crystallography.[10] The corresponding cobalt analogue, as expected, has only two carbon atoms in the polyhedron (**15**).[10c]

Application of the concepts based on compatibility of orbitals of the rings and caps to borane anions, metal clusters, and organic reaction mechanisms are currently being investigated.

Conclusions

The electronic structure of *closo*-carboranes follows a six-electron rule. The relative stability of position isomers is determined by the matching of the rings and caps that formally constitute the carborane. CH prefers to be the cap on three- and four-membered boron rings. BH prefers to be the cap on five-membered rings. These preferences are dictated by the greater overlap enjoyed by a cap having more diffuse orbitals to the orbitals of a larger ring. The most stable isomer satisfies these preferences as far as possible. Even the BH group does not have orbitals sufficiently diffuse to be appropriate caps on six-membered borocycles. Caps can be selected to stabilize polyhedra based on larger rings.

Acknowledgment. We thank Professor Paul von Ragué Schleyer for constructive criticisms, helpful suggestions, and several enlightening discussions. The University of Hyderabad is thanked for providing research facilities.

Registry No. 1a, 20693-66-7; **1b**, 23777-70-0; **1c**, 30396-61-3; **2a**, 20693-67-8; **2b**, 20693-68-9; **3a**, 25036-79-7; **3b**, 25036-76-4; **3c**, 20693-69-0; **3d**, 30347-95-6; **6a**, 23653-23-8; **6b**, 41655-27-0; **6c**, 23704-81-6; **7a**, 20644-12-6; **7b**, 16872-09-6; **7c**, 16986-24-6; **12**, 83435-74-9; **14**, 83435-75-0; **15**, 52649-56-6.

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(10) (a) Pipal, J. R.; Grimes, R. N. *Inorg. Chem.* **1978**, *17*, 6. (b) Maxwell, W. M.; Weiss, R.; Sinn, E.; Grimes, R. N. *J. Am. Chem. Soc.* **1977**, *99*, 4016. (c) Evans, W. J.; Hawthorne, M. F. *J. Chem. Soc., Chem. Commun.* **1974**, 38. (d) Maxwell, W. M.; Sinn, E.; Grimes, R. N. *Ibid.* **1976**, 389.

Surface Organometallic Chemistry: Formation of $HFe_3(CO)_{11}^-$ from $Fe_3(CO)_{12}$ and $Fe(CO)_5$ on Silica, Alumina, Magnesia, and Zinc Oxide

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Received November 30, 1981

Abstract: This paper describes, at a molecular level, the organometallic chemistry that occurs during the adsorption of $Fe_3(CO)_{12}$ and $Fe(CO)_5$ on silica, alumina, magnesia, and zinc oxide. $Fe(CO)_5$ and $Fe_3(CO)_{12}$ are only weakly adsorbed on silica. In contrast on alumina, magnesia, and zinc oxide there is formation of the anionic hydride $HFe_3(CO)_{11}^-M^+$ (M = Al, Mg, Zn), which has been characterized in the adsorbed state by infrared, UV, and ^1H NMR spectroscopy and which has been extracted from the surface by ion exchange with Et_4NCl. The results indicate that the surface hydroxyl group of alumina, magnesia, or zinc oxide can make a nucleophilic attack at the coordinated CO as it occurs in solution with formation of the stable surface hydrido cluster. The result is also the first example of a grafted cluster where the grafting occurs by ionic interaction with a surface cation of the oxide lattice. It is possible that the anionic cluster interacts with such a surface cation via the oxygen lone pair of the bridging carbonyl ligand.

Surface organometallic chemistry can be considered as a major aspect of surface science and heterogeneous catalysis. Because of the intrinsic difficulties in the study of surface chemistry, few basic phenomena or elementary steps have been elucidated at a molecular level. Direct interaction between molecular cluster carbonyls and the surface hydroxyl groups of highly divided oxides is a possible approach to study the reactivity of metal–metal or metal–ligand bonds of carbonyl clusters toward the hydroxyl groups of a surface.

Surface hydroxyl groups of alumina can oxidize zerovalent rhodium in $Rh_6(CO)_{16}$ to surface $Rh^I(CO)_2$ complex with simultaneous release of hydrogen,[2] but surface hydroxyl groups of silica cannot oxidize zerovalent rhodium of $Rh_4(CO)_{12}$ or $Rh_6(CO)_{16}$.[3] Surface hydroxyl groups of silica, alumina, and magnesia can oxidatively add to the Os–Os bonds of $Os_3(CO)_{12}$ or $Os_3(CO)_{10}(CH_3CN)_2$ with formation of the grafted cluster (H) $Os_3(CO)_{10}$ (O-M) (M = Si, Al, Mg).[4-9]

We report here on the reactivity of $Fe_3(CO)_{12}$ (and $Fe(CO)_5$) with the hydroxyl groups of silica, alumina, magnesia, and zinc oxide. In some cases the OH groups of the oxide behave as

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(1) For typical results related to surface organometallic chemistry, see for example (a) C. M. Friend, R. M. Gavin, E. L. Muetterties, and M. C. Tsai, *J. Am. Chem. Soc.* **102**, 1717 (1980); (b) C. M. Friend, J. Stein, and E. L. Muetterties, *ibid.*, *103*, 767 (1981); (c) C. M. Friend and E. L. Muetterties, *ibid.*, *103*, 773 (1981); (d) Y. I. Yermakov, *Catal. Rev. Sci. Eng.*, **13**, 77 (1976); (e) D. G. H. Ballard, *Adv. Catal.*, **23**, 267 (1973); (*f*) A. Brenner and R. Burwell, *J. Catal.*, **52**, 353 (1978); (g) E. L. Muetterties, *Angew. Chem., Int. Ed. Engl.*, **17**, 545 (1978); (h) J. M. Basset, Y. Ben Taarit, J. L. Bilhou, J. Bousquet, R. Mutin, and A. Theolier, *Proc. Int. Cong. Catal. 6th* **1**, 570 (1977); (i) F. Correa, R. Nakamura, R. E. Stimson, R. L. Burwel Jr., and D. F. Shriver, *J. Am. Chem. Soc.*, **102**, 5114 (1980); (j) W. M. Bowser and W. H. Weinberg, *ibid.*, **103**, 1453 (1981); (k) W. M. Bowser and W. H. Weinberg, *ibid.*, **102**, 4720 (1980).

(2) A. K. Smith, F. Hugues, A. Theolier, J. M. Basset, R. Ugo, G. M. Zanderighi, J. L. Bilhou, V. Bougnol, and W. F. Graydon, *Inorg. Chem.*, **18**, 3104 (1979).

(3) A. Theolier, A. K. Smith, M. Leconte, J. M. Basset, G. M. Zanderighi, R. Psaro, and R. Ugo, *J. Organomet. Chem.*, **191**, 415 (1980).

(4) R. Ugo, R. Psaro, G. M. Zanderighi, J. M. Basset, A. Theolier, and A. K. Smith, *Fund. Res. Homogeneous Catal.* [*Proc. Int. Workshop*], **3**, 579 (1979).

(5) B. Besson, B. Moraweck, A. K. Smith, J. M. Basset, R. Psaro, A. Fusi, and R. Ugo, *J. Chem. Soc., Chem. Commun.*, 569 (1980).

(6) A. K. Smith, B. Besson, J. M. Basset, R. Psaro, A. Fusi, R. Ugo, *J. Organomet. Chem.*, **192**, C31 (1980). R. Psaro, R. Ugo, G. M. Zanderighi, B. Besson, A. K. Smith, and J. M. Basset, *ibid.*, **213**, 215 (1981).

(7) A. Theolier, A. Choplin, L. D'Ornelas, J. M. Basset, G. M. Zanderighi, R. Ugo, R. Psaro, and C. Sourisseau, submitted.

(8) M. Deeba and B. Gates, *J. Catal.* 67, 303 (1981).

(9) P. L. Watson and G. L. Schrader, *J. Mol. Catal.*, **9**, 125 (1980).

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nucleophiles toward coordinated CO with concomitant formation of $[HFe_3(CO)_{11}]^-M^+$, M = Al^+, Mg^+, Zn^+, in a similar way to the behavior observed in solution. Thermal decomposition of such supported clusters into very small metal particles and the catalytic properties of such small particles in Fischer–Tropsch synthesis will be reported in subsequent papers.[10]

Experimental Section

Materials and Procedures. The following supports were used in this study: the silica, Aerosil type, was obtained from Degussa; its surface area was 200 $m^2\ g^{-1}$. The γ-alumina was obtained from Degussa; its surface area was 100 $m^2\ g^{-1}$. The porous η-alumina (average diameter of pores 30 Å) was obtained by thermal activation of aluminum trihydroxide at 500 °C; its surface area was equal to 315 $m^2\ g^{-1}$. The magnesia support (96 $m^2\ g^{-1}$) was obtained by decomposition, under high vacuum at 400 °C, of high purity $Mg(OH)_2$. Zinc oxide was obtained from Cadox. Its surface area was 75 $m^2\ g^{-1}$. $Fe(CO)_5$ was obtained from Strem Chemicals and used as received. $Fe_3(CO)_{12}$ (Strem Chemicals) was purified before use by recrystallization from toluene or by sublimation. The various solvents used were distilled and stored under argon over activated molecular sieves. All experiments were carried out in vacuo or under dehydrated and deoxygenated argon. The iron contents of the supports were determined by atomic absorption (after dissolution of the sample in $HF/HNO_3/HCl$).

Before adsorption of the iron complex, the supports were treated in the following way: the support was heated slowly under vacuum (10^{-4} torr) up to a temperature T (T = 500 °C for alumina, 400 °C for magnesia, and 300 °C for zinc oxide). It was then subjected to several cycles of oxygen treatment ((500 torr), 0.5 h) and vacuum treatment ((10^{-4} torr), 14 h) at the same temperature T. This procedure allowed the support to be degassed and dehydrated and reduced the amount of carbonate present. The supports obtained in this way could be rehydrated by introduction of water vapor ((18 torr) at 25 °C) for 2 h and then treatment under vacuum (10^{-4} torr) at a given temperature T' between 25 and 500 °C, allowing the degree of hydration to be varied in a controlled manner.

The supports were impregnated with the iron complexes either by stirring a pentane or hexane solution of the complex with the support followed by evaporation of the solvent or by subliming the iron complex onto the support. In both cases, the addition was carried out in the strict absence of oxygen and water, using vacuum-line and break-seal techniques. Infrared spectra were recorded on a Perkin-Elmer 225 spectrometer, with the sample pressed into a 16-mm disk and placed in a cell as described previously.[2] In some cases the infrared spectra of the adsorbed cluster were recorded with a Fourier transform Bruker IFS 110 spectrometer. This spectrometer allowed the substraction of the background spectrum of the alumina support and the observation of bands of low intensity in the bridging ν(CO) region.

Diffuse reflectance UV spectra were recorded on an Optica Milano CF4 DR spectrophotometer, with the sample pressed into a 30-mm disk. ^1H NMR spectra of the supported complexes were obtained with a Bruker CXP 100 instrument equipped with a high-power probe.

Adsorption of $Fe_3(CO)_{12}$ and $Fe(CO)_5$ on Silica. When $Fe_3(CO)_{12}$ was sublimed onto silica pretreated at 25, 250, or 500 °C, the solid acquired the characteristic green color of $Fe_3(CO)_{12}$. The infrared spectra (Figure 1) showed bands at 2110, 2053, 2033, and 2013 cm^{-1} characteristic of a mixture of $Fe(CO)_5$ and $Fe_3(CO)_{12}$. Treatment of the support under vacuum at 25 °C removed the $Fe(CO)_5$, and the solid showed only two bands in the ν(CO) frequency range of the infrared spectrum, at 2053 and 2027 cm^{-1}, which are characteristic of $Fe_3(CO)_{12}$ in frequency and intensity. When the silica was stirred with a hexane solution of $Fe_3(CO)_{12}$, only a very slight decoloration of the solution occurred; the evaporation of the solvent, however, transferred all the $Fe_3(CO)_{12}$ onto the solid which thus became dark green. However, decoloration of the solid occurred when it was washed with hexane.

When $Fe(CO)_5$ was adsorbed onto silica, pretreated at 25 or 500 °C, from hexane solution or from the vapor phase, the support became pale yellow. Treatment under vacuum at 25 °C, however, produced a solid which showed no ν(CO) bands in the infrared spectrum. Furthermore, chemical analysis showed only trace amounts of iron on the support.

Adsorption of $Fe_3(CO)_{12}$ on Hydrated Alumina. When a hexane solution of $Fe_3(CO)_{12}$ was mixed with alumina (η or γ), pretreated at 25 °C under vacuum, the alumina became rose colored, and the initially green solution was decolorized. The same pink color was obtained when $Fe_3(CO)_{12}$ was sublimed onto the hydrated alumina. The adsorption process was therefore studied quantitatively. When 2.0 g of η-alumina was mixed with $Fe_3(CO)_{12}$ (0.10 g, 0.20 mmol) in hexane, the solution was completely decolorized after about 1 h of stirring. An analysis of the gas phase showed the presence of only a small amount of CO (~0.1 mol/(mol cluster)) and CO_2 (~0.05 mol/(mol cluster)), suggesting that the cluster did not decompose significantly in the presence of alumina. The pink-colored alumina thus obtained could be washed several times with hexane, and no extraction of the cluster occurred. The maximum quantity of cluster that could be chemisorbed onto the alumina in this way varied with the nature of the alumina used. For example, with γ-alumina (100 $m^2\ g^{-1}$ surface area) and η-alumina (315 $m^2\ g^{-1}$ surface area), the maximum amounts corresponded to 2.0% and 2.5% Fe, respectively. Further adsorption of $Fe_3(CO)_{12}$ onto an alumina already "saturated" with $Fe_3(CO)_{12}$ led to reversible physisorption of the cluster. In view of this, all studies were carried out with less than the maximum amount of cluster, so that only chemisorption and no physisorption could take place.

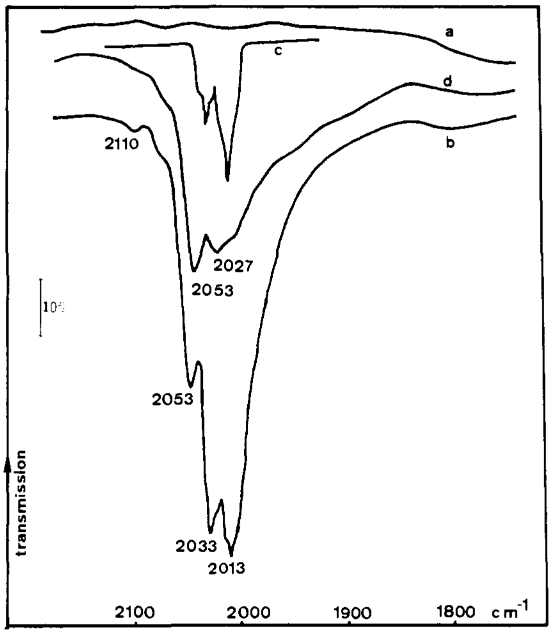

Figure 1. Infrared spectra corresponding to the adsorption of $Fe_3(CO)_{12}$ on $silica_{500}$ (a) silica sample (with an identical sample in the reference beam); (b) after sublimation of $Fe_3(CO)_{12}$ at room temperature; (c) gas-phase corresponding to (b); (d) after vacuum (10^{-4} torr) treatment at 25 °C for 1 h.

The characterization of the rose-colored adsorbed species I was achieved by using a variety of spectroscopic techniques. The Fourier transform infrared spectrum of adsorbed species I obtained by subtraction of the original spectrum of the alumina support, shown in Figure 2, gave a shoulder of medium intensity at 2082 cm^{-1}, two broad and intense bands at 2020 and 2008 cm^{-1}, a band of medium intensity at 1598 cm^{-1}, and shoulders of smaller intensity at 2115, 2052, and 1970 cm^{-1} (Figures 2 and 3). Bands of very weak intensity were also observed at 1250, 1400, and 1480 cm^{-1}, presumably due to CO_2 adsorbed on the support (Figure 3).

The visible spectrum of the adsorbed species showed an absorption maximum at 550 nm. The solid-state ^1H NMR spectrum of the adsorbed species showed a broad intense band centered at around 3.2 ppm downfield of tetramethylsilane and a less intense band at −13.6 ppm. The broad band at 3.2 ppm is due to OH groups of the alumina support. This band could be removed from the spectrum of the complex in two ways: (i) substraction of the signal recorded from the equivalent quantity of blank sample of alumina and (ii) a pulse sequence designed to suppress the proton signal of the support based on differences in T_1.

Species I could not be extracted from the alumina surface by CH_2Cl_2, $CHCl_3$, CH_3OH, or C_2H_5OH. However, when the rose-colored alumina was stirred with a dichoromethane solution of tetraethylammonium chloride (in excess with respect to the amount of $Fe_3(CO)_{12}$ initially used), after several minutes the alumina was decolorized and the solution became red. The alumina was completely decolorized after three successive washings with the Et_4NCl solution. The red solution was filtered, evaporated to dryness, and washed with water to remove the excess

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[10] A preliminary report of this work was published recently: (a) F. Hugues, J. M. Basset, D. Commereuc, and Y. Chauvin, *J. Chem. Soc., Chem. Commun.*, 68 (1980); Fe carbonyls have already been used to prepare highly dispersed metal particles supported on highly divided oxides; see for example (b) A. Brenner, *ibid.*, 251 (1979); (c) A. Brenner and D. A. Hucul, *Inorg. Chem.*, **18**, 2836 (1979); (d) J. B. Nagy, M. Van Eenoo, and E. G. Derouane, *J. Catal.*, **58**, 230 (1979).

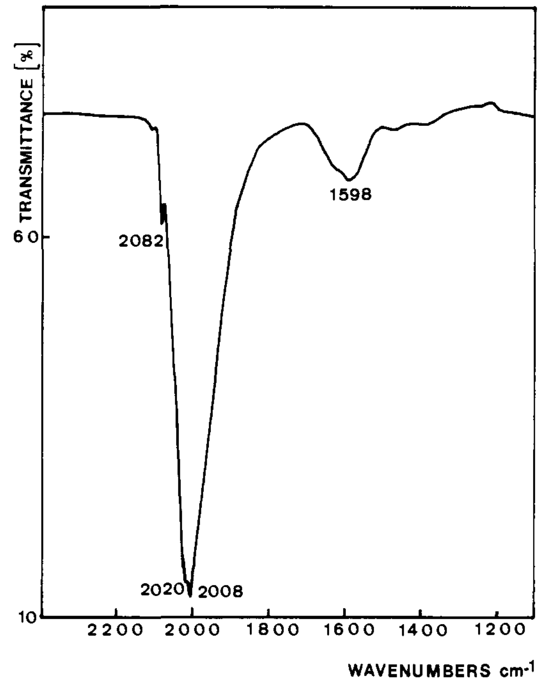


Figure 2. Infrared spectrum resulting from the ratio of alumina$_{25}$-supported $Fe_3(CO)_{12}$ vs. starting alumina$_{25}$. (The cluster $Fe_3(CO)_{12}$ was adsorbed from a hexane solution which was removed by treatment under vacuum (10^{-4} torr) at 25 °C for 1 h.)

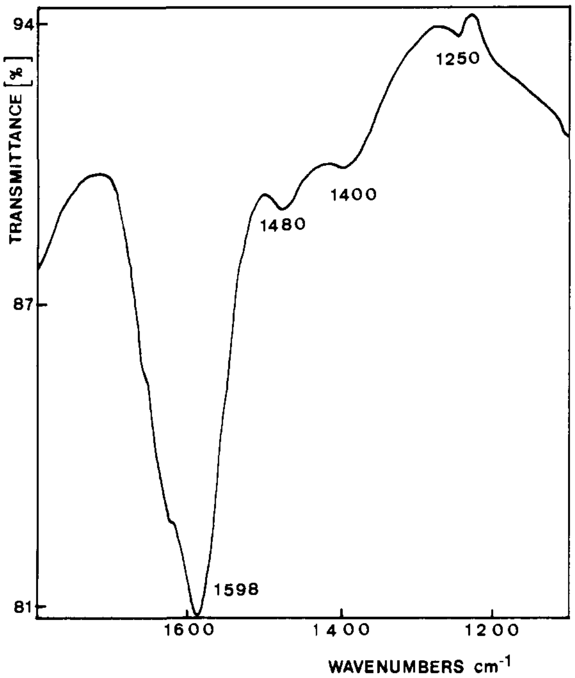


Figure 3. Same as Figure 1 with expansion of the ordinates in the range 1100–1800 cm^{-1}.

$(C_2H_5)_4NCl$. The remaining red solid (70% yield based on the starting $Fe_3(CO)_{12}$) was recrystallized from methanol. This red solid was characterized as $[HFe_3(CO)_{11}][N(C_2H_5)_4]$: ^1H NMR (CD_2Cl_2) 15 ppm (downfield from Me_4Si); UV λ_{max} (CH_2Cl_2) 543 nm; IR (CH_2Cl_2) ν(CO) 2072 (w), 2002 (s), 1971 (m), 1945 (sh), 1712 (m). Anal. Calcd for $[HFe_3(CO)_{11}][N(C_2H_5)_4]$: C, 37.31; H, 3.52; N, 2.33; Fe, 27.83. Found: C, 37.60; H, 3.49; N, 2.31; Fe, 27.60. An analysis of the alumina for iron before (1.7% Fe) and after (0.30%) the extraction indicated that 80% of the iron could be extracted by this ion-exchange reaction.

Adsorption of $Fe(CO)_5$ on Alumina. When a hexane solution of $Fe(CO)_5$ was stirred with γ-alumina or η-alumina (pretreated at 25 °C under vacuum), the support became pale rose in color after 4 h, while the initially yellow solution was slightly decolorized. After the support was washed with hexane to remove any physisorbed $Fe(CO)_5$, the solvent was evaporated under reduced pressure to leave a pale red solid. Extraction of the surface species with a dichloromethane solution of Et_4NCl, gave $[HFe_3(CO)_{11}][Et_4N]$ characterized by its infrared spectrum.

Protonation of the Chemisorbed Species I. When aqueous HCl (0.2 M) was added to an alumina sample (2 g) containing species I obtained by adsorption of $Fe_3(CO)_{12}$ (0.32 mmol) in hexane solution, the alumina rapidly changed color from rose to green and hydrogen (0.29 mmol of H_2) was evolved. The solution remained colorless. When the alumina was washed repeatedly with water to remove the acid and dried at 25 °C under vacuum, the green color was maintained. However, extraction with dichloromethane gave a green solution characterized as $Fe_3(CO)_{12}$ from its infrared spectrum.

Adsorption of $Fe_3(CO)_{12}$ and $Fe(CO)_5$ on Magnesia. When a hexane solution of $Fe_3(CO)_{12}$ was stirred at room temperature with magnesia (pretreated at 25 ° under vacuum), the solution was rapidly decolorized and the support became red. An analysis of the gas phase showed the presence of CO (0.3 mol/(mol cluster)) and CO_2 (0.05 mol/(mol cluster)). After removal of the solvent, the supported cluster could not be extracted by washing with hexane. The maximum amount of cluster that could be chemisorbed onto the magnesia corresponded to 2.7% Fe. Further adsorption of $Fe_3(CO)_{12}$ onto the magnesia was reversible. The adsorbed species II was characterized by its infrared spectrum: ν(CO) at 2078 (w), 2010 (s, br), 1950 (sh); weak bands were also observed at 1910 and 1860 cm^{-1}. Extraction of the surface species II with Et_4NCl in dichloromethane gave a red solution from which $[Et_4N][HFe_3(CO)_{11}]$ was recrystallized (60% yield). An analysis of the iron content of the magnesia showed that 85% of the iron was extracted in this way (from 2.7% Fe before extraction to 0.4% after extraction).

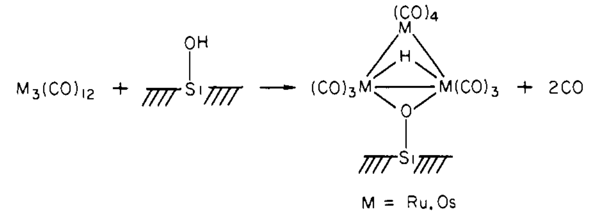
The addition of aqueous HCl to surface species II by adsorption of $Fe_3(CO)_{12}$ on magnesia as described above led to a color change from red to green, and hydrogen was evolved (1.1 ± 0.1 mol H_2 per mol cluster). The extraction of the green complex with CH_2Cl_2, under the same conditions as were used for alumina, gave a green solution which showed infrared bands characteristic of $Fe_3(CO)_{12}$.

When a hexane solution of $Fe(CO)_5$ was stirred with magnesia (pretreated at 25 °C under vacuum), the initially yellow solution was slightly decolorized and the support became pale rose in color. Species III which was thus formed could be extracted from the surface by a solution of $N(C_2H_5)_4Cl$ in excess to give $[N(C_2H_5)_4][HFe_3(CO)_{11}]$.

Adsorption of $Fe_3(CO)_{12}$ on Zinc Oxide. When a hexane solution of $Fe_3(CO)_{12}$ was stirred with hydrated zinc oxide (pretreated at 25 °C under vacuum), the solution became decolorized after several minutes, and the solid became red. An analysis of the gas phase indicated the presence of CO (0.1 mol/(mol cluster)) and CO_2 (<0.05 mol/(mol cluster)). The red supported complex obtained after removal of the solvent could not be extracted into hexane. This behavior was similar to that observed with hydrated alumina and magnesia. Very strong absorptions in the ν(CO) region of the infrared spectrum by the zinc oxide precluded an infrared spectroscopic study of the complexes on this support. However, a red complex could be extracted by ion exchange into a Et_4NCl solution and was then characterized as $[Et_4N][HFe_3(CO)_{11}]$ by its infrared and UV–vis spectra.

Results and Discussion

Although some decomposition to gaseous $Fe(CO)_5$ occurs, the adsorption of $Fe_3(CO)_{12}$ on silica is mainly a reversible process as determined by infrared spectroscopy (Figure 1) and by quantitative extraction of the adsorbed cluster by hexane. This reversible adsorption occurs on silica$_{25}$, silica$_{300}$, and silica$_{500}$. It indicates the low reactivity of the silanol groups of the support toward the carbonyl ligands of the cluster or toward the metallic frame. This is in contrast to the behavior of silanol groups of silica toward $Ru_3(CO)_{12}$ or $Os_3(CO)_{12}$ where the following reaction takes place:[4-9]

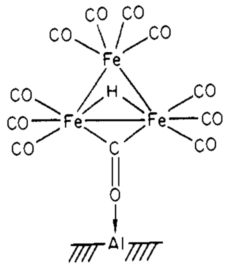


In the case of iron the lower stability of the metal–metal bond leads to the easy formation of $Fe(CO)_5$ by sublimation of $Fe_3(CO)_{12}$ at 60 °C. The formation of $Fe(CO)_5$ by heating unsupported $Fe_3(CO)_{12}$ or $Fe_2(CO)_9$ has also been observed by Brenner.[10c] This very low reactivity of the silanol groups is also observed in the adsorption of $Fe(CO)_5$ on silica, which is also a reversible process regardless of the pretreatment temperature of the support between 25 and 500 °C.

On alumina we have observed two types of adsorption of $Fe_3(CO)_{12}$. First, a chemisorption process corresponding to the transfer of the green cluster from a hexane solution to the alumina support with formation of a pink-colored supported species that we shall subsequently refer to as species I. Second, at high loading (>2%), a simple physisorption occurs: the supported cluster is identical with the initial carbonyl complex $Fe_3(CO)_{12}$ and can be extracted into a hexane solution. The maximum quantity of $Fe_3(CO)_{12}$ that can be chemisorbed in the form of species I on γ- and η-alumina is 2.0 and 2.5%, respectively. In the case of nonporous γ-alumina, the whole surface is theoretically accessible to the cluster. This means that statistically there is a distribution of 0.72 molecule of supported cluster per 100 Å^2. This is not far from a complete covering of the surface since $Fe_3(CO)_{12}$ may be estimated as having a "surface area" of 80 Å^2. In the case of the porous η-alumina, the smaller amount of cluster distributed over the surface (0.25 molecule per 100 Å^2) is undoubtedly due to the fact that some of the pores (mean diameter 30 Å) are not easily accessible to the cluster.

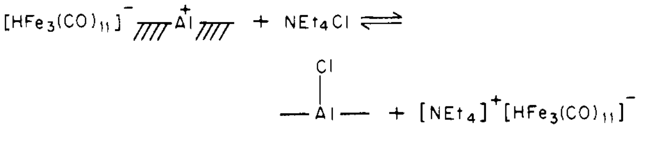
The mass balance deduced from the analysis of the gas phase during chemisorption of the cluster indicates that no significant amounts of CO or CO_2 are evolved during this chemisorption process (respectively 0.1 and 0.05 mol/(mol cluster)). This lack of CO evolution is a meaningful result since it is well-known that CO does not chemisorb significantly on hydrated alumina.[11] The absence of CO_2 in the gas phase is not significant due to the adsorption process of CO_2 on hydrated alumina at room temperature. (Infrared data are not of great help in this respect because we have found in separate experiments carried out with hydrated alumina that if the amount of CO_2 chemisorbed corresponds to less than 1 CO_2/100 Å^2, it cannot be easily detected by infrared spectroscopy[12].) Therefore if we except the uncertainty due to possible, but not detectable, CO_2 adsorption on the support, the mass balance data indicate that the number of CO ligands in species I is not far from that of the starting cluster $Fe_3(CO)_{12}$.

Species I has been characterized in the solid state by infrared, ^{1}H NMR, and UV spectroscopy. The values obtained for such species are in fair agreement with those expected for the anionic hydrido species $[HFe_3(CO)_{11}]^-$ although differences are observed with respect to the values observed for the well-known cluster $[NR_4][HFe_3(CO)_{11}]$.[13] The IR spectrum (Figures 2 and 3) shows three main absorptions at 2082, 2020, and 2008 cm^{-1} for the linear carbonyls and a broad band of smaller intensity in the bridging region at 1598 cm^{-1} whereas ν(CO) bands at 2073 (w), 2008 (s), 2000 (s) and 1709 (m) (C_6H_6 solvent) are observed with the parent cluster $[N(Et)_4][HFe_3(CO)_{11}]$.[13] In fact, it is known that the stretching frequency of the bridging carbonyl ligand in $[(C_2H_5)_3NH][HFe_3(CO)_{11}]$ varies with the polarity of the solvent from 1639 cm^{-1} in benzene to 1742 cm^{-1} in acetonitrile.[13] In nonpolar solvents such as benzene, there is formation of a tight ion-pair complex in which the bridging carbonyl ligand is interacting with the proton of the ammonium cation. On the alumina surface, a similar interaction probably occurs with the aluminum cation leading to the formation of the hypothetical surface cluster.[14]



Such complexation would be responsible for the shift of about 100 cm^{-1} to lower frequency of the ν(CO) band corresponding to the bridging carbonyl and for the small shift of about 10 cm^{-1} to higher frequency of the ν(CO) bands corresponding to the linear carbonyls.

The anionic character of species I is in agreement with the impossibility of extracting it by any solvent (CH_2Cl_2, $CHCl_3$, CH_3OH, or C_2H_5OH). In contrast, it was possible to extract it by ion exchange with a hexane solution of $[N(C_2H_5)_4]Cl$, presumably according to the equilibrium



$$[HFe_3(CO)_{11}]^- \; \overset{+}{Al} + NEt_4Cl \rightleftharpoons \overset{\overset{\textstyle Cl}{|}}{-Al-} + [NEt_4]^+[HFe_3(CO)_{11}]^-$$

The yield of such an extraction process (80% based on the iron content of the alumina support before and after extraction; 70% based on the yield of $[NEt_4][HFe_3(CO)_{11}]$) indicates clearly that species I has a formula very close to $[HFe_3(CO)_{11}]^-$.

The hydridic character of species I is confirmed by the observation in the solid-state ^{1}H NMR spectrum of a high-field proton resonance at 13.6 ppm relative to Me_4Si, whereas values of 14.6, 15, and 15.5 ppm are observed, respectively, for $[(Ph_3P)_2N][HFe_3(CO)_{11}]$, $[H_3O^+, {}_nH_2O][HFe_3(CO)_{11}]$, and $[NEt_4][HFe_3(CO)_{11}]$.[13,15-17] This difference in chemical shift is probably due to the interaction between the cluster and the surface cation via the bridging carbonyl ligand. The presence of a hydride in species I is also confirmed by the quantitative evolution of H_2 observed during the protonation of such species by aqueous HCl (0.2 M). Simultaneously $Fe_3(CO)_{12}$ is formed on the surface and can be extracted by CH_2Cl_2. The reactivity of the surface anionic hydride is therefore similar to that observed in solution.[18]

The UV–visible spectrum of species I in the solid state exhibits a maximum at 543 nm whereas a value of 540 nm is observed

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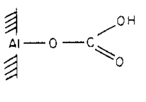
(11) Infrared and volumetric measurements did not indicate a significant and detectable chemisorption of CO on hydrated alumina, see also R. P. Eischens and V. A. Pliskin, *Adv. Catal.*, **10**, 1 (1958).

(12) The adsorption of CO_2 on hydrated alumina was studied carefully by Parkyns (N. D. Parkyns, *J. Chem. Soc. A*, 410 (1969)). We found that if CO_2 was adsorbed on our γ-alumina in such a way that the amount adsorbed was about 1 CO_2/100 Å^2 (value corresponding to the maximum amount of $Fe_3(CO)_{12}$ which could be chemisorbed on γ-alumina) bands of very weak intensity could be observed at 1645, 1445, and 1240 cm^{-1}. However, those bands almost disappeared after vacuum treatment at room temperature for 1 h. Those bands were also observed by N. D. Parkyns (vide supra) and they were attributed to hydrogeno carbonates of the type



Such bands were also observed by Fourier transform infrared upon adsorption of $Fe_3(CO)_{12}/Al_2O_3$, but their intensity was very weak in agreement with their low extinction coefficient.

(13) J. R. Wilkinson and L. J. Todd, *J. Organomet. Chem.*, **118**, 199 (1976); H. A. Hodali, C. Arcus, and D. F. Shriver, *Inorg. Synth.*, **20**, 218 (1980).

(14) For a review of the interaction between various Lewis acids with the oxygen lone pair of a coordinated CO, see for example D. F. Shriver and Sr. A. Alich, *Coord. Chem. Rev.*, 8 (1972); J. S. Kristoff and D. F. Shriver, *Inorg. Chem.*, **13**, 499 (1974); D. F. Shriver, S. Onaka, and D. Strope, *J. Organomet. Chem.*, **117**, 277 (1976). Concerning the interaction between carbonyl ligands and Lewis acid sites present at the surface of oxides, see for example ref 1(h) or 1(i).

(15) M. L. H. Green, *Angew. Chem.*, **72**, 719 (1960).

(16) H. A. Hodali, D. F. Shriver, and C. A. Ammlung, *J. Am. Chem. Soc.*, **100**, 5239 (1978).

(17) W. Hieber and H. Beutner, *Z. Naturforsch.*, **176**, 211 (1962).

(18) In solution the protonation of $HFe_3(CO)_{11}^-$ leads to the formation of H_2 and $Fe_3(CO)_{12}$ according to the following equation:

$$12HFe_3(CO)_{11}^- + 18H^+ \rightarrow 11Fe_3(CO)_{12} + 15H_2 + 3Fe^{2+}$$

R. Doedens and L. F. Dahl, *J. Am. Chem. Soc.*, **88**, 4847 (1966).

in the parent cluster $[NMe_4][HFe_3(CO)_{11}]$.[17]

Although less data are available on magnesia, it seems that chemisorption of $Fe_3(CO)_{12}$ and $Fe(CO)_5$ on fully hydroxylated magnesia gives rise more rapidly than on alumina to the formation of the red complex $[HFe_3(CO)_{11}]^-Mg^+$ characterized by its infrared spectrum. Such supported cluster could be extracted only by ion exchange with $[NEt_4]Cl$ which gave almost quantitative extraction of the surface cluster $[NEt_4][HFe_3(CO)_{11}]$. The supported cluster obtained by chemisorption of $Fe_3(CO)_{12}$ on magnesia can also be protonated by HCl with concomitant formation of 1 mol of H_2 per mol of supported cluster with partial regeneration of $Fe_3(CO)_{12}$ which can be extracted from the surface by CH_2Cl_2.

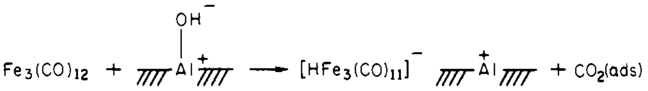
Similar data are observed during the chemisorption of $Fe_3(CO)_{12}$ on hydroxylated zinc oxide. Although infrared spectroscopy cannot be easily used with such support, the chemisorption of $Fe_3(CO)_{12}$ is irreversible and gives a red supported species without significant decomposition of the starting cluster into gaseous CO or CO_2. The red complex can be extracted by ion exchange with NEt_4Cl and can be characterized as $[NEt_4][HFe_3(CO)_{11}]$.

In conclusion, all the data available on alumina concerning species I indicate that such species can be formulated best as $[HFe_3(CO)_{11}]^-$ interacting via the bridging carbonyl with some acidic center. In basic solution the formation of $[HFe_3(CO)_{11}]^-$ from $Fe_3(CO)_{12}$ or $Fe(CO)_5$ is carried out according to the reactions:[19,20]

$$Fe_3(CO)_{12} + OH^- \xrightarrow[\text{MeOH}]{\text{KOH, 25 °C}} [HFe_3(CO)_{11}]^- + CO_2$$

$$3Fe(CO)_5 + NR_3 + 2H_2O \xrightarrow{\text{80 °C}} [HFe_3(CO)_{11}]^- \, NHR_3^+ + 2CO_2 + 2CO + H_2$$

On the alumina surface, two possibilities may be envisaged: (i) nucleophilic attack by a surface hydroxyl group;

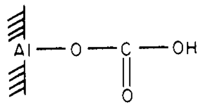


$$Fe_3(CO)_{12} + \overset{OH^-}{\underset{|}{}}\!\!-\overset{+}{Al}- \longrightarrow [HFe_3(CO)_{11}]^- \; -\overset{+}{Al}- + CO_2(ads)$$

(ii) nucleophilic attack by water present on the alumina surface.

$$Fe_3(CO)_{12} + 2H_2O \rightarrow [HFe_3(CO)_{11}]^- \, [H_3O]^+ + CO_2(ads)$$

Two experimental results suggest that the former alternative is more likely. First, the anionic hydrido species is also observed on supports that do not contain molecular water $Al_2O_3(300)$ and $Al_2O_3(500)$;[21] second, only ion-exchange techniques, using Et_4NCl, have enabled the surface species to be extracted, suggesting that the cation is a surface site ($-Al^+-$) and not H_3O^+. The basic character of the hydroxyl groups on alumina has been shown by Knözinger[22] and Che.[23] It is probable from infrared data that most of the CO_2 remains adsorbed on alumina as a hydrogeno carbonate of the type



$$Al-O-\underset{\underset{O}{\|}}{C}-OH$$

which has a very low extinction coefficient.[12] The overall reaction scheme for the adsorption of $Fe_3(CO)_{12}$ and $Fe(CO)_5$ on alumina is shown in Figure 4.

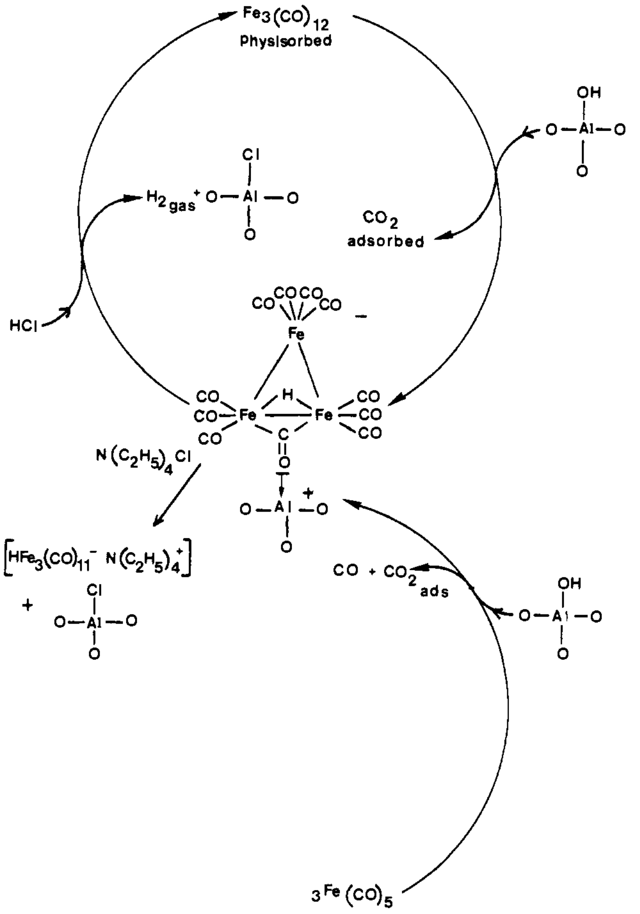


Figure 4. Overall reactions occurring with $Fe_3(CO)_{12}$ and $Fe(CO)_5$ with the alumina surface.

The formation of $HFe_3(CO)_{11}^-$ by adsorption of $Fe(CO)_5$ or $Fe_3(CO)_{12}$ on fully hydroxylated magnesia is much faster than on alumina. This must be ascribed to the more basic character of the surface hydroxyl group of magnesia.[24] Furthermore, the maximum quantity of $Fe_3(CO)_{12}$ that can be chemisorbed on magnesia corresponds to 0.9 molecule of cluster per 100 Å^2, a value even closer to complete coverage than is achieved on γ-alumina. Hydroxylated zinc oxide seems to be less basic than magnesia, but the general behavior is the same as that of alumina and magnesia.

Registry No. $Fe_3(CO)_{12}$, 17685-52-8; $Fe(CO)_5$, 13463-40-6; $HFe_3(CO)_{11}^-$, 55188-22-2; SiO_2, 7631-86-9; Al_2O_3, 1344-28-1; MgO, 1309-48-4; ZnO, 1314-13-2.

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(19) W. McFarlane and G. Wilkinson, *Inorg. Synth.*, **8**, 181 (1966).

(20) W. Hieber and G. Brendel, Zeit. Anorg. Chem., **289**, 324 (1957).

(21) On alumina$_{300}$ and alumina$_{500}$, ν(CO) bands corresponding to the anionic hydrido species were also observed, but simultaneously other bands could be detected. Studies are still in progress to fully characterize those species.

(22) H. Knözinger and B. Stubner, *J. Phys. Chem.*, **82**, 1526 (1978).

(23) M. Che, C. Naccache, and B. Imelik, *J. Catal.*, **24**, 328 (1972).

(24) H. Knözinger, *Adv. Catal. Rel. Subj.*, **25**, 184 (1976).