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was achieved with broad-band modulated decoupling.

^{1}H NMR spectra were recorded on the same instrument as above with a 5-mm ^{1}H observe probe. A broad-band decoupling coil tuned to ^{125}Te and set on the frequency of ^{125}Te in 1,3-ditellurole at 4 W of power was used to decouple ^{125}Te. Proton spectra were referenced to internal Me$_4$Si. ^{13}C NMR spectra were recorded on a JEOL FX270 spectrometer at 27.14 MHz in 16K of memory with a spectral width of 15 kHz (1.8 Hz/data point; pulse repetition time, 0.5 s) and a pulse width of 4 μs. Samples were run deuterium locked and were referenced to internal Me$_4$Si. Proton decoupling was broad band.

Spectra were simulated with a Bruker Aspect 2000 computer in the program PANIC, part of the Bruker software package. Line broadening of 1 Hz was added to the simulated spectra.

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Surface Organometallic Chemistry: Formation of the Grafted Anionic Clusters $[HFeOs_3(CO)_{13}]^-$, $[HFeRu_3(CO)_{13}]^-$, and $[FeCo_3(CO)_{12}]^-$ on a Hydroxylated Magnesia

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The reaction of the mixed hydrido carbonyl $H_2FeM_3(CO)_{13}$ (M = Ru, Os) and $HFeCo_3(CO)_{12}$ with the surface of partially hydroxylated magnesia has been studied in situ by IR spectroscopy, evolution of gases, and extraction of the adsorbed complexes. At room temperature, $H_2FeM_3(CO)_{13}$ (M = Ru, Os) and $HFeCo_3(CO)_{12}$ are deprotonated at the surface of magnesia to give the anions $[HFeM_3(CO)_{13}]^-$ (M = Ru, Os) and $[FeCo_3(CO)_{12}]^-$ with virtually no disproportionation to other cluster species. The anions $[HFeM_3(CO)_{13}]^-$ (M = Ru, Os) were also synthesized by proton abstraction by KOH and by KH. It is suggested that on the surface of the magnesia the deprotonation occurs via surface OH groups. From IR spectra apparently there is no tight ion pair between the anions on the surface and the Lewis centers which is in contrast with that which is observed for $[HFe_3(CO)_{11}]^-$ (M = Fe). A mechanistic explanation is proposed. Thermal decomposition of the surface-bound anions has been studied.

Introduction

Earlier studies have shown that $Fe_3(CO)_{12}$ reacts with surface OH groups of alumina,[1] magnesia,[1] zinc oxide,[1] or NaY zeolite[2] to give the corresponding anionic hydride $[HFe_3(CO)_{11}]^-$ linked to the surface cation, M^{n+} (M^{n+} = Al^{3+}, Mg^{2+}, Zn^{2+}) via a tight ion pair. The formation of this anionic hydride corresponds to a nucleophilic attack of surface OH groups at coordinated CO followed by β-H elimination and formation of CO_2 adsorbed as carbonate. We report here the results of a study which shows that certain anionic mixed-metal clusters linked to basic surfaces can be obtained through proton abstraction by surface OH groups.[17] The OH groups of a magnesia [surface] deprotonate the mixed-metal hydrido clusters $H_2FeM_3(CO)_{13}$ (M = Ru, Os) or $HFeCo_3(CO)_{12}$, to the corresponding anions $[HFeM_3(CO)_{13}]^-\cdot{}^1/_2Mg^{2+}$ [surface] (M = Ru, Os) and $[FeCo_3(CO)_{12}]^-\cdot{}^1/_2Mg^{2+}$ [surface] without significant formation of secondary products. These conclusions are based upon the absence of gas evolution in placing the cluster on the magnesia support, IR spectra of adsorbed species, and IR spectra of species extracted from the surface. The relative absence of secondary products is of importance in delineating thermal stabilities of bound species and products from thermal decomposition, and in the ultimate production of metal particles which has also been explored in this investigation.

Table I. Infrared Spectra (CO Stretching Region, cm^{-1})

Surface-Bound Species	Extracted Anion ($[PPN]^+$ Salt)
$[HFeOs_3(CO)_{13}]^-$	$[HFeOs_3(CO)_{13}]^-$
2078 w, 2036 ms, 2016 s, 1997 s, 1975 sh, 1941 sh, 1788 w (br)[a]	2078 w, 2037 s, 2013 s, 1997 s, 1964 m, 1940 m, 1794 w
2077 w, 2035 s, 2013 s (br), 1998 s (br), 1937 sh, 1792 w (br)[b]	
$[HFeRu_3(CO)_{13}]^-$	$[HFeRu_3(CO)_{13}]^-$
2070 w, 2030 s (br), 2007 s (sh), 1990 s, 1972 sh[a]	2070 w, 2032 s, 2013 s, 1998 s, 1970 sh, 1940 sh, 1844 w, 1809 w (br)
$[FeCo_3(CO)_{12}]^-$	$[FeCo_3(CO)_{12}]^-$
2065 w, 2004 s, 1968 m (br), 1928 w, 1888 m (br), 1814 w (br)[a]	2062 w, 2003 vs, 1967 w, 1928 w, 1888 m (br), 1811 m (br)

[a] Before extraction. [b] Material on surface after extraction.

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(1) Hugues, F.; Basset, J. M.; Ben Taarit, Y.; Choplin, A.; Primet, M.; Rojas, D.; Smith, A. K. *J. Am. Chem. Soc.* **1982**, *104*, 7020.

(2) Iwamoto, M.; Kusano, H.; Kagawa, S. *Inorg. Chem.* **1983**, *22*, 3336.

(3) Budge, J. R.; Scott, J. P.; Gates, B. C. *J. Chem. Soc., Chem. Commun.* **1983**, 342.

(4) Budge, J. R.; Lücke, B. F.; Gates, B. C.; Toran, J. *J. Catal.* **1985**, *91*, 272.

(5) Guglielminotti, E.; Osella, D.; Stanghellini, P. L. *J. Organomet. Chem.* **1985**, *281*, 291.

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Experimental Section

1. **General Procedures.** All experiments were carried out under strict exclusion of air, via standard techniques for handling air-sensitive compounds (Schlenk tube under Ar or vacuum (10^{-5} torr)).

For IR spectra, a cell was constructed which permitted the addition of the cluster to the support in the cell under controlled conditions of vacuum or Ar atmosphere. The adsorbed cluster was not exposed to the air prior to obtaining its IR spectrum which was produced with either a Perkin-Elmer 225 or a Nicolet MDX spectrometer. Gases evolved during cluster adsorption on the support were sampled for analysis by gas chromatography using an apparatus in which the sample syringe was not permitted to come in contact with the adsorbed cluster.[6] Traces of H_2, CO, CO_2, and hydrocarbons corresponding to less than 0.1 mol/mol of cluster could be quantitatively analyzed. The ^1H NMR spectra of the extracted clusters were obtained by using a Varian XL 100 spectrometer.

All experiments were carried out by using magnesia (100 m^2/g) taken from the same batch which had been treated under O_2 (1 atm) for 10 h at 400 °C and then under vacuum (10^{-5} torr for 16 h) at 400 °C. This procedure eliminated most of the surface carbonate. The solid was then equilibrated with H_2O at 25 °C for 16 h ($mgO_{25 °C}$) and placed under vacuum at 25 °C overnight. In some cases it was subsequently dehydrated at 200 °C under vacuum (10^{-5} torr) overnight ($MgO_{200 °C}$).

2. **Extraction Experiments. a. $H_2FeOs_3(CO)_{13}$/Magnesia(25 °C).** In a typical experiment, 2 g of $MgO_{25 °C}$ was placed in contact with a solution of $H_2FeOs_3(CO)_{13}$ (0.03 mmol) in CH_2Cl_2 (10 mL) in a Schlenk tube under Ar. The orange solution was instantaneously decolorized, and the solid turned red within a few seconds. The in situ IR (Table I) spectrum of the solid indicated the presence of $[HFeOs_3(CO)_{13}]^-\cdot{}^1/_2Mg^+$ [surface]. Simultaneously, no gas evolution (CO, H_2, or CO_2) could be detected. The solid was then thoroughly washed three times with 5-mL aliquots of CH_2Cl_2 in order to remove any unreacted cluster. No detectable amounts of any carbonyl species could be removed from the surface. The solid was then treated with 0.06 mmol of (PPN)Cl ($[N(PPh_3)_2]Cl$) in CH_2Cl_2 (10 mL); the resulting solution contained $[PPN]^+[HFeOs_3(CO)_{13}]^-$, characterized by comparison of its infrared (Table I) and ^1H NMR spectra (δ ($CDCl_3$) 7.5 (m, 30 H), −19.5 (s, 1 H)) with those of an earlier report.[7]

Only 60% of the initial cluster was extracted as $[PPN]^+[HFeOs_3(CO)_{13}]^-$. The species remaining on the surface was characterized by its IR spectrum (Table I); it exhibited bands as expected for $[HFeOs_3(CO)_{13}]^-\cdot{}^1/_2Mg^{2+}$ [surface].

b. $H_2FeRu_3(CO)_{13}$/Magnesia(25°C). When a red solution of $H_2FeRu_3(CO)_{13}$ (0.048 mmol) in CH_2Cl_2 (10 mL) was placed in contact with 2 g of MgO_{25} in a Schlenk tube under Ar, the solution decolorized immediately while the solid turned red. Simultaneously, no evolution of CO, H_2, or CO_2 could be detected. The in situ IR spectrum (Table I) of the solid indicated the presence of $[HFeRu_3(CO)_{13}]^-\cdot{}^1/_2Mg^{2+}$ [surface]. While carbonyl species could not be extracted by CH_2Cl_2, (PPN)Cl (0.055 mmol) in CH_2Cl_2 (10 mL) produced a red extract, which was purified by column chromatography. The resulting solution contained $[PPN]^+[HFeRu_3(CO)_{13}]^-$ which was characterized by comparison of its IR (Table I) and ^1H NMR spectra (δ ($CDCl_3$) 7.4 (m, 30 H), −15.1 (s, 1 H)) with an earlier report.[8] Analysis of the residual Fe and Ru at the surface of magnesia showed that 80% of the starting cluster had been extracted.

c. $HFeCo_3(CO)_{12}$/Magnesia(25°C). A violet solution of $HFeCo_3(CO)_{12}$ (0.08 mmol) in CH_2Cl_2 (10 mL) was decolorized within a few seconds after it was placed in contact with $MgO_{25 °C}$. The in situ IR spectrum (Table I) of the solid indicated the presence of $[FeCo_3(CO)_{12}]^-\cdot{}^1/_2Mg^{2+}$ [surface]. No carbonyl species could be removed from the resulting violet solid by washing it with 5-mL aliquots of CH_2Cl_2. The solid was then treated with 0.14 mmol of (PPN)Cl in CH_2Cl_2 (10 mL); the resulting solution contained $[PPN]^+[FeCo_3(CO)_{12}]^-$,[9] characterized by its IR spectrum (Table I). A minor component $[PPN]^+[Co(CO)_4]^-$[10] was identified from a weak band at 1888 cm^{-1}. No ^1H NMR signal could be observed in the range examined (+10 to −25 ppm).

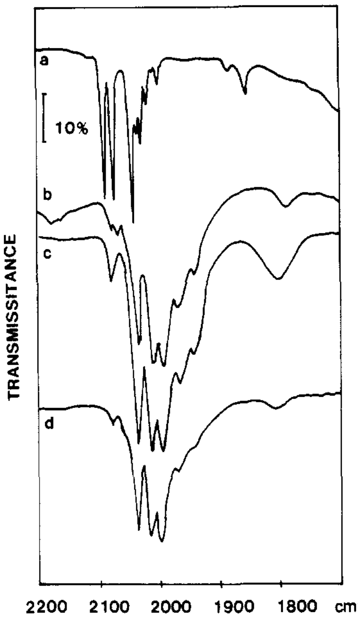

Figure 1. Interaction of $H_2FeOs_3(CO)_{13}$ with $MgO_{25 °C}$: infrared spectra in the ν(CO) region of (a) $H_2FeOs_3(CO)_{13}$ (CH_2Cl_2 solution), (b) $H_2FeOs_3(CO)_{13}$ after impregnation on a $MgO_{25 °C}$ disk, (c) b extracted by $(PPN)Cl/CH_2Cl_2$, and (d) $HFeOs_3(CO)_{13}^-$ PPN^+ (CH_2Cl_2 solution) from reaction of $H_2FeOs_3(CO)_{13}$ with KOH/MeOH.

3. **Syntheses of $[PPN]^+[HFeM_3(CO)_{13}]^-$ (M = Ru, Os) by Metathesis Reactions. a. Deprotonation Using KOH.** In a typical experiment, a methanolic solution of KOH (0.06 mmol) was added to $H_2FeM_3(CO)_{13}$ (0.033 mmol) in 10 mL of CH_2Cl_2, and the system was allowed to reflux for 3 h. Metathetical reaction with PPNCl (0.048 mmol) in 10 mL of CH_2Cl_2 yields salts almost quantitatively. They were characterized by their IR[7,8] and ^1H NMR spectra. **$[PPN]^+[HFeOs_3(CO)_{13}]^-$**: ν(CO) ($cm^{-1}$) 2077 w, 2036 s, 2013 s, 1997 s, 1964 m (sh), 1941 w (sh), 1810 w; δ ($CDCl_3$) 7.5 (m, 30 H), −19.5 (s, 1 H). **$[PPN]^+[HFeRu_3(CO)_{13}]^-$**: ν(CO) ($cm^{-1}$) 2068 w, 2030 s, 2012 s, 1996 s, 1968 m, 1944 w, 1838 w (sh), 1807 m (br); δ ($CDCl_3$) 7.5 (m, 30 H), −15.1 (s, 1 H).

b. Deprotonation Using KH. In a typical synthesis, 25 mL of THF was condensed into a vessel which was equipped with a stir bar, $H_2FeM(CO)_{13}$ (0.101 mmol), and KH (0.444 g, 0.111 mmol). The reaction mixture was placed in an oil bath at 55 °C and stirred for 20 h. Noncondensable gas from the reaction solution was collected (ca. 85% of theory) intermittently by using a Toepler pump and analyzed (H_2 by mass spectrometry). The solution was then filtered in a vacuum line extractor, THF was pumped away, and 10 mL of hexane was added in order to wash the precipitate. Yields of salts were about 80%. The IR and ^1H NMR spectra of the potassium salts are consistent with spectra produced by the PPN salts. **$K^+[HFeOs_3(CO)_{13}]^-$**: ν(CO) (cm^{-1}) 2071 w, 2035 s, 2012 s, 1995 vs, 1966 m, 1942 m (sh), 1816 w (br); δ (CD_2Cl_2) 7.5 (m, 30 H), −19.3 (s, 1 H). **$K^+[HFeRu_3(CO)_{13}]^-$**: ν(CO) (cm^{-1}) 2078 w, 2026 s, 2011 s, 1995 vs, 1968 m, 1942 m, 1822 w (br); δ (CD_2Cl_2): 7.5 (m, 30 H), −15.4 (s, 1 H). Metathetical reactions of $K^+[HFeOs_3(CO)_{13}]^-$ and $K^+[HFeRu_3(CO)_{13}]^-$ with (PPN)Cl (0.081 mmol) were carried out in CH_2Cl_2 to obtain $[PPN]^+[HFeOs_3(CO)_{13}]^-$ and $[PPN]^+[HFeRu_3(CO)_{13}]^-$ almost quantitatively.

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[6] Smith, A. K.; Besson, B.; Basset, J. M.; Psaro, R.; Fusi, A.; Ugo, R. *J. Organomet. Chem.* **1980**, *192*, C31.

[7] Eadie, D. T.; Holden, H. D.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1984**, 301.

[8] Taskusagawa, F.; Fumagalli, A.; Koetzle, T. F.; Steinmetz, G. R.; Rosen, R. P.; Gladfelter, W. L.; Geoffroy, G. L.; Bruck, M. A.; Bau, R. *Inorg. Chem.* **1981**, *20*, 3823.

[9] Chini, P.; Colli, L.; Perraldo, M. *Gazz. Chim. Ital.* **1960**, *90*, 1005.

[10] Ruff, J. K.; Schlientz, W. F. *Inorg. Synth.* **1974**, *15*, 84.

[11] Drezdon, M. A.; Tessier-Youngs, C.; Woodcock, C.; Blonsky, P. M.; Leal, O.; teo, B. K.; Burwell, R. L., Jr.; Shriver, D. F. *Inorg. Chem.* **1985**, *24*, 2349.

[12] Basset, J. M.; Choplin, A. *J. Mol. Catal.* **1983**, *21*, 95.

[13] Choplin, A.; Huang, L.; Theolier, A.; Gallezot, P.; Basset, J. M.; Siriwardane, U.; Shore, S. G.; Mathieu, R. *J. Am. Chem. Soc.*, in press.

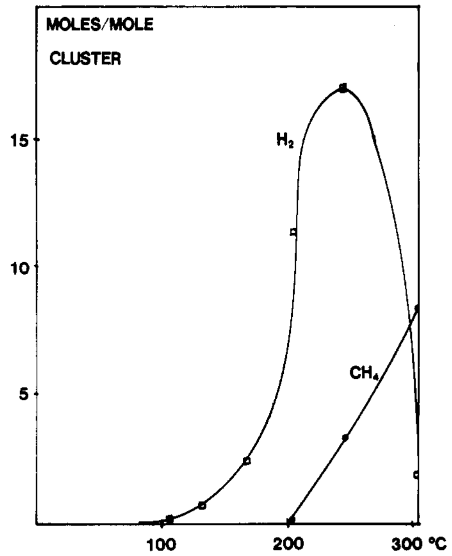

Figure 2. Gas evolution during thermal treatment under vacuum (10^{-5} mmHg) of $H_2FeOs_3(CO)_{13}/MgO_{200°C}$.

Results

1. Interaction of $H_2FeOs_3(CO)_{13}$ with Magnesia (25°C). The IR spectrum of $H_2FeOs_3(CO)_{13}$ in CH_2Cl_2 is shown in Figure 1a. Placing this solution in contact with magnesia, pretreated at 25 °C, results in fast and quantitative chemisorption of the cluster on the support without detectable evolution of any gas (CO, H_2, or CO_2). The infrared spectrum of the supported species (Table 1, Figure 1b) exhibits bands which are typical for the $[HFeOs_3(CO)_{13}]^-$ ion.[7] This ion was extracted as $[PPN]^+[HFeOs_3(CO)_{13}]^-$, using (PPN)Cl in CH_2Cl_2. The IR spectrum of the extract (Table I, Figure 1c) agrees very well with the IR spectrum of the surface-bound species in the ν(CO) stretching region. Approximately 60% of the surface-bound anion was extracted; the spectrum of the remaining surface-bound species was still characteristic of the $[HFeOs_3(CO)_{13}]^-$ anion (Table I, Figure 1d), indicating that the surface ion-exchange process is slow or an equilibrium.

Evolved gases were analyzed as a function of temperature in the thermal decomposition of the adsorbed anionic cluster $[HFeOs_3(CO)_{13}]^-$ (Figure 2). Only above 120 °C does H_2 begin to appear in the gas phase. Above 200 °C methane is formed. Surprisingly gaseous CO is not formed during the thermal decomposition experiment. This result suggests a stoichiometric water-gas shift reaction between the carbonyl ligands and the adsorbed water with formation of gaseous H_2 and carbonates adsorbed on the magnesia support. At 300 °C most of the gaseous hydrogen has been transformed into methane. Electron microscope measurements show that at 300 °C after treatment under H_2 metallic particles shown to be bimetallic are formed,[13] well dispersed; their size ranges between 20 and 50 Å.

2. Interaction of $H_2FeRu_3(CO)_{13}$ with Magnesia (25°C). The IR spectrum of $H_2FeRu_3(CO)_{13}$ in CH_2Cl_2 is shown in Figure 3a. The behavior of this cluster on a hydroxylated magnesia is very similar to that observed for $H_2FeOs_3(CO)_{13}$. The cluster is instantaneously chemisorbed on the surface of magnesia as $[HFeRu_3(CO)_{13}]^-$ on the basis of the IR[8] spectrum of the adsorbed species in the CO stretching region (Table I, Figure 3b). No concomitant gas evolution (CO, H_2, or CO_2) is observed. Extraction of the anionic cluster by surface ion exchange with a slight excess of (PPN)Cl in CH_2Cl_2, yields $[PPN]^+[HFeRu_3(CO)_{13}]^-$ (Table I, Figure 3c), confirming the formation of this anionic mixed-metal species on the surface of magnesia. About 80% of the surface-bound anion was extracted. The remaining material could not be analyzed owing to its high air sensitivity.

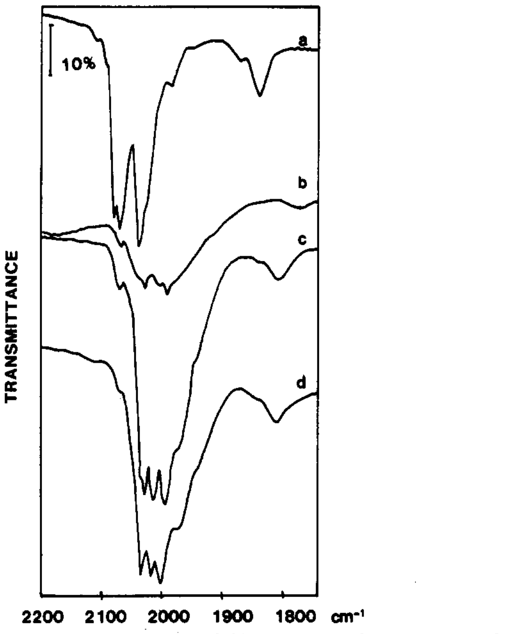

Figure 3. Interaction of $H_2FeRu_3(CO)_{13}$ with $MgO_{25°C}$: infrared spectra in the ν(CO) region of (a) $H_2FeRu_3(CO)_{13}$ (CH_2Cl_2 solution), (b) $H_2FeOs_3(CO)_{13}$ after impregnation on a $MgO_{25°C}$ disk, (c) b extracted by $(PPN)Cl/CH_2Cl_2$, and (d) $HFeRu_3(CO)_{13}^-$ PPN^+ (CH_2Cl_2 solution) from reaction of $H_2FeOs_3(CO)_{13}$ with KOH/MeOH.

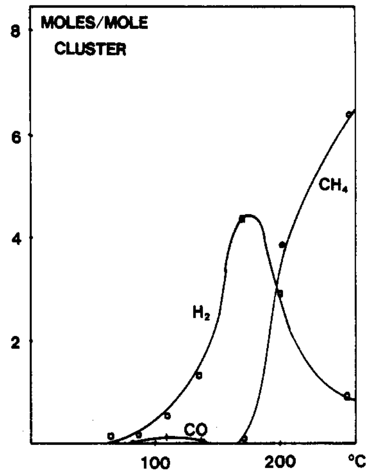

Figure 4. Gas evolution during thermal treatment under vacuum (10^{-5} mmHg) of $H_2FeRu_3(CO)_{13}/MgO_{25°C}$.

Above ca. 120 °C metal particles are formed (shown by electron microscopy to have an average diameter of 15 Å) in the thermal decomposition of the adsorbed cluster anion $[HFeRu_3(CO)_{13}]^-$. Gases evolved were analyzed as a function of temperature. Evolution of H_2 with only trace amounts of CO (less than 0.1 mol/mol of cluster) suggests the occurrence of a stoichiometric water-gas shift reaction between the carbonyl ligands of the adsorbed cluster anion and the surface water, but at a lower temperature than in the case of the adsorbed $[HFeOs_3(CO)_{13}]^-$ ion. The CO_2 arising from this reaction is likely adsorbed as carbonate. It is hydrogenated to methane above 200 °C, very likely on the metallic particles.

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[14] Lavigne, G.; Kaesz, H. D. *J. Am. Chem. Soc.* **1984**, *106*, 4467.

[15] Hughes, F.; Basset, J. M.; Ben Taarit, Y.; Choplin, A.; Primet, M.; Rojas, D.; Smith, A. K. *J. Am. Chem. Soc.* **1982**, *104*, 7020.

[16] Wilkinson, J. R.; Todd, L. J. *J. Organomet. Chem.* **1976**, *118*, 199.

[17] A very recent report has shown that $H_2Os(CO)_4$ is deprotonated by basic magnesium oxide surface. Lamb, H.; Gates, B. C. *J. Am. Chem. Soc.* **1986**, *108*, 81.

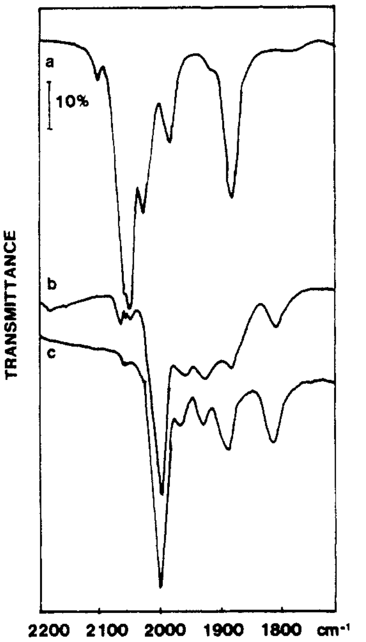


Figure 5. Interaction of $HFeCo_3(CO)_{12}$ with $MgO_{25°C}$: infrared spectra in the ν(CO) region (a) $HFeCo_3(CO)_{12}$ (CH_2Cl_2 solution), (b) $HFeCo_3(CO)_{12}$ after impregnation on a $MgO_{25°C}$ disk, and (c) b extracted by (PPN)Cl/CH_2Cl_2.

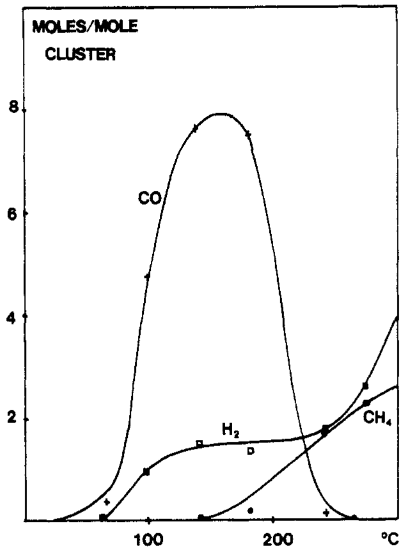
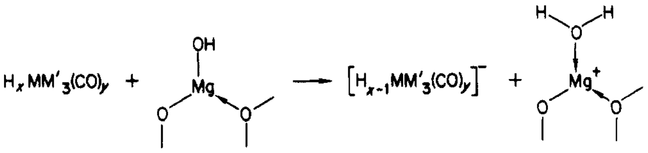


Figure 6. Gas evolution during thermal treatment of $HFeCo_3(CO)_{12}/MgO_{25°C}$.

3. Interaction of $HFeCo_3(CO)_{12}$ with Magnesia (25°C). The IR spectrum of $H_2FeCo_3(CO)_{12}$ in CH_2Cl_2 is shown in Figure 5a. After addition of this solution to a hydroxylated magnesia pretreated at 25 °C, there is a fast and quantitative chemisorption of the cluster on the support without detectable evolution of any gas (CO, H_2, or CO_2). The IR spectrum (Table I, Figure 5b) of the surface-bound species is very close to that reported for $[FeCo_3(CO)_{12}]^-$,[9] indicating that this is the primary product. However, the band at 1888 cm^{-1} suggests the presence of some $[Co(CO)_4]^-$ as a possible decomposition product.[10] Surface ion exchange by extraction with a slight excess of (PPN)Cl in CH_2Cl_2 gives an extract with an IR spectrum which is very similar to that of the surface-bound species (Table I, Figure 5c).

The supported anionic cluster $[FeCo_3(CO)_{12}]^-$ is much less thermally stable than $[HFeOs_3(CO)_{13}]^-$ and $[HFeRu_3(CO)_{13}]^-$ (Figure 6). It starts to decompose to gaseous CO and H_2 at 50 °C. Methane is formed above 200 °C, probably by hydrogenation of CO over metal particles.

Scheme I



Discussion

Surface organometallic chemistry deals with the reactivity of organometallic compounds with the functional groups present at the surface of oxides. Thus far, most of the published work has been concerned with the reactivity of CO, μ-CO, μ_3-CO, CH_2R, μ-CR,[11] η^3-allyl ligands with OH, O^{2-} groups, or Lewis centers.[12] Regarding the reactivity of the metal itself, most studies have been devoted to mononuclear or polynuclear monometallic complexes and the chemistry derived from such studies parallels fairly well the coordination chemistry in solution.

The study of the interaction between neutral hydrido mixed-metal cluster with the surface of oxides was undertaken in this study to obtain information on two important parameters relevant to heterogeneous catalysis. (A) What is the behavior, on a support, of hydrogen coordinated to a cluster frame? (B) What is the stability of a heterobimetallic cluster frame at the surface of an oxide?

With respect to question A, this work shows that hydroxylated magnesia can readily abstract a proton from $H_2FeOs_3(CO)_{13}$, $H_2FeRu_3(CO)_{13}$, and $HFeCo_3(CO)_{12}$ to give surface-bound anionic species which are the conjugate bases of the parent hydrido cluster. The IR spectra indicate that $[HFeOs_3(CO)_{13}]^-$ and $[HFeRu_3(CO)_{13}]^-$ are formed essentially quantitatively, while $[FeCo_3(CO)_{12}]^-$ is formed as the principal product. Similar results were also obtained on partially hydoxylated magnesia ($Mg_{200°C}$) as well.

Concerning question B, the ability to obtain one cluster species on the support rather than a mixture of clusters is of importance for later studies concerning stabilities of surface-bound species, gaseous products produced during thermal decomposition studies, and the nature of the metallic particles formed upon complete decomposition. Earlier studies on $H_2RuOs_3(CO)_{13}$,[3] $H_2FeOs_3(CO)_{13}$,[4] and $HFeCo_3(CO)_{12}$[5] on alumina give evidence for incomplete reaction, probably due to the lower basicity of the support compared to magnesia. While the earlier study[5] of $HFeCo_3(CO)_{12}$ on magnesia revealed complete consumption of the cluster, the IR spectrum suggests a less pure product than that obtained in the present study. This might be due to the difference in sampling procedures rather than an inherent problem of loading the sample on the support.

Surface ion exchange and extraction of the anions with (PPN)Cl in 60–80% yields reveal the lability of the surface-bound species. The ease of extraction parallels the expected basicity of the anion. Since (PPN)Cl is known to deprotonate hydrido carbonyl clusters,[14] it is important to note that in this study the anionic species on the support were first identified before (PPN)Cl was added.

The mechanism of formation of these anions can be reasonably assumed to be a proton abstraction by the basic OH groups of the surface of magnesia, as suggested by Scheme I. Proton abstraction by a base such as KOH is a well-known reaction, and as shown in the examples $H_2FeOs_3(CO)_{13}$ and $H_2FeRu_3(CO)_{13}$ they are readily deprotonated in KOH/MeOH solution. Concerning the nature of the interaction between the anionic cluster and the surface, it should be noted that the ν(CO) frequencies of the bridged carbonyl in the adsorbed anions are very close to the values observed for the extracted PPN salts

Table II. Comparison of [ν(CO)] Frequencies of Some Hydrido Carbonyl Anionic Clusters Supported on Magnesia and in a CH_2Cl_2 Solution as Their PPN Salt

anion	adsorbed on magnesia	PPN salt	ref
$HFeOs_3(CO)_{13}^-$	1788	1794	this work
$HFeRu_3(CO)_{13}^-$	1772	1809	this work
$FeCo_3(CO)_{12}^-$	1814	1811	this work
$HFe_3(CO)_{11}^-$	1598	1709	15, 16

(Table II). It is unlikely that the adsorbed anions are bound to the magnesia through tight ion pairing since such an interaction generally produces a shift to a lower bridge carbonyl stretching frequency. Such behavior is observed for $[HFe_3(CO)_{11}]^-$ on the surface of magnesia (Table II). Where the tight ion pairs have been formed, the OH group on the magnesia is believed to function as a nucleophile to attack the coordinated CO in the well-known reaction of a metal carbonyl with a hydroxyl group to generate carbonate and hydrido carbonyl anion. In the present case it is reasonable to assume that proton abstraction results in the formation of adsorbed water which remains coordinated to the Mg^+ site and the interaction with the anion is not as strong or as specific as in the case of the tight ion pair.

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Registry No. $H_2FeOs_3(CO)_{13}$, 12563-74-5; $H_2FeRu_3(CO)_{13}$, 12375-24-5; $HFeCo_3(CO)_{12}$, 21750-96-9; $[PPN]_+[HFeOs_3(CO)_{13}]^-$, 89716-81-4; $K_+[HFeOs_3(CO)_{13}]^-$, 102588-90-9; $[HFeOs_3(CO)_{13}]^-$, 89716-80-3; $[PPN]^+[HFeRu_3(CO)_{13}]^-$, 78571-90-1; $K^+[HFeRu_3(CO)_{13}]^-$, 102588-91-0; $[HFeRu_3(CO)_{13}]^-$, 74128-10-2; $[PPN]^+[FeCo_3(CO)_{12}]^-$, 80883-51-8; $[FeCo_3(CO)_{12}]^-$, 53240-35-0; $[PPN]^+[Co(CO)_4]^-$, 53433-12-8; MgO, 1309-48-4; Fe, 7439-89-6; Ru, 7440-18-8; Os, 7440-04-2; Co, 7440-48-4.

Organotin(IV) Compounds Derived from $2\text{-}Me_2NC_6H_4CH_2Li$ and Its Chiral α-Me_3Si Derivative. X-ray Structure of Pentacoordinate [{2-(Dimethylamino)phenyl}(trimethylsilyl)methyl-*C*,*N*]methylphenyltin Bromide Having a Chiral Sn Center

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A series of triorganotin halides, RR′SnBr(*C-N*), and a series of tetraorganotin compounds, R_3Sn(*C-N*), have been synthesized in which *C-N* is either monoanionic $2\text{-}Me_2NC_6H_4CH_2^-$ or novel, monoanionic $2\text{-}Me_2NC_6H_4CH(SiMe_3)^-$. ^1H and ^{13}C NMR data indicate that the tin center in the R_3Sn(*C-N*) compounds is tetracoordinate whereas this center in the RR′SnBr(*C-N*) derivatives is pentacoordinate as a result of intramolecular Sn–N coordination. Pentacoordination in a trigonal-bipyramidal manner with axial N and Br atoms has also been established by the X-ray structure determination of $2\text{-}Me_2NC_6H_4CH(SiMe_3)$-SnMePhBr (**4c**): $C_{19}H_{28}BrNSiSn$; monoclinic; $P2_1/n$, $a = 13.085$ (4) Å, $b = 16.127$ (5) Å, $c = 10.437$ (3) Å; $\beta = 99.88$ (2)°; $V = 2170$ (1) Å; $Z = 4$; μ(Mo Kα) = 29.4 cm^{-1}; $R = 0.0307$ for 3185 [$I \geq 2.5\sigma(I)$] reflections. Compound **4c** contains two chiral centers, which are formed stereospecifically during the reaction of $2\text{-}Me_2NC_6H_4CH(SiMe_3)Li$ with $PhMeSnBr_2$ and have either the R_C, R_{Sn} or the S_C, S_{Sn} combination of configurations at the benzylic C and five-coordinate Sn centers. The structure shows that the chelate ring conformation is such that it places the bulky Me_3Si substituent both out of the plane of the aryl ring and, furthermore, at the side of the less bulky methyl ligand. It is suggested that the unusual high configurational stability of the RR′SnBr(*C-N*) compounds arises from the rigidity of the $2\text{-}Me_2NC_6H_4CH(Z)^-$ ligand which holds the $2\text{-}Me_2N$ group in close proximity of the tin center. If Z is the bulky $SiMe_3$ group also, the SnR_2Br grouping is locked in a fixed position with respect to the N donor site.

Introduction

It has been well-established that the configurational stability of the tin center in triorganotin halides can be increased considerably by using potentially bidentate organo ligands $C\frown Y$,[1] in which Y is a heteroatom-containing substituent, e.g., $-NR_2$,[2] $-P(=O)R_2$,[3] $-C(=O)R$,[4] or $=NOR$.[5] These compounds, $SnC_2(C\frown Y)X$ (X = halide), have a trigonal-bipyramidal structure[2-5] in which the electronegative ligands Y and X occupy apical sites and the three carbon ligands C equatorial sites.

The existence of an equilibrium in solution between the two possible situations, i.e., with and without intramo-

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(1) van Koten, G.; Noltes, J. G. *J. Am. Chem. Soc.* **1976**, *98*, 5393.

(2) (a) van Koten, G.; Jastrzebski, J. T. B. H.; Noltes, J. G.; Pontenagel, W. M. G. F.; Kroon, J.; Spek, A. L. *J. Am. Chem. Soc.* **1978**, *100*, 5021. (b) Jastrzebski, J. T. B. H.; Knaap, C. T.; van Koten, G. *J. Organomet. Chem.* **1983**, *255*, 287.

(3) Weichmann, H.; Mügge, C.; Grand, A.; Robert, J. B. *J. Organomet. Chem.* **1982**, *238*, 343.

(4) Kuivila, H. G.; Dixon, J. E.; Maxfeld, P. L. Scarpa, N. M.; Topka, T. M.; Tsai, K. H.; Wursthorn, K. L. *J. Organomet. Chem.* **1975**, *86*, 89.

(5) Abbas, S. Z.; Poller, R. C. *J. Organomet. Chem.* **1976**, *104*, 187.

0276-7333/86/2305-1551$01.50/0