PEt₃)₂. ^c Determined by total PV measurements in combination with GLC studies and mass spectral studies of materials collected during the GLC traces. ^d A partially reduced dimer of HFB. It is probably the cyclic dimer



substance in the vacuum system. This substance was the same as the large portion of hexane-soluble red-brown material removed from the reactor and crystallized from hexane. Elemental analysis indicated the product to be Pd₄(CO)₄(HFB)₃, but molecular weight (osmometry in acetone) indicated a Pd₄(CO)₄(HFB)₂ formula. IR and NMR studies showed close similarities to the analogous Ni₄ cluster. Attempts to correlate the molecular weight (found) of 855 with the elemental analysis did not yield reasonable structures, and it seems likely that in acetone solution one HFB ligand is dissociated at least partially (mol wt HFB = 162 + 855 = 1017; Pd₄(CO)₄(HFB)₃ requires 1021).

The formation of the Pd₄ cluster is a slow process and only occurred in toluene or alkane solutions, not in acetone. If the Pd-HFB-CO matrix after warmup was immediately washed with acetone, the material taken up was not in the form of a cluster. Molecular weight studies in freezing acetophenone indicated a molecular weight (found) of 260, which is somewhat lower than that expected for Pd(CO)₂(HFB) (mol wt 324).

Palladium with HFB (no CO) yielded a labile complex that was moderately soluble in toluene and very soluble in acetone (purple solution). The compound in toluene solution or as a solid readily yielded C₆(CF₃)₆ as a decomposition product. However, with immediate acetone wash, the products could be taken up in the absence of C₆(CF₃)₆ (as determined by IR). Furthermore, by dissolving in acetone followed by vacuum removal of all volatiles and then pyrolysis of the powder, HFB, (CF₃)₆C₆, and acetone were evolved in comparable amounts. Molecular weight studies and HCl decomposition studies (cf. Table II) indicated an apparent formula of Pd₂(HFB)₂(solvent).

Pt, Cu, Au HFB/CO. The metals Pt, Cu, and Au all formed moderately stable, soluble, darkly colored HFB complexes. The complexes did not take up CO under the same conditions that Ni and Pd-HFB complexes did. These materials also decomposed to yield C₆(CF₃)₆ and metal in several hours at room temperature.

Ge, Sn HFB. Germanium deposited with HFB yielded an amber matrix that remained amber upon warming. This material was insoluble in pentane or toluene, but soluble in acetone and upon standing for several hours in acetone yielded a precipitate (not C₆(CF₃)₆) through slow decomposition. The amber substance was air sensitive in solution and melted over a broad range near 150 °C with darkening. ¹⁹F NMR yielded two broad resonances at 63.0 and 55.7 ppm upfield from CFCl₃. Infrared analysis showed $\nu_{C\equiv C}$ at 1710–1720 cm⁻¹. Mass spectral analysis yielded only ions resulting from decomposition during heatup, some of which contained Ge. Decomposition with HCl yielded two organic products, HFB (17%) and C₈F₁₂H₂ (83%), but a M:organics ratio was not obtained owing to the complexity and nonquantitative nature of the HCl reaction. Analysis of the compound yielded C₁₁H₆F₁₂OGe₃, which is close to [Ge₃(HFB)₂(acetone)]_n.

Tin vapor with HFB yielded a dark brown, acetone-soluble material that decomposed at ~150 °C, was very air sensitive, and slowly decomposed (3 h) in acetone or the solid state, $\nu_{C\equiv C}$ at 1700 cm⁻¹.

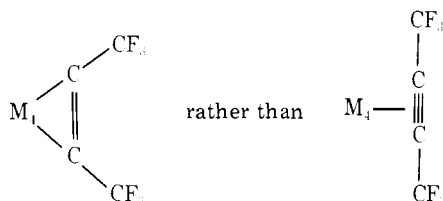
Other metals Al, In, Zn, Pb, and Sb yielded no apparent reaction or products when condensed with HFB.

Germanium cocondensed with 2-butyne or 1-propyne yielded high polymers incorporating some Ge. These polymers were resistant to concentrated HCl and room temperature aqua regia, and insoluble in all common organic solvents.

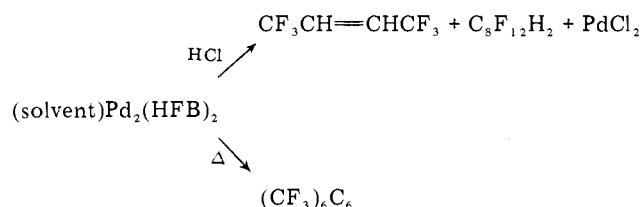
Discussion

The $\text{Pd}_4(\text{CO})_4(\text{HFB})_3$ cluster is similar to the analogous Ni_4 cluster in that it is thermally sensitive with CO loss occurring readily. No sensible mass spectrum could be obtained (mass spectrometric studies of the Ni_4 cluster initially led to a $\text{Ni}_4(\text{CO})_3(\text{HFB})_3$ formulation⁶). In the IR, $\nu_{\text{C}=\text{O}}$ frequencies (Table II) are slightly lower for the Ni_4 compound indicating a slightly stronger Ni–CO interaction than for Pd–CO. The same trend is observed in comparing $\nu_{\text{C}\equiv\text{C}}$ for these compounds. Thus, as would be expected, Ni donates better to the π^* orbitals of CO and HFB than Pd. This stronger binding to Ni explains our qualitative observation concerning the greater stability and lifetime of $(\text{HFB})\text{Ni}(\text{CO})_2$ vs. $(\text{HFB})\text{Pd}(\text{CO})_2$, and the tendency of $\text{Pd}_4(\text{CO})_4(\text{HFB})_3$ to dissociate in solution.

For these compounds the observed $\nu_{\text{C}\equiv\text{C}}$ frequencies are so low that the bonding should be considered more σ in character than π :



The very strong bonding interaction of HFB alone is striking, and HFB is certainly an excellent π -acid ligand, comparable to CO and in some respects superior to CO, especially for the heavy metals. Thus, we find that HFB formed room temperature stable, but labile complexes with a variety of d-electron-rich metals including Co, Ni, Pd, Pt, Cu, and Au. However, we were very surprised at the apparent stoichiometries of M:HFB of 1:1 for Ni and Pd. We cannot speculate as to the bonding in these compounds, but in the solid form surely they must be bridging or telomerized to satisfy open coordination sites, as well as cause them to be nonvolatile. Similarities to the recently described bis(diphenylacetylene)platinum(0) complex⁸ are apparent, although stoichiometries are somewhat different. Also, in our system the HCl decomposition studies indicate that HFB and/or HFB dimer could be involved as ligands (however, the dimerization could have been induced upon HCl addition). We do not believe that HFB trimer $[(\text{CF}_3)_6\text{C}_6]$ binds to Ni or Pd since we have not observed it as a product in the HCl studies. It is formed by thermal decomposition, however, and it seems likely that once formed it dissociates from the metal center.



It is instructive to compare the spectral data for the Ni, Pd, Pt, and Au HFB complexes (Table II). The strength of the bonding interaction, as measured by the lowering of the $\nu_{\text{C}\equiv\text{C}}$ stretch, is in the order $\text{Pd} \gtrsim \text{Ni} > \text{Au} \gtrsim \text{Pt}$. Thus, Ni and Pd interact strongly while Pt and Au less strongly. Since the Pt and Au complexes do not take up CO, it would appear that the

metals that strongly bind CO will also strongly bind HFB.⁹ However, HFB can stabilize some metals in atomic or small cluster form more effectively than CO!

In the main group series, the metals Ge and Sn interact with HFB apparently by radical pathways, rather than by simple coordination. This is not surprising since the ground 3p electronic state ($:\dot{\text{Ge}}$) would be expected to react through radical pathways.¹⁰ Thus, onset of polymerization takes place with Ge–HFB and Sn–HFB system, and total polymerization occurs with Ge–2 butyne and Ge–propyne, and in the latter cases very high molecular weight polymers incorporating some Ge were formed. However, the polymerization is very sensitive sterically since we found that 3-hexyne did not polymerize with Ge. And in the case of HFB, some polymerization occurs, but not to the extent with 2-butyne or 1-propyne, and a large amount of Ge is incorporated, analysis indicating $\text{Ge}_3(\text{HFB})_2$ ratios.

Experimental Section

Analytical Methods. Elemental analyses were performed by Dornis and Kolbe, 433 Mulheim a, d, Ruhr, Hohenweg, West Germany (samples were manipulated under argon). Osmometric molecular weight studies were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich. Molecular weight determinations performed in our laboratory were done by a freezing point depression method as described by Reilly and Rae¹¹ with modifications employing continuous automatic mechanical stirring and continuous slow N_2 flush. All solutions were prepared using deoxygenated solvents in a Vacuum Atmospheres inert atmosphere (N_2) box.

Solvents. Pentane and hexane were shaken with KMnO_4 solution and concentrated H_2SO_4 , washed with water, dried over CaCl_2 , and then continually refluxed over benzophenone ketyl under N_2 so that fresh dry, deoxygenated samples were always available for immediate use. Toluene was also continually refluxed over benzophenone ketyl. Acetone was dried over CaSO_4 and continuously refluxed under N_2 over CaSO_4 .

Metal Atom Apparatus. Our simple synthetic scale reactors have been described previously.¹² The metals Co, Ni, Pd, Cu, Au, Ge, and Sn were all vaporized by resistive heating of Al_2O_3 –W intergral crucibles (Sylvania Emissive Products, CS-1002A, power input about 6 V, 65 A). Pt was vaporized directly from a thick W wire. These reactors are now available commercially from Kontes–Martin Glass Co.

Preparation of $\text{Ni}_4(\text{CO})_4(\text{HFB})_3$. Hexafluoro-2-butyne (HFB) (from PCR, Inc.) was distilled into a 2-L bulb, degassed, and placed on the metal atom reactor system. In 45 min 90 mmol of HFB was codeposited with 0.26 g of Ni (4.50 mg-atoms) at -196°C resulting in a dark purple-black matrix. While still at -196°C , 600 mm of CO was inletted, the liquid nitrogen removed, and the reactor allowed to slowly warm while maintaining the overall pressure at about 600 mm by intermittent and rapid opening of the vacuum system to the pump through a -196°C cold trap. Magnetic stirring was continued throughout the experiment. The excess HFB slowly moved out of the reactor to the cold trap, and when the reactor had reached about -10°C , the liquid HFB had disappeared. Then with two -196°C cold traps in series to condense all HFB, the CO was slowly pumped out. **Caution—vent vacuum pumps to a good hood.** An orange-brown, volatile material pumped over. After the excess HFB was fractionated away, this orange-brown product distilled around the vacuum system for a short while before it spontaneously formed a red-brown solid, $(\text{Ni}_4(\text{CO})_4\text{HFB})_3$. This product was taken up in hexane and crystallized.

The nonvolatile reactor contents were washed with two 20-mL portions of dry, deoxygenated hexane, combined, and filtered and the product was crystallized from hexane yielding the major portion (80%) of $\text{Ni}_4(\text{CO})_4(\text{HFB})_3$ (0.19 g, 20% based on Ni vaporized/4). For spectra cf. Table I.

Preparation of $\text{Pd}_4(\text{CO})_4(\text{HFB})_3$. The above procedure was followed, and 90 mmol of HFB was codeposited with 1.0 g of Pd (9.6 mg-atoms) yielding a very small amount of volatile brown organometallic which moved under vacuum to a cold trap and there spontaneously formed $\text{Pd}_4(\text{CO})_4(\text{HFB})_3$. A large amount of red-brown solid was left behind in the reactor, and was washed thoroughly with vigorous stirring with

three 20-mL portions of dry, deoxygenated hexane; these were combined and filtered under N_2 , the hexane was reduced under vacuum to about 15 mL, and the product was crystallized as a dark red-purple solid (0.23 g, 10% based on Pd vaporized/4), mp 90–92 °C (darkens ~80 °C). Anal. Calcd for $Pd_4(CO)_4(HFB)_3$: C, 18.7; F, 33.4. Found: C, 17.84; F, 33.42. For spectra cf. Table I. Mol wt (osmometry in acetone) 855.

Preparation of Ni–HFB–Solvent Complex. In a 1.5-h period 25 mmol of HFB and 0.423 g (7.22 mg-atoms) of Ni were codeposited at –196 °C followed by slow warming and vacuum removal of excess HFB. The resulting purple-black residue was washed with 20 mL of dry, deoxygenated acetone and filtered under N_2 , followed by solvent reduction and drying under vacuum. These manipulations should be completed as rapidly as convenient to avoid excessive formation of $(CF_3)_6C_6$. Mol wt (in freezing acetophenone, average of several determinations) 374. For spectra cf. Table I.

Preparation of $(Pd)_2(HFB)_2$ –Solvent. In a 2-h period 30 mmol of HFB and 0.455 g (7.74 mg-atoms) of Pd were codeposited at –196 °C followed by slow warming and vacuum removal of excess HFB. The resulting purple-black residue was washed with three 20-mL portions of dry, deoxygenated acetone and filtered under N_2 followed by solvent reduction, crystallization, and drying under vacuum. These manipulations should be completed in 1 day, and the sample stored under N_2 in a refrigerator, to avoid excessive formation of $(CF_3)_6C_6$. Mol wt (in freezing acetophenone, average of several determinations) 580. For spectra cf. Table I.

Preparation of Co, Pt, Cu, and Au HFB Complexes. Procedures analogous to those given for Ni–HFB and $Pd_2(HFB)_2$ were employed. Spectra are given in Table I.

HCl Decompositions of Ni–HFB and Pd–HFB Complexes. The M–HFB complexes were prepared as described above, but no solvent was added. Instead 380 mm of dry HCl was inletted on the samples in the metal atom reactor, and with magnetic stirring the reactor contents was allowed to stand for 3 h. Then the volatiles were slowly fractionated through pentane slush (–131 °C) and then liquid N_2 (–196 °C) cold traps. The pentane slush trap contained the $CF_3CH=CHCF_3$ and $C_8F_{12}H_2$, and these were separated and their relative amounts determined on a 10-ft SE-30 GLC column operating at 25 °C and 60 mL/min He flow. They were collected and IR and MS studies carried out: $CF_3CH=CHCF_3$ (cis); IR (gas) cm^{-1} 1425 (s), 1330 (vs), 1170 (s); mass spectrum m/e (%) 164 (5), 145 (15), 95 (98), 69 (100), 51 (10), $CF_3CH=CHCF_3$ (trans); mass spectrum m/e (%) 164 (13), 145 (32), 95 (93), 44 (100), $C_8F_{12}H_2$; IR (gas) 2990 (vs), 1950 (w), 1340 (vs), 1270 (vs), 1155 (vs, broad), 1030 (m), 900 (vs, broad), 820 (vs); mass spectrum m/e (%) 326 (2), 307 (7), 257 (15), 219 (4), 207 (6), 169 (9), 119 (9), 116 (7), 115 (6), 113 (6), 96 (59), 81 (100), 69 (27), 47 (92).

The MCl_2 left in the metal atom reactor was allowed to react with PEt_3 by inletting 2 mL of PEt_3 under vacuum followed by standing for 3 h. The excess PEt_3 was removed under vacuum, and the residue

washed exhaustively with several 20-mL portions of solvent followed by solvent reduction and crystallization of $MCl_2(PEt_3)_2$ (for Ni washed and crystallized from 1-butanol and for Pd washed and crystallized from hexane. For results cf. Table II).

Ge–HFB. In a 1-h period 25 mmol of HFB was codeposited with 0.221 g (3.04 mg-atoms) of Ge to yield an amber matrix at –196 °C. Warming and vacuum removal of excess HFB left an amber solid. Direct removal of this solid was accomplished by disassembling the reactor within a N_2 -filled glovebag with good N_2 flushing, and scraping the product. Table I lists the IR data for this solid.

The amber solid could also be dissolved in acetone under N_2 and removal by syringe followed by filtration, solvent reduction, and crystallization (powder) at –78 ° (cf. Table I for ^{19}F NMR). Anal. Calcd for $[Ge_3(HFB)_2(acetone)]_n$: C, 22.0; H, 1.00; F, 38.1. Found: C, 22.95; H, 1.10; F, 36.25. Molecular weight studies were not carried out because of continuous decomposition problems.

Acknowledgments. Support of the National Science Foundation (CHE-7402713) is acknowledged with gratitude. We also thank Dr. Alan Wilks of UOP Corp. for stimulating discussions.

References and Notes

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