and hexane. It was then dissolved in 15 mL of benzene and the solution was filtered. Addition of hexane and cooling to 0° C gave dark red crystals: yield 0.3 g (45%); 210 °C dec (DTA); ^{31}P NMR (C_6D_6) δ 32.06 (s). Anal. Calcd for $C_{60}H_{48}P_4Pd$: C, 72.10; H, 4.84; Pd, 10.64. Found: C, 72.04; H, 4.95; Pd, 10.45.

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Registry No. 1, 85318-45-2; 2, 85318-46-3; 3, 85318-47-4; 4, 85318-48-5; 5, 85318-49-6.

Supplementary Material Available: Listing of the structure factors for 4 (20 pages). Ordering information is given on any current masthead page.

Reactions of Nickel Atoms with Substituted Ethylenes

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Nickel atoms have been codeposited with substituted ethylenes at −196 °C in an attempt to synthesize new organometallics capable of depositing metallic films at moderate temperatures. Thermally unstable homoleptic nickel–olefin complexes with the stoichiometry $Ni(olefin)_3$ were formed, but not isolated. Reaction of these complexes with trifluorophosphine at low temperatures led to the partial displacement of olefin and the isolation and characterization of three new $(PF_3)_3Ni(olefin)$ compounds. The $(PF_3)_3Ni(olefin)$ compounds were found to decompose between −16 and +6 °C to give $Ni(PF_3)_4$, olefin, and nickel metal.

The decomposition of organometallic compounds by pyrolytic[1] and photolytic[2,3] techniques has received considerable attention as a method of depositing metallic films. Both of these approaches have inherent disadvantages associated with the inclusion of impurities in either the film structure, the substrate, or both. We have recently been interested in the synthesis of new organometallics with moderate thermal stability that can be decomposed controllably at relatively low temperatures (e.g., below 100 °C) to produce metallic films. This paper describes our attempt to use the metal-vapor technique to synthesize such compounds containing nickel.

The importance of metal-vapor chemistry in organometallic syntheses has been discussed in detail in recent review articles.[4,5] In addition to its direct synthetic utility, it has also been combined with matrix isolation techniques in spectroscopic studies to suggest new, potentially fruitful areas for synthesis work. For example, the low-temperature optical spectra of homoleptic nickel–olefin complexes have led Ozin and Power to propose that such complexes might be stable enough for macroscale syntheses.[6] We have investigated some of these systems further to determine their suitability as synthetic reactions.

Experimental Section

General Data. The metal-atom vapor apparatus is similar to that described in detail elsewhere.[7] Vacuum system manipulations were carried out in a Pyrex system with greaseless Kontes glass/Teflon valves. Routine infrared spectra were recorded on a Perkin-Elmer 457 spectrometer using a 5-cm glass cell with KBr windows. Attempts to obtain infrared spectra of isolable, but thermally unstable, products were made by using a Digilab FTS-15C Fourier transform interferometer. NMR spectra were recorded on a Varian EM-390 spectrometer operating at 90 MHz for proton and 84.68 MHz for fluorine nuclei and equipped with an EM-3940 variable-temperature accessory calibrated with a methanol sample.

Propene, vinyl chloride, and vinyl fluoride were obtained from Matheson Gas Products and used as received. Trifluoropropene, fluorobenzene, trifluoromethylbenzene, *m*-bis(trifluoromethyl)benzene, and hexafluorobenzene were purchased from PCR and used without further purification. The arenes were stored under vacuum over activated 4A molecular sieves. Trifluorophosphine was obtained from Ozark-Mahoning and purified by vacuum distillation through a −160 °C trap.

Reactions of Ni Atoms with Olefins. The same general procedure was followed in all reactions of nickel atoms with olefins and will be described in detail for the reaction with trifluoropropene. Nickel metal (6.27 mmol) was vaporized under a dynamic vacuum from a tungsten/alumina crucible and codeposited over 1.75 h with trifluoropropene (47.38 mmol) at liquid-nitrogen temperatures to form a dark brown matrix. At this point, the reactor was closed off and the liquid nitrogen removed to allow gradual warming. When the matrix melted, streaks of brown liquid collected in the bottom of the reactor which was then immersed in a toluene slush bath at −96 °C. After 15 min, the reactor was opened to a trap at liquid-nitrogen temperatures, and the volatile material was collected during a 1.25 h period. The −96 °C bath was then removed and the reactor allowed to warm gradually to ambient temperatures with any remaining volatile materials bring collected in a separate trap at −196 °C. The volatile materials collected at −96 °C (35.88 mmol) and between −96 °C and ambient (10.37 mmol) were identified as trifluoropropene.

Synthesis of $(PF_3)_3Ni(FCH{=}CH_2)$. The reaction of nickel vapor with $FCH{=}CH_2$ and PF_3 described here was representative of those reactions involving other olefins. Nickel metal (2.79 mmol) was vaporized and codeposited with $FCH{=}CH_2$ (41.53 mmol) at liquid-nitrogen temperatures during 1.5 h. The reactor was closed off and the dark brown matrix warmed slightly until it melted producing streaks of brown liquid that collected at the

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bottom of the reactor. A toluene slush bath at -96 °C was placed around the reactor for 0.5 h before the reactor was opened to a trap cooled to -196 °C, and the volatile materials were collected during a 1-h period ($FCH{=}CH_2$, 35.38 mmol). The reactor was again cooled to -196 °C and PF_3 (18.34 mmol) added. After this mixture was allowed to stand for 0.5 h at -96 °C, materials that were volatile at this temperature were collected in a separate trap. The toluene slush was removed and the reactor warmed gradually to ambient temperatures as additional volatile materials were collected at -196 °C.

The materials obtained from the reactor at -96 °C after PF_3 was added were separated by fractional condensation through traps at -160 and -196 °C. The -196 °C fraction was identified as PF_3 (14.13 mmol) and that at -160 °C as $FCH{=}CH_2$ (2.89 mmol).

A chlorobenzene slush bath at -45 °C was placed around the trap containing volatile materials collected on warming the reactor from -96 °C to ambient, and the more volatile components were transferred to another trap at -196 °C. Separation of this latter material by fractional condensation using traps at -96 °C and -196 °C produced $FCH{=}CH_2$ (2.85 mmol) and $Ni(PF_3)_4$ (0.69 mmol). The $Ni(PF_3)_4$ was identified by gas-phase molecular weight measurements (407.7 vs. 410.6 calcd) and its infrared spectrum.[8]

The clear yellow liquid (106.1 mg) remaining in the trap at -45 °C was transferred *in vacuo* to a tared vessel at -196 °C and warmed to ambient conditions. Within 1-2 min, a black deposit and fine black particles were visible. This was followed by the slow formation of a reflective metallic coating over the walls of the vessel. After being left at ambient conditions for nine days, the volatile materials were transferred to the vacuum system and separated by fractional condensation using traps at -96 and -196 °C to yield $FCH{=}CH_2$ (-196 °C, 0.27 mmol) and $Ni(PF_3)_4$ (-96 °C, 0.22 mmol); the weight of the tared vessel increased by 2.4 mg. The molecular stoichiometry determined from the decomposition products was $Ni_{1.0}(PF_3)_{3.4}(C_2H_3F)_{1.0}$ which corresponded to a 10.3% yield based on the amount of nickel metal evaporated.

Results and Discussion

Reactions of Ni Atoms with Olefins. Nickel atoms were cocondensed at -196 °C with an excess (usually 10:1 or greater) of various substituted ethylenes, $XCH{=}CH_2$ where X = Cl, F, CF_3, and CH_3 to give dark brown matrices. The volatile materials collected at various stages during the warmup of these matrices provided evidence for the formation of nickel-olefin complexes on a macrosynthetic scale. All complexes proved to be thermally unstable and decomposed well below ambient temperarures, thus discouraging attempts to isolate them directly. However, indirect evidence for their existence was obtained by collecting significant quantities of each olefin (3-10 mmol depending on the amount of nickel evaporated) after removal of the excess ligand at low temperatures and subsequent warming of the reaction mixture to ambient. This is similar to the method used by Klabunde and coworkers to identify unstable Pd(olefin)$_3$ intermediates in reactions of palladium atoms with perfluoroolefins.[9] The nickel-olefin stoichiometry could not be determined directly in our work because of the nature of metal-vapor experiments in which some metal was effectively lost in coating parts of the reactor during varporization. However, on the basis of experiments in which PF_3 displaced some of the olefin, as discussed below, we have concluded that the majority of the materials were present as the π-bonded tris(olefin) complexes as suggested by the spectroscopic studies of Ozin and Power[6] and found by Wilke for the ethylene compound.[10]

Thermal stabilities of the complexes varied according to the olefin substituent. The vinyl chloride and fluoride materials proved to be the least stable, decomposing between -96 and -45 °C, whereas those of propene and trifluoropropene decomposed slowly at -45 and -30 °C, respectively. Nonvolatile materials remaining in the reactor were analyzed qualitatively only in the case of the vinyl chloride complex which could not be trapped with PF_3 (see below). In this instance, the residue gave positive tests for chloride and nickel ions, suggesting the formation of nickel chloride, presumably via a decomposition route involving oxidative insertion of nickel atoms into the C-Cl bonds at some point. It should be noted that Ozin and Power found no evidence for this behavior in smaller scale matrix experiments at temperatures up to -48 °C.[6] None of the complexes investigated here proved to be as stable as tris(ethylene)nickel which was reported to exist up to 0 °C.[10] The reason for this difference in behavior is not readily apparent and will require additional experimental and theoretical work.

Reactions of Ni Atoms with Olefins and PF_3. Nickel atoms were cocondensed with the particular olefin at -196 °C, and the matrix was warmed to -96 °C where the excess olefin was removed. Upon recooling to -196 °C, PF_3 was added to the reactor, and the contents were warmed to -96 °C again where the volatile materials were collected and separated. In all cases except vinyl chloride, further warming to ambient conditions produced a volatile liquid that decomposed below ambient temperatures to yield nickel films and volatile decomposition products consisting of $Ni(PF_3)_4$ and the olefin.

Trifluorophosphine was chosen as the trapping ligand in these systems primarily for two reasons. First, being a good π acceptor and a rather weak σ donor, it would be expected to impart some degree of stability to the metal-olefin bond without displacing the olefin from the nickel entirely. Second, because of the high volatility of PF_3, it was likely that any product containing it would also be volatile; this would facilitate handling if the product proved to be unstable.

The effect of adding PF_3 to the preformed nickel-olefin complex at -96 °C was to displace some, but not all, of the olefin. Yields based on the amount of nickel evaporated ranged from 10 to 38% and, as often happens in metal-vapor reactions, appeared to be dependent on the rate of evaporation of the nickel. In general, the molar quantities of PF_3 consumed were substantially more than the olefin displaced, with most values of the PF_3:olefin ratio falling between 1.75 and 1.45. If the complexes most likely to be present under these reaction conditions were the bis- and tris(olefins), then the subsequent reaction with PF_3 to form a PF_3-nickel-olefin complex would be described by one of the equations (1)-(4). The experimental data are in

$$\mathrm{Ni(olefin)_2 + 2PF_3 \rightarrow (PF_3)_2Ni(olefin) + 1\,olefin} \quad (1)$$

$$\mathrm{Ni(olefin)_2 + 3PF_3 \rightarrow (PF_3)_3Ni(olefin) + 1\,olefin} \quad (2)$$

$$\mathrm{Ni(olefin)_3 + 2PF_3 \rightarrow (PF_3)_2Ni(olefin) + 2\,olefin} \quad (3)$$

$$\mathrm{Ni(olefin)_3 + 3PF_3 \rightarrow (PF_3)_3Ni(olefin) + 2\,olefin} \quad (4)$$

closer agreement with the 3:2 ratio shows in (4), suggesting the formation of an original tris(olefin) complex that was converted to an 18-electron compound upon reacting with PF_3. Presumably, the olefin remained π bonded to the nickel, making it effectively four-coordinate, although this was not confirmed by infrared spectra due to the low thermal stabilities as indicated below. Although the L_3Ni(olefin) stoichimetry is somewhat unusual in comparison to that of the more commonly found 16-electron

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Table I

	δ_{H}[a]	δ_{F}[b]	$J_{H\text{-}F}$[c]	$J_{P\text{-}F}$[c,d]
PF_3		33.3		1418
$FCH{=}CH_2$	5.93,[e] 5.33, 3.48	115.7	85 (gem) 35 (trans) 20 (cis)	
$(PF_3)_3Ni(FCH{=}CH_2)$[f]	6.20,[e] 2.75 (2.2) (1.0)	21.3, 134.8 (9.6) (1.0)	74	1284
$CF_3CH{=}CH_2$	4.47, 4.12[e]	68.6	4	
$(PF_3)_3Ni(CF_3CH{=}CH_2)$[f]	6.38,[g] 5.67[g] (2.0) (1.0)	20.8, 63.0 (3.0) (1.0)		1305
$CH_3CH{=}CH_2$	8.35,[e] 5.07,[e] 4.23[g]			
$(PF_3)_3Ni(CH_3CH{=}CH_2)$[f]	8.25,[h] 6.32,[g] 5.15[g] (3.0) (2.0) (1.0)	20.3		1270
$Ni(PF_3)_4$[f]		16.9		1316

[a] ^{1}H chemical shifts are relative to internal Me_4Si at $\tau = 10$. Sample concentration is 15-20 mol %. [b] ^{19}F chemical shifts are upfield relative to external CCl_3F. [c] Coupling constants are expressed in Hz. [d] Measured between the most intense peaks of the multiplets. [e] Chemical shift of center peak in multiplet. [f] Spectra recorded at −45 °C. [g] Chemical shift of most intense peak of multiplet. [h] Quintet.

L_2Ni(olefin) complexes, examples such as $(t\text{-}BuNC)_3Ni$(olefin),[11] $CH_3C(CH_2P(C_6H_5)_2)_3Ni(C_2F_4)$,[12] and $(Et_3P)_3Ni(N_2)$[13] have been reported.

In the reaction of PF_3 with the nickel–vinyl chloride complex, the products collected on warming the reactor from −96 °C to ambient included $Ni(PF_3)_4$, C_2H_3Cl, PF_3, and a small amount of brown residues. The absence of a nickel mirror that was observed in reactions with other olefins suggested that no nickel–olefin–PF_3 material had transferred from the reactor.

For the reactions with vinyl fluoride, trifluoropropene, and propene, liquid products were collected at liquid-nitrogen temperatures on warming the reactor from −96 °C to ambient. The trifluoropropene complex collected just above the liquid-nitrogen level in an orange ring which formed a yellow liquid upon melting. The propene complex also gave a yellow liquid upon melting. All of these materials decomposed as they were warmed to ambient temperatures to yield nickel metal, primarily as uncharacterized films, $Ni(PF_3)_4$, and olefin. In at least the propene and trifluoropropene complexes, the decomposition was not complete and gave indications of being photoassisted. The ratio of olefin to $Ni(PF_3)_4$ recovered in this decomposition was 1.2:1.0 which is in good agreement with a value of 1.3:1.0 based on eq 5 and a stoichiometry as given by 1. Thus, the results from both the

$$\underset{1}{4(PF_3)_3Ni(\text{olefin})} \rightarrow 3Ni(PF_3)_4 + 4\,\text{olefin} + Ni \tag{5}$$

olefin displacement reactions described in eq 4 and the thermal decomposition studies are consistent with the formation of tris(trifluorophosphine)nickel–olefin complex. Further support for this stoichiometry comes from low-temperature NMR work as discussed below.

The low decomposition temperatures of these materials made it impossible to obtain elemental analyses and infrared or mass spectral data. An attempt was made to collect infrared spectra rapidly using a Fourier transform system as the samples warmed from −196 °C; however, only bands for $Ni(PF_3)_4$ and olefin were observed.

NMR data for the complexes were obtained conveniently at low temperatures and are summarized in Table I with values for the free ligands and $Ni(PF_3)_4$. Spectra were initially recorded in the −45 to −50 °C range and contained evidence of at least traces of $Ni(PF_3)_4$ impurity at the outset. No changes were detected in either the proton or fluorine spectra as the probe temperature increased until it approached 0 °C. Monitoring the PF_3 resonances in the product complexes and in $Ni(PF_3)_4$ proved to be the most convenient way of detecting decomposition. The vinyl fluoride complex was determined to be the least stable of the three, decomposing at −16 °C, followed by the trifluoropropene (+2 °C) and propene (+6 °C) materials. Decomposition could not be followed to completion due to the loss of signals when nickel coatings formed on the walls of the tube.

The variation in complex stability with olefin substituents in the PF_3-containing compounds was somewhat different from that encountered in the simple binary nickel–olefin complexes described above. For example, the nickel–vinyl fluoride and chloride complexes appeared to be of comparable stability with both decomposing between −96 and −45 °C, whereas only the vinyl fluoride–nickel–PF_3 complex was stable enough to be isolated. Moreover, the propene–nickel–PF_3 complex demonstrated an even greater increase in stability than those of other olefins and in particular greater than that of trifluoropropene.

The ratios of integrated areas in both proton and fluorine spectra were of particular interest in these systems. Proton ratios of 1:2:3 for the propene complex were consistent with the presence of a metal-bonded propene structure and not that of an allyl hydride. Furthermore, no evidence for a hydride type of hydrogen was found as far as 40-ppm upfield from Me_4Si, nor were the spectra found to change on warming from −196 °C to a probe temperature of −60 °C and above until decomposition was detected at +6 °C. This was in contrast to the temperature-dependent allyl–hydride–propene equilibrium found by Bonneman for $F_3PNiC_3H_6$.[14] The presence of two additional PF_3 groups around the nickel atom appeared to discourage such an equilibrium, possibly through increased steric requirements.

Spin–spin decoupling of the hydrogen and the adjacent methyl group reduced the methyl quintet to a quartet. The quintet was apparently the product of overlapping bands arising from similar P–H and H–H coupling constants, whereas the quartet resulted from three equivalent phosphorus nuclei in the molecule. This equivalency arose either from rapid rotation of the propene about the nickel–olefin bond or from rapid ligand exchange. The 3:1 ratio

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of PF_3 to olefin was also suggested for the vinyl fluoride and trifluoropropene complexes based on the relative integrated areas of the PF_3 and olefin fluorine resonances.

Reactions of Ni Atoms with Olefins and Arenes. In an attempt to obtain a stable π-arene–nickel–olefin complex, nickel atoms were cocondensed at −196 °C with trifluoropropene and various arenes, including toluene, fluorobenzene, trifluoromethylbenzene, *m*-bis(trifluoromethyl)benzene in methylcyclohexane, and hexafluorobenzene in methylcyclohexane. Although Ni(0)–π-arene complexes have generally proved to be thermally unstable.[15,16] we believed that a mixed-ligand environment, particularly one with arenes having a electron-withdrawing groups, might provide the necessary stability to isolate a complex. Reactions were carried out by forming the nickel–trifluoropropene complex initially before adding the arene and vice versa with trifluoropropene being added to the nickel–arene complex. Upon warming these mixtures to ambient, no evidence was obtained for the formation of (π-arene)nickel–olefin complexes.

Conclusions

We have shown that nickel atoms reacted on a macrosynthetic scale with substituted ethylenes at −196 °C to form homoleptic nickel-olefin complexes analogous to $Ni(C_2H_4)_3$. In contrast to suggestions based on earlier spectroscopic studies, these complexes did not have sufficient thermal stability to be isolated by using standard metal-vapor-chemistry techniques.

We reacted the nickel–olefin complexes with trifluorophosphine at low temperatures in an attempt to obtain materials with increased thermal stability. The products isolated in these reactions were assigned the general formula $(PF_3)_3Ni$(olefin) based on thermal decomposition and low-temperature NMR studies. Although these complexes decomposed below ambient conditions, they proved to be more thermally stable than the initial binary complexes. Moreover, their ability to produce nickel films during decomposition was encouraging with respect to our stated objective of obtaining metallic films at relatively low temperatures.

Attempts to introduce a π-bonded arene into the nickel-olefin system instead of PF_3 groups were not successful. This was probably the result of the weak nickel-arene interaction.[17] Further studies are being conducted with these ligands and other metal atoms to determine if moderately stable organometallics capable of producing metal films can be synthesized.

Registry No. $(PF_3)_3Ni(FCH{=}CH_2)$, 85318-60-1; $(PF_3)_3Ni(CF_3CH{=}CH_2)$, 85318-61-2; $(PF_3)_3Ni(CH_3CH{=}CH_2)$, 85318-62-3; $Ni(PF_3)_4$, 13859-65-9.

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Chemistry of the Interaction of Some Metal Carbonyl Clusters with Metal Oxide Surfaces. $[CpFe(CO)]_4$, $Cp_3Ni_3(CO)_2$, and $[CpNi(CO)]_2$ on Alumina

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The nature of the interactions between $[CpFe(CO)]_4$, $Cp_3Ni_3(CO)_2$, and $[CpNi(CO)]_2$ with nearly fully dehydroxylated alumina were investigated by infrared spectroscopy, gas evolution, and other chemical means. A donor–acceptor interaction occurs between a carbonyl oxygen and the surface Al^{3+} in the case of $[CpFe(CO)]_4$ and $Cp_3Ni_3(CO)_2$ and possibly in the case of $[CpNi(CO)]_2$. The stability of these simple surfaces adducts increases in the order $[CpNi(CO)]_2 < Cp_3Ni_3(CO)_2 < [CpFe(CO)]_4$ with the γ-Al_2O_3·$[CpFe(CO)]_4$ adduct being stable for weeks and the adduct with $[CpNi(CO)]_2$ rapidly decomposing to $Ni(CO)_4$, CO, and other products. The chemistry of these metal clusters with an active alumina surface strongly parallels the reactions with aluminum bromide.

Introduction

Metal carbonyls and other organometallics supported on metal oxide surfaces have attracted considerable attention because of the catalysts derived from many of these systems.[1] There have been a number of attempts to characterize the nature of the species resulting from these interactions,[1] but precise identification is often difficult because of the formation of multiple surface species and because of problems inherent in characterizing surface species. The present research was undertaken with compounds that might interact in a simple manner with the alumina surface, thus optimizing the chances that the surface species might be characterized.

Several different types of simple interactions have been observed or proposed for metal carbonyls on activated alumina surfaces: basicity of the carbonyl oxygen toward surface Al^{3+},[2-5] electrophilic interaction of the carbonyl

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