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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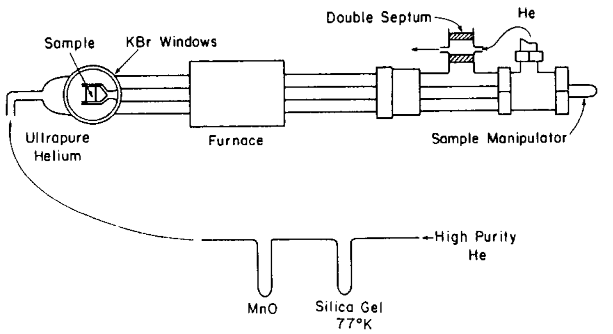

Figure 1. Infrared cell for surface studies.

carbon toward surface oxide,[6,7] and displacement of CO ligands by surface oxides.[1,2,5,7,8] In the present research we picked $[CpFe(CO)]_4$ for study on an alumina surface, because this compound is highly robust,[9] the triply bridging CO ligand is basic toward molecular Lewis acids,[10,11] and the carbonyl carbon in this type of compound should not be susceptible to attack by nucleophiles on both electronic[12] and steric grounds. To round out the chemistry of these types of clusters, we also investigated two less robust metal cyclopentadiene carbonyls $Cp_3Ni_3(CO)_2$ and $[CpNi(CO)]_2$, which are heterogenous catalyst precursors.

Experimental Section

Materials. The complexes $Cp_3Ni_3(CO)_2$ and $[CpNiCO]_2$ were prepared and purified by the procedure of Fishcher and Palm.[13] The trimeric nickel complex was also obtained by pyrolysis of a toluene suspension of $[CpNiCO]_2$ at 100–110 °C for 3 h. Toluene was removed, and extraction of the residue with cyclohexane gave $Cp_3Ni_3(CO)_2$ in 70% yield. King's procedure[14] was employed for the synthesis of $[CpFeCO]_4$, and the product was recrystallized from either diethyl ether or benzene. The compounds were judged pure by comparison of their infrared spectra with published spectra and by elemental analysis. Aluminum bromide was sublimed twice under vacuum. Transparent alumina films were prepared from Al(O-i-Pr)$_3$ (Apache Chemicals) by the method of Yoldas.[7,15] In some experiments, commercial alumina, PHF high purity γ-alumina extrudate (American Cyanamid, 80–100 mesh, surface area 160 $m^2\ g^{-1}$ [16]), was used. Hydrocarbon solvents were treated with concentrated sulfuric acid and distilled from benzophenone ketyl. Dichloromethane was distilled from P_2O_5. Pyridine was dried over and distilled from barium oxide.

General Procedures. Solids were transferred in a nitrogen-purged drybox. Unless otherwise indicated, all other manipulations involved the use of standard Schlenk and syringe inert atmosphere techniques. Infrared spectra were obtained with a Nicolet 7199 Fourier transform spectrometer at 4-cm^{-1} resolution. Solution spectra were monitored by using matched CaF_2 windowed cells (1-mm path length). Spectra of volatile components were obtained by using a gas cell with NaCl windows (10-cm path length). Spectra of solids were obtained as Flurolube mulls on KBr plates.

Surface Infrared Experiments. The infrared cell employed in the surface studies, a modification of an earlier design,[7] is shown in Figure 1. The furnace and fused silica midsection of the cell permitted activation of the alumina at temperatures up to 950 °C. A flushed double septum assembly permitted the introduction of solutions onto the alumina film. The alumina film was housed in a fused silica holder. A fused silica rod attached to the holder served as the sample manipulator. Commercial high purity helium was further purified by passing it through a silica gel trap at 77 K and an MnO/SiO_2 trap.[18] The helium then flowed through the cell, and any leakage was detected by means of a second MnO/SiO_2 trap on the exit helium stream. In a typical experiment, an alumina film was nearly fully dehydroxylated by heating to 940 ± 15 °C for 0.5 h under helium flow. This material is referred to as dehydroxylated alumina, DA. During this process the downstream MnO/SiO_2 trap was bypassed. The sample holder was positioned in the infrared beam, and a spectrum was recorded. Typically, 50 μL of a saturated solution was injected onto the film. For the three compounds $[CpNiCO]_2$, $Cp_3Ni_3(CO)_2$, and $[CpFeCO]_4$ this corresponds to 5.3, 1.4, and 4.8 μmol, respectively, from dichloromethane solution or 1.3, 0.68, and 1.4 μmol from benzene. The alumina films weighed 0.1–0.2 g. After most of the solvent had evaporated from the surface (5–10 min), the sample was repositioned and the infrared spectrum was monitored as a function of time. Spectra were referenced to the empty cell. Similar results were obtained with both dichloromethane or benzene. These more polar solvents were used because the complexes do not possess sufficient solubility in aliphatic hydrocarbons.

Gas Evolution Experiments. Volatile compounds produced from the interaction of metal carbonyl complexes with γ-alumina were analyzed in a vacuum line system described previously.[16,19,20] Helium carrier gas was purified as described above. The flow rate of helium was 30 mL min^{-1} during dehydroxylation and 60 mL min^{-1} throughout the rest of the experiment. The amount of O_2 in the carrier gas was less than 0.01 μmol h^{-1} at a flow rate of 60 mL min^{-1}. Commercial (American Cyanamid Co.) PHF γ-alumina (0.25 ± 0.004 g) was used.

Infrared and gas evolution experiments indicate that the PHF material is chemically equivalent to our alumina films in its interactions with metal carbonyls. Experiments were conducted on a 17–26 μmol scale by using 1.7–2.5 mL of dichloromethane solutions. The solutions were injected on DA that had been previously cooled to –78 °C. Gases liberated into the flowing helium were monitored at this temperature, at 0 °C, and then at room temperature. Gases produced from the interaction of the solvent (1.5 mL) with DA were determined in a similar fashion. There has been some controversy on the reactivity of chlorinated hydrocarbons toward activated alumina.[21-23] Contact of these solvents with activated alumina has been reported to produce carbon monoxide, hydrogen, and other gases[21] as well as a chlorinated alumina surface.[24,25] We have found that the interaction of 1.5 mL of dichloromethane with 0.25 g of DA produces 0.15 μmol of carbon monoxide as the only gaseous product. This amount of carbon monoxide is greater than that produced when dichloromethane solutions of $[CpFeCO]_4$ and $Cp_3Ni_3(CO)_2$ interaction with 0.25 g of DA. This indicates that the carbonyl complexes effectively compete with dichloromethane for reaction sites on DA and that the modification of the surface by the chlorinated solvent is minimal in our experiments.

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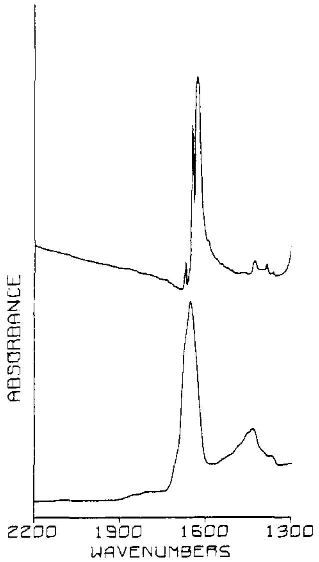


Figure 2. Upper figure: infrared spectrum (Fluorolube mull) of $[CpFeCO]_4$. Lower figure: infrared spectrum of $[CpFeCO]_4$ on dehydroxylated alumina (DA).

Figure 3. Upper figure: infrared spectrum (Flurolube mull) of $Cp_3Ni_3(CO)_2$. Lower figure: infrared spectrum of $Cp_3Ni_3(CO)_2$ on a DA surface (spectrum of DA subtracted out). This spectrum was obtained on a region of the sample having no free $Cp_3Ni_3(CO)_3$.

Total Absorption Experiments. These experiments were conducted to assure that chemisorption rather than simple physisorption had taken place. Their scale was similar to that of the gas evolution experiments. Crushed alumina films were dehydroxylated under vacuum in a fused silica tube. Dichloromethane solutions of the metal carbonyls were injected onto the DA surface, and the length of time required to decolorize the solution was noted. An infrared spectrum of the volatile components was recorded. In the case of $[CpFeCO]_4$ and $Cp_3Ni_3(CO)_2$, mull spectra of the alumina films were recorded. About 1 mL of pyridine was injected into the silica tube. The resulting solution was filtered from the DA surface, the solvent was removed, and the resulting solid and DA were examined by infrared spectroscopy.

Reaction with $AlBr_3$. The tendency of the nickel complexes to form Lewis acid–base adducts with $AlBr_3$ was determined. Reactions were conducted on a 0.1–1.0-mmol scale by using a vacuum-tight grease-free H-type Schlenk tube[11] and standard high vacuum techniques. A toluene solution of $AlBr_3$ was added to a toluene solution or slurry of the nickel dimer or trimer. The infrared spectrum of the solution above the resulting solid was recorded within 10 min. Removal of the volatile components under vacuum resulted in the formation of a brown solid in all cases. The infrared spectra of the voltaile components and the brown solid were recorded. The brown solid was then treated with an excess of pyridine, typically 1–2 mL. The volatile components and the solid products were examined by infrared spectroscopy. The pyridine adduct of $AlBr_3$, obtained as a white insoluble solid, was formed by reacting 1 mmol of $AlBr_3$ with 1 mL of pyridine in toluene solution.

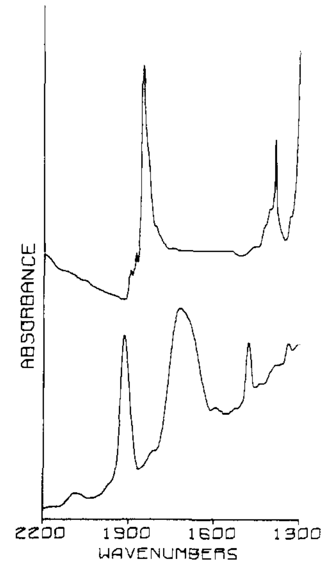
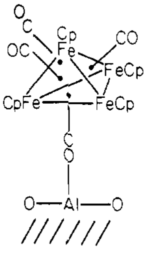


Figure 4. Upper figure: infrared spectrum (Fluorolube mull) of $[CpNiCO]_2$. Lower figure: infrared spectrum of $[CpNiCO]_2$ on a DA surface.

Results and Discussion

Initial Carbonyl–Surface Interactions. Infrared spectra in the carbonyl region for the products of the interactions between $[CpFeCO]_4$, $Cp_3Ni_3(CO)_2$, or $[CpNiCO]_2$ and dehydroxylated alumina (DA) within the first 10 min are compared with spectra of the parent complexes in Figures 2–4. The parent complexes show one band or one main band with weaker shoulders (Flurolube mulls). Upon interaction with the DA surface, two bands are observed with respect to the band of the parent complex: a fairly sharp band at higher frequency and a broad band at lower frequency. These spectra suggest presence of the expected surface adducts between carbonyl oxygens and aluminum cations I, II, and III. Similar spectral changes are observed when these complexes interact with Lewis acids in solution.[10,11] The presence of several types of acidic aluminum cations on the alumina surface[24] may account for the broadness of the surface bands when compared to analogous solution spectra. Changes are observed in the hydroxyl region of the infrared spectra, but the spectra in this region revert to their original appearance when the solvent (benzene or dichloromethane) has completely evaporated from the surface. Similar changes in the spectra of surface hydroxyl groups have been observed when benzene interacts with a partially dehydroxylated



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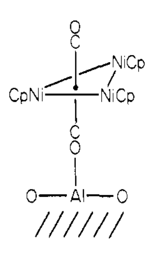

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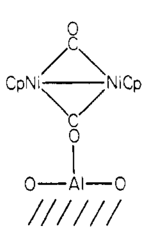


III

Table I. Gas Evolution Data for Metal Carbonyl Complexes on DA

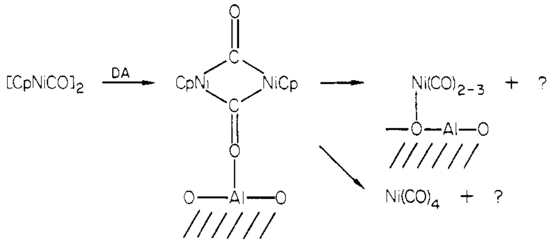
complex	temp, °C	time, min	mol of CO/mol of complex
$[CpNiCO]_2$	−78	30	0.0
	0	10	<0.002
		10	0.018
		30	0.054
	23	60	0.045
		90	0.022
		137	0.015
			0.155^a
$Cp_3Ni_3(CO)_2$	−78	10	0.0
	0	10	0.0
		30	0.001
	24	45	<0.001
			0.002^a
$[CpFeCP]_4$	−78	30	0.0
		10	<0.001
	0	30	0.001
		15	0.005
		30	0.004
		60	0.002
			0.013^a

[a] Total mol of CO/mol of complex.

alumina surface (dehydroxylation temperature 650 °C).[26] Gas evolution data (Table I) also support the assignment of the infrared spectra. The most reactive complex $[CpNiCO]_2$ produces only 0.02 mol of carbon monoxide/mol of complex after 10 min on the surface. No hydrogen or methane is detected when any of these complexes interact with DA.

In addition to carbonyl bands attributable to surface adducts, both $[CpFeCO]_4$ and $Cp_3Ni_3(CO)_2$ on DA often show bands attributable to crystalline phases of the parent complexes.[27] (These spectra are not shown.) The strongest CO stretching frequency of the parent is observed as a shoulder on the high-frequency band for the DA adduct of $[CpFeCO]_4$. In the case of $Cp_3Ni_3(CO)_2$ on DA the spectrum of the uncomplexed parent compound is usually the strongest feature in the CO stretching region. Confirmation for the viewpoint that two phases are present comes from visual inspection of the films of DA supported complex. Evaporation of solutions of $[CpFeCO]_4$ or $Cp_3Ni_3(CO)_2$ onto DA does not give a homogeneous layer of the carbonyl complex, as evidenced by varying intensities of color and apparent rings of deeper color. When the infrared spectrum of areas that are less intensely colored, shown in the figures, is observed the bands due to the parent complex are of low intensity and occasionally are absent. In the case of $Cp_3Ni_3(CO)_2$, surface spectra free of parent complex bands were very weak. The spectrum shown in Figure 3 could be observed only after the spectrum of the DA surface was subtracted out. The relatively large amount of crystalline $Cp_3Ni_3(CO)_2$ on the surface is consistent with its substantially lower solubility than that of the other two complexes. Sublimation of the compounds onto the surface might give more uniform samples; however, these metal clusters are not sufficiently volatile to permit the use of this technique. There is evidence that the adsorption of the larger complexes is slow. For example, when a DA film is placed in dichloromethane solution of $[CpNiCO]_2$, the solution completely decolorizes within a few minutes with no stirring required. Complete decolorization of solutions of $Cp_3Ni_3(CO)_2$ and $[CpFeCO]_4$ requires several hours under the same conditions, which is consistent with the observation of uncomplexed parent compound in the infrared spectra. Infrared examination of the DA films obtained after complete adsorption shows none of the bands attributable to the parent complexes.

Stability and Reversibility of Surface Adducts. The relative stabilities of these surface adducts and the reversibility of adduct formation have been investigated. The adduct formed when $[CpFeCO]_4$ interacts with a DA surface is the most stable. The infrared spectrum of this surface species remains unchanged for at least 1 h and 0.01 mol of carbon monoxide/mol of tetrameric complex is the only volatile species isolated after one hour. Complete decoloration of a $[CpFeCO]_4$ solution by DA indicates that a fairly strong interaction takes place. This interaction can be completely reversed by the addition of an excess of a strong base such as pyridine. The DA surface loses its green color, and its infrared spectrum shows only DA-bound pyridine,[28] and the parent complex can be isolated unchanged from this solution. The adduct formed when $Cp_3Ni_3(CO)_2$ interacts with DA is less stable. After a variable interval of 10 min–1 h, a broad band in the infrared spectrum at about 2040–2060 cm^{-1} is obsreved, indicating the presence of a terminal carbonyl. Complete decolorization and adsorption of a solution of $Cp_3Ni_3(CO)_2$ by DA is not a reversible process. A substantial amount of a volatile nickel compound, presumably $Ni(CO)_4$ (infrared band at 2057 cm^{-1}), is formed. Only part of the surface-bound species is displaced by pyridine as the parent complex, and none is displaced by PMe_3. These results might appear to contradict gas evolution data which indicate that surface-bound $Cp_3Ni_3(CO)_2$ is very stable. However, this result may reflect in part the large proportion of unreacted parent on the surface and the lack of CO evolution resulting from the surface reaction. The least stable surface adduct is that formed from $[CpNiCO]_2$. Its decomposition is accompanied by color changes and can be followed by infrared spectroscopy as shown in Figure 5. The spectrum of the surface adduct loses intensity. Decay of the 1908-cm^{-1} band, attributed to the free bridging carbonyl, follows either zero- or first-order kinetics. The broad band at about 1700 cm^{-1}, attributed to the carbonyl bound to the DA surface, shifts to lower frequency as it decays. A very broad band centered at 2080 cm^{-1} and a weak band at 1832 cm^{-1} gain intensity over about 1 h. These new bands agree well with the spectrum of $Ni(CO)_4$ on an alumina surface that had been dehydroxylated at 450 °C.[29] Nickel carbonyl and 0.15 mol of carbon monoxide/mol of $[CpNiCO]_2$ are the volatile components isolated after about 2 h. Nickel carbonyl on alumina gives an unstable mixture of nickel dicarbonyl and tricarbonyl species.[30] The following reaction scheme can be proposed for $[CpNiCO]_2$ on a DA surface (eq 1). The



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cyclopentadienyl rings remain on the surface, as shown by

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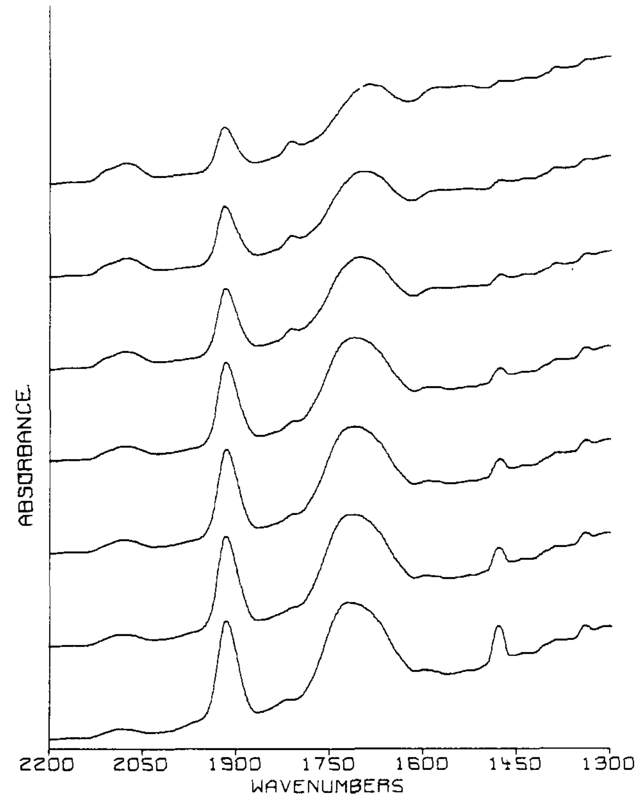

Figure 5. Decomposition of $[CpNiCO]_2$ on a DA surface. The lower tracing was obtained ca. 8 min after deposition of the sample, and the times at which succeeding spectra were obtained (bottom to top) are 11, 13, 16, 27, 35, and 51 min.

infrared spectroscopy and by gas evolution experiments, indicating that no mono- or dicyclopentadiene or other unsaturated organic compounds are produced.

Model Reactions with $AlBr_3$. Previous studies have shown that $[CpNiCO]_2$, $Cp_3Ni_3(CO)_2$, and $[CpFeCO]_4$ each form at least a 1:1 adduct with trialkylaluminum compounds[10] and that $[CpFeCO]_4$ forms adducts of all four possible stoichiometries with $AlBr_3$.[11] The possibility of observing adduct formation between the nickel complexes and $AlBr_3$ had not been investigated. The interaction of 1:1 molar ratios of $Cp_3Ni_3(CO)_2$ and $AlBr_3$ in toluene results in the formation of a brown solid of low solubility. The infrared spectrum of the toluene solution above the precipitated solid shows three bands all of roughly the same intensity at 2042, 1799, and 1521 cm^{-1}. The bands at 1799 and 1521 cm^{-1} correspond well with the expected spectrum of $Cp_3Ni_3(CO)(COAlBr_3)$, but the band at 2042 cm^{-1} indicates that a terminal carbonyl is also present. The volatile components from this reaction mixture contain $Ni(CO)_4$ and a trace of a volatile green solid, presumably Cp_2Ni. This observation indicates that decomposition processes are taking place. After removal of solvent a brown solid is isolated. The bands attributable to the 1:1 adduct appear to be split in the solid state. In addition, a weak band at 2040 cm^{-1} is observed. Treatment of the brown solid with pyridine results in the regeneration of the parent trimer and in the formation of the pyridine adduct of $AlBr_3$. A small amount of an unidentified volatile blue compound is also formed. From these experiments we conclude that, even though some decomposition takes place, $Cp_3Ni_3(CO)_2$ forms a 1:1 adduct with $AlBr_3$.

The reaction of one mole of $Cp_3Ni_3(CO)_2$ with 2 mol of $AlBr_3$ gives a brown solid for which the infrared spectrum consists of a main band at 1507 cm^{-1} and weak bands at 2040, 1800, and 1739 cm^{-1}. The volatile components again contain $Ni(CO)_4$ and a trace of Cp_2Ni. Treatment of the brown solid with pyridine gives $Cp_3Ni_3(CO)_3$ and the pyridine adduct of $AlBr_3$. These observations are consistent with the formation of a 1:2 adduct as the major product, a small amount of the 1:1 adduct, unreacted starting material, and some decomposition products. Similar reactions between the nickel trimer and an exess of trialkylaluminum produced the 1:1 adduct as an impurity.[10]

Table II. CO Stretching Frequency Shifts on Adduct Formation[a]

	Lewis acid		
compd	$Al(C_2H_5)_3$	γ-Al_2O_3[b]	$AlBr_3$
$[CpNiCO]_2$	+25[c]	+36 (7)[d]	
	−116	−170 (2)	
$Cp_3Ni_3(CO)_2$	+34[c]	+45 (4)[d]	+48[d]
	−124	−171 (15)	−230
$[CpFeCO]_4$	+4[c]	+11 (5)[d]	+33[e]
	−102	−185 (15)	−257

[a] Frequency shifts with respect to solution spectra of the parent compound. [b] Values in parentheses represent the errors in determining the maxima of broad surface bands. [c] Reference 10. [d] This research. [e] Reference 11.

Reaction of $[CpNiCO]_2$ with $AlBr_3$ in a 1:1 ratio in toluene leads to an immediate color change from red to brown even at −78 °C and a brown solid precipitate forms after a few minutes. The infrared spectrum of the solution contains three bands at 2042, 1799, and 1521 cm^{-1}, which are in frequency identical with those observed for the 1:1 interaction of the trimeric nickel complex and $AlBr_3$. However, the 2042-cm^{-1} band is considerably stronger for the nickel dimer product. The volatile components contain $Ni(CO)_4$ and a trace of Cp_2Ni. Treatment of the brown solid with pyridine produces the trimeric complex. It thus appears that a simple stable adduct $[CpNiCO]_2 \cdot AlBr_3$ is not formed in significant amounts.

Comparison with Other Systems. The infrared frequency shifts observed when $[CpNiCO]_2$, $Cp_3Ni(CO)_2$, and $[CpFeCO]_4$ interact with DA are listed along with data for other Lewis acid adducts in Table II. The magnitude of the shifts for DA adducts is intermediate between the corresponding AlR_3 and $AlBr_3$ adducts. This indicates the relative electron pair acceptor strength: $AlBr_3 > DA > AlR_3$. The long-term stability of these adducts is related to the inherent stability of the parent carbonyl complex. All the adducts of the iron tetramer are stable for considerable length of time consistent with the fact that the $[CpFeCO]_4$ moiety remains intact under a variety of conditions.[9] The adducts of the nickel complexes are considerably less stable. The production of surface-bound nickel carbonyl (eq 1) by $[CpNiCO]_2$ on DA is reminiscent of the types of reaction that this complex undergoes when treated with carbon monoxide or various phosphines, to form $Ni(CO)_2L_2$ and Cp_2Ni.[31] This suggests that the Lewis base character of the DA surface is responsible for the decomposition. We did not expect to isolate Cp_2Ni from such a surface reaction because Cp_2Ni reacts with both Lewis acids and bases.[32] In fact, the interaction of Cp_2Ni, a green solid, with a DA surface produces a brown surface species. The color of the surface species produced from $[CpNiCO]_2$ and DA after about 0.5 h is also brown, but the breadth of the infrared bands coupled with the lack of sensitivity to structural changes of the infrared bands in the cyclopentadienyl C–H stretching region does not

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permit firm conclusions on the nature of the surface cyclopentadienyl species. The reaction of $[CpNiCO]_2$ with $AlBr_3$ to produce the nickel trimer parallels the foramtion of a Cp_3Ni_3 moiety from $[CpNiCO]_2$ by thermolysis[13,33] (see Experimental Section), by metal reduction,[13,34] or by reaction with nucleophiles.[35,36] The fact that both nucleophiles and electrophiles promote the formation of trimeric nickel compounds from the dimer suggests that this process might be especially favored by a DA surface. The various IR bands for alumina mask possible IR bands of the adsorbed trimer so no decision can be made on its presence. It is more difficult to rationalize the decomposition of the $Cp_3Ni_3(CO)_2$ adducts simply because little is known about the chemistry of the parent compound. The DA adduct is the least stable adduct formed by the trimer in this study. This suggests that the nucleophilicty of the substituent bound to the aluminum, rather than the Lewis acidity of the aluminum compound, is the factor responsible for the decomposition. These results for the nickel complexes can be compared to a preliminary report of their interaction with a silica surface.[37] Hydroxylated silica shows no Lewis acid or base properties and mild Brønsted acidity.[24] Decomposition of the nickel complexes on silica required 80–120 °C and resulted in stoichiometric production of carbon monoxide and cyclopentadiene.[37] Similar interactions have been proposed for the ethylene oligomerization catalyst prepared from $Cp_3Ni_3(CO)_2$ and a hydroxylated silica–alumina surface.[38]

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Registry No. $[CpNiCO]_2$, 12170-92-2; $Cp_3Ni_3(CO)_2$, 12194-69-3; $[CpFeCO]_4$, 12203-87-1; γ-Al_2O_3, 1344-28-1; $AlBr_3$, 7727-15-3.

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Oxidation of Dodecamethylcyclohexasilane by *m*-Chloroperbenzoic Acid

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Oxidation of dodecamethylcyclohexasilane (I) by *m*-chloroperbenzoic acid leads to six oxidation products that possess respectively one, two, three, four, five, and finally six oxygen atoms as well as all of the atoms originally present in I. The structures of these products as well as their formation are discussed.

The oxidation of silicon–silicon single bonds of disilanes by peracids,[1-9] tertiary amine oxides,[2,10] nitrogen oxides,[16] ozone,[17] sulfoxides,[11-13] and peroxides[4-7,14] as well as by molecular oxygen in both the singlet[15] and triplet[5,14] states to yield disiloxanes has been reported. On the other hand, much less work has been presented on the oxidation of silicon–silicon single bonds of polysilanes. The air oxidation of octamethylcyclotetrasilane to yield 1-oxa-2,2,3,3,4,4,5,5-octamethyl-2,3,4,5-tetrasilacyclopentane[18] and the recent report of the peracid oxidation of various 1,2,3,4-tetra-*tert*-butyl-1,2,3,4-tetramethylcyclotetrasilane isomers[9] are among the few previous results in this area.

We have been interested in the oxidation of silicon–silicon single bonds[8,11-13] and would like to report our work on the reactions of *m*-chloroperbenzoic acid (MCPBA) with dodecamethylcyclohexasilane (I). Oxidation of 1 equiv of I with 2 equiv of MCPBA leads to formation of six oxidation products as well as significant amounts (~60%) of unreacted I. These possess respectively one, two, three, four, five, and finally six oxygen atoms as well as all of the atoms originally present in I. These products may result from the sequential insertion of oxygen atoms into the silicon–silicon single bonds of I.

There are a number of possible isomeric monocyclic compounds that possess a framework of six silicon and from one to six oxygen atoms. For example, there are three isomers that possess a framework skeleton of six silicon and three oxygen atoms. Likewise, there are three isomeric compounds that have six silicon and two oxygen atoms as well as three isomers that possess four oxygen and six

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