Reaction of [NEt$_4$][3] with NaOMe. A 100-mL flask was charged with NaOMe (0.022 g, 0.407 mmol), which was then suspended in hexamethylphosphoramide (5 mL). A yellow-orange solution of [NEt$_4$][3] (0.400 g, 0.411 mmol) in hexamethylphosphoramide (5 mL) was generated in a separate flask and subsequently added to the NaOMe suspension via cannula. After being stirred for 1 h, the reaction had evolved into a homogeneous, dark orange solution. The reaction vessel was evacuated to remove any volatiles formed during the reaction. Addition of pentane (50 mL) to the remaining orange solution resulted in the formation of a white precipitate, probably NEt$_4$I or NaI. The light orange solution was filtered away from the precipitate, and the precipitate was washed with pentane (2 × 50 mL). Cooling the light yellow hexamethylphosphoramide/pentane solution to −35 °C yielded an orange oil. The colorless supernatant was decanted, and the oil was washed with pentane (2 × 25 mL). After excess pentane was removed by evacuation, the oil was dissolved in diethyl ether (5 mL). Cooling the resulting yellow solution to −78 °C afforded yellow crystals (0.110 g). Infrared and ^{1}H NMR spectroscopies showed peaks that are consistent with the stoichiometry $[Na(HMPA)_{4.5}][(CO)_5WSi(SnMe_3)_3]$.

X-ray Structure Determination of [NEt$_4$][3]. A pale yellow fragment of approximate dimensions 0.22 mm × 0.34 mm × 0.50 mm was cut from a much larger crystal and was mounted in a thin-walled glass capillary under N$_2$. Centering of 25 randomly selected reflections with $15° \leq 2\theta \leq 30°$ provided the unit cell dimensions. Axial photographs confirmed the lattice assignment as monoclinic. A summary of the data collection and refinement is provided in Table I. The data were corrected for a 9% decay in the intensities of three check reflections, Lorentz and polarization effects, and absorption. The space group was uniquely determined by systematic absences. Solution was achieved by direct methods, and the structure was refined by using full-matrix least-squares methods (SHELXTL PLUS computer programs, Nicolet Instrument Corp., Madison, WI). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated, idealized positions with fixed isotropic thermal parameters (d(C–H) = 0.96 Å, H thermal parameter approximately equal to 1.2 times the isotropic thermal parameter of the parent carbon atom).

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Supplementary Material Available: Tables of crystal, data collection, and refinement parameters, complete atomic coordinates, complete bond distances and angles, anisotropic thermal parameters, and hydrogen atom coordinates (6 pages); listings of observed and calculated structure factors (23 pages). Ordering information is given on any current masthead page.

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Formation and Chemical Reactions of Ruthenium Tricarbonyls Adsorbed on Metal Oxides. Use of Chemical Reactions as a Method of Surface Structure Determination

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The adsorption of $Ru(CO)_3Cl_2(THF)$ onto the surface of hydroxylated metal oxides yields one of two surface metal carbonyls depending on the metal oxide. Depending on the nature of the metal oxide, the surface species either retains or loses coordinated chloride. The surface species may be described as $[Ru(CO)_3Cl_2(HO–)]$ and $[Ru(CO)_3(HO–)(O–)_2]$, where HO– and O– represent surface hydroxyl and oxo groups, respectively. Although the exact nature of the ligands provided by the surface remains unknown in the adsorbed complexes, the ligands shown provide for the formation of a neutral carbonyl fragment when ruthenium remains in the +2 oxidation state. The former species is generated on silica and NaY zeolite, and the latter is generated upon adsorption on alumina and MgO. The proposed structures are consistent with the reactions of the surface species with bipyridine and tetracarbonylcobaltate(1−). The more strongly adsorbed species, $[Ru(CO)_3(HO–)(O–)_2]$, generated on alumina and MgO does not react with tetracarbonylcobaltate(1−), while the more weakly adsorbed species, $[Ru(CO)_3Cl_2(HO–)]$, on silica and NaY zeolite reacts to yield a bimetallic cluster.

Much of the interest in the chemistry of metal carbonyls with solid metal oxides stems from the observation that metal carbonyls offer alternative starting materials for the preparation of supported metal catalysts.[1] Metal carbonyls themselves, when supported on metal oxides, also have been shown to be catalytically active for a wide range of reactions.[2] Furthermore, heterogeneous catalysts derived from metal carbonyls give, in some cases, higher selectivity and activity than those prepared from metal salts.[3] Supported ruthenium carbonyls and the catalysts derived from them have been shown to be active for the catalytic reduction of CO,[4] the water gas shift reaction,[5] and the hydrogenation of olefins.[6]

One problem that plagues the study of adsorbed metal carbonyls is the determination of the composition and structure for the adsorbed species. It is important to determine the structure of the adsorbed carbonyls, since this may influence the catalytic activity of materials derived from the carbonyls. Structures for adsorbed carbonyls are typically deduced from spectroscopic data and by comparison of this data with known compounds that serve as models for the adsorbed carbonyls. Preferably a variety of spectroscopic techniques are applied to the supported carbonyl; a consistent set of results from several methods is most likely to give a reliable indication of the structure of the supported carbonyl.

The formation of ruthenium tricarbonyl on many metal oxides has been implicated in the surface chemistry of ruthenium carbonyls under a variety of conditions.[7–11] The starting material for the adsorbed carbonyls is typically $Ru_3(CO)_{12}$ although $[Ru(CO)_3Cl_2]_2$[8] and $Ru(CO)_3Cl_2THF$[11] have also been used.

Bell et al. have shown that $Ru_3(CO)_{12}$ readily sublimes onto untreated SiO$_2$ to yield initially physisorbed $Ru_3(CO)_{12}$.[7] The physisorbed cluster can then be fragmented under H$_2$ at 500 K to give mononuclear and dinuclear ruthenium carbonyls. Basset et al. have demonstrated that the oxo-bridged cluster $[HRu_3(CO)_{10}OSi–]$ can be formed on hydroxylated SiO$_2$.[8] Furthermore, they showed that the grafted cluster can be fragmented at high

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temperature to yield the mononuclear carbonyls $Ru(CO)_2$(ads) and $Ru(CO)_3$(ads). (The term ads is used to denote ruthenium carbonyl fragments chemically bonded to the metal oxide surface.) Decomposition at temperatures greater than 373 K followed by recarbonylation led to the formation of Ru(CO)(ads). The assignment of these surface subcarbonyls was made on the basis of the position and intensity of the carbonyl bands in the infrared spectrum.

Darensbourg et al. have shown that $Ru_3(CO)_{12}$ reacts with partially dehydroxylated alumina to yield the hydrido cluster $[HRu_3(CO)_{11}]^-$.[9] Reaction of this adsorbed cluster with hydrogen at 473 K led to a surface species postulated to be $Ru(CO)_2]_n$(ads). This is similar to the chemistry proposed by Bell et al. to occur on SiO_2. The dicarbonyl species absorbs CO to yield what is postulated to be $[Ru(CO)_x]_n$(ads), where $x = 3$ or 4. Exposure to hydrogen regenerates the species assigned as $[Ru(CO)_2]_n$(ads).

Zecchina et al. propose that the grafted cluster $[HRu_3(CO)_{10}OAl^-]$ can be obtained on hydroxylated alumina.[10] This can then be decomposed to form three different types of ruthenium dicarbonyl groups depending on the reaction conditions: under vacuum $Ru^0(CO)_2$(ads); under oxygen, $Ru^{II}(CO)_2$(ads); under oxygen followed by exposure to CO, $Ru^n(CO)_2$(ads), where n is greater than 2.

A potentially cleaner route to a supported tricarbonyl group is through the reaction of a precursor that already contains the desired group. For example, reaction of $(\eta^6\text{-}C_6H_6)Mo(CO)_3$ with alumina has been shown to be consistent with the formation of $Mo(CO)_3$(ads).[12] Ugo et al. have suggested that $Os(CO)_3$(ads) can be formed on MgO from $[Os(CO)_3Cl_2]_2$.[13] The metal oxide in this reaction serves as a halide acceptor to yield the simple tricarbonyl group. A similar species is obtained from the carbonylation of $OsCl_3$ adsorbed on MgO.[13]

Silica has also been proposed to play the role of halide acceptor in the adsorption of $[Ru(CO)_3Cl_2]_2$.[8b] We have shown previously that $Ru(CO)_3Cl_2$(THF) adsorbs onto hydroxylated alumina surfaces to yield a species best described as $Ru^{II}(CO)_3$(ads).[11] Again the surface appears to act as a halide acceptor to yield a simple tricarbonyl group. The evidence for this comes in part from the observed chemical reactivity of the resulting tricarbonyl group. In this case reaction with CO leads to the adsorbed anion $[HRu_3(CO)_{11}]^-$ under exceptionally mild conditions.[11] The determination of the structure on SiO_2 was based on the infrared spectrum of the adsorbed species.[8b]

Classic methods of structure determination in chemistry rely heavily on the formation of derivatives of known composition and the synthesis of new compounds by alternative pathways. These methods have not seen much application in the determination of surface structures for adsorbed carbonyls. In this paper we describe the synthetic routes to adsorbed ruthenium tricarbonyl groups and use chemical tests to determine if the supported carbonyl contains Ru–Cl bonds.

Experimental Section

The aluminum oxide used in this study was CATAPAL SB (Conoco). This was sieved to <200 mesh and calcined at 350 °C. This procedure yields a pseudo-γ-alumina[14] with a surface area of 200 $m^2\ g^{-1}$. The surface was hydroxylated by passing helium saturated with water vapor over the freshly calcined support at 100 °C for 0.5 h. The other supports, SiO_2 (Davison-62) and MgO and NaY zeolite (Strem), were treated similarly to yield hydroxylated surfaces. The supports also obtained some adsorbed water, as judged by infrared spectroscopy. The surface of MgO is probably best described as $Mg(OH)_2$ under these reaction conditions. The NaY zeolite is fully hydrated under these reaction conditions. Thus, the adsorption of ruthenium carbonyls is most likely to occur on the external surfaces of the zeolite.

The ruthenium compounds $[Ru(CO)_3Cl_2]_2$,[15] $Ru(CO)_3Cl_2(THF)$,[16] and $[RuCo_3(CO)_{12}]^-$[17] were prepared by literature methods. Sodium tetracarbonylcobaltate(1−), $Na[Co(CO)_4]$, was prepared from $Co_2(CO)_8$ by a literature method.[18]

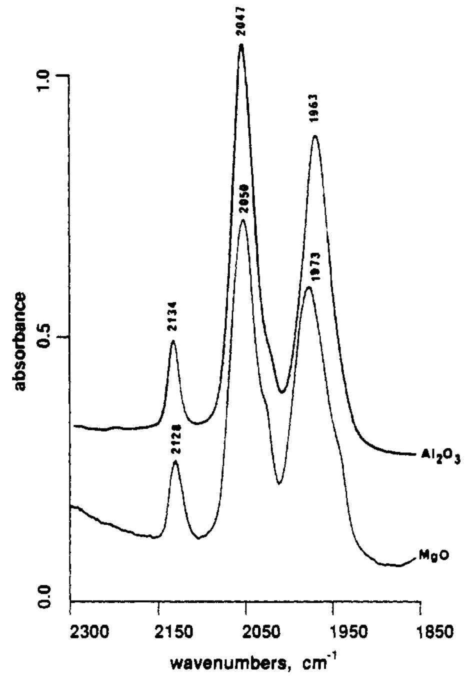

Figure 1. Infrared spectra for adsorbed ruthenium tricarbonyl on MgO (lower trace) and Al_2O_3 (upper trace).

Tetrahydrofuran and pentane were distilled immediately before use from potassium–benzophenone ketyl. Dichloromethane was distilled from P_2O_5 and stored over molecular sieves; prior to use CH_2Cl_2 was degassed by three freeze–pump–thaw cycles. Bipyridine and (PPN)Cl were obtained from Aldrich and used without further purification.

The adsorption of $Ru(CO)_3Cl_2$(THF) onto the supports was carried out by two different methods. In a typical batch reaction 1.3 mg of $Ru(CO)_3Cl_2$(THF) was dissolved in 5 mL of THF and the solution added by syringe to 200 mg of support in a helium flow reactor. The reactor has been described previously.[19-21] This enabled the determination and quantitation of evolved gases. At this loading the ruthenium complex was quantitatively removed from solution. After removal of solvent the solid contained 0.2% ruthenium. Other reactants could be added to the support after the initial adsorption of $Ru(CO)_3Cl_2$(THF), and the evolved gases from any reactions on the support could also be identified and quantitated. In addition to the batch reactions described above the adsorption could be monitored by in situ infrared spectroscopy in a cell designed for the impregnation of solids with solutions of metal carbonyls.[21] In a typical experiment 15 mg of support was pressed into a self-supporting wafer at 1500 psi in a standard infrared die. The wafer was transferred to the cell and pretreated to yield a hydroxylated surface. Immersion of the wafer into a 0.01 M THF solution of $Ru(CO)_3Cl_2$(THF) yielded the adsorbed carbonyl. The adsorption process could be monitored by infrared spectroscopy. All spectra were recorded on a Nicolet 5 DXB spectrometer. Subsequent reactions were initiated by syringing a solution of the desired reactant onto the wafer in the infrared beam.

Both the batch reactions and the in situ experiments were performed under ultrapure helium (Airco 99.995) that had been passed over MnO on silica to remove oxygen.[19] Blank reactions were done on each of the supports. In all cases contacting the solids with THF, CH_2Cl_2, or pentane at room temperature did not yield any evolved gases.

Results

The ruthenium complex $Ru(CO)_3Cl_2$(THF) (**1**) is spontaneously adsorbed by each of the supports, Al_2O_3, SiO_2, MgO, and NaY zeolite, from THF solution at room temperature. Very little

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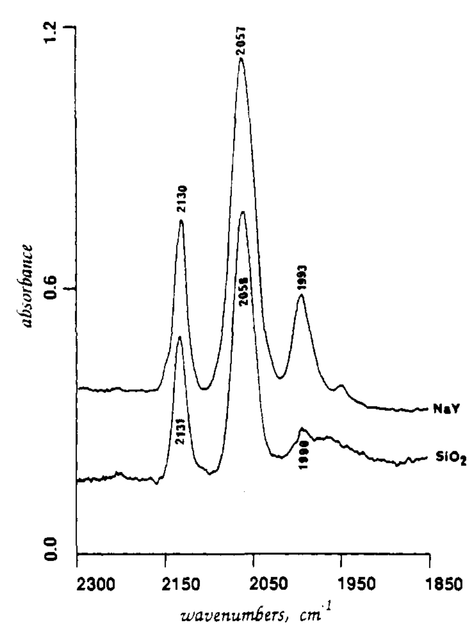


Figure 2. Infrared spectra for ruthenium tricarbonyl on SiO_2 (lower trace) and NaY (upper trace). The solution infrared spectrum of **1** in THF is superimposable on the spectrum for $Ru(CO)_3Cl_2$(ads) on SiO_2.

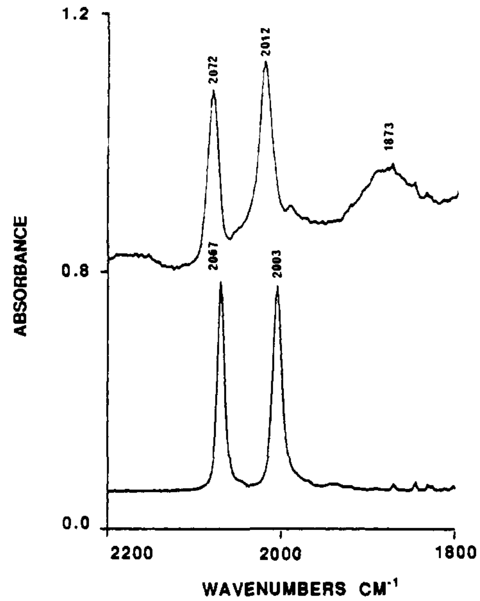


Figure 3. Infrared spectra obtained after the addition of bipyridine to **2a** on SiO_2 (upper trace) and NaY (lower trace). The broad absorbance at 1873 cm^{-1} in the upper trace is due to silica. The two bands of nearly equal intensity are consistent with a cis arrangement of carbonyls in $Ru(CO)_2bpyCl_2$.

CO loss from the ruthenium complex was observed during the adsorption and for a period of up to 4 h under flowing helium after the adsorption was complete. The average quantity of CO evolved for 17 experiments was 0.06 equiv CO/ruthenium. After adsorption of **1** and the removal of excess solvent the support was obtained as a dry free-flowing powder, which was pale yellow or light tan in color. The supported ruthenium complex is stable at room temperature for long periods of time provided that oxygen is rigorously excluded from the sample.

The infrared spectra obtained upon adsorption of **1** onto Al_2O_3 and MgO are shown in Figure 1. Although the spectra are very similar, small shoulders are observed at low wavenumbers for the most intense peaks in the spectrum obtained on MgO. Figure 2 presents the infrared spectra obtained when **1** is adsorbed onto SiO_2 and NaY zeolite.

The infrared spectra that result when **1**, adsorbed onto a support, is reacted with bipyridine are shown in Figures 3 and 4 for SiO_2 and NaY and Al_2O_3, respectively. Reaction of adsorbed **1** with $Co(CO)_4^-$ leads to a Ru–Co cluster only on zeolite and silica. A representative spectrum for the in situ formed product is shown in Figure 5.

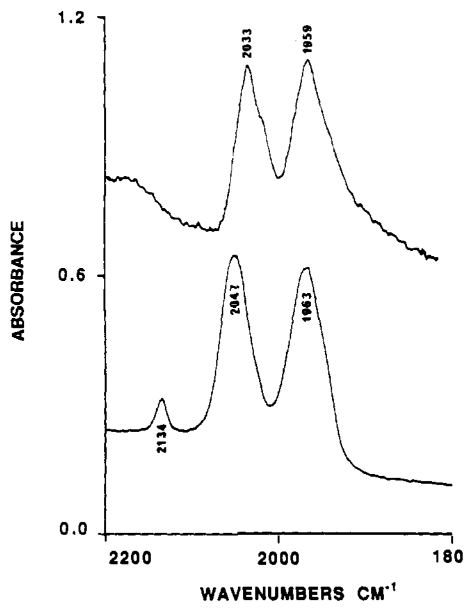


Figure 4. Infrared spectrum of **2b** on Al_2O_2 (lower trace). After the addition of bipyridine, the spectrum shown in the upper trace is obtained.

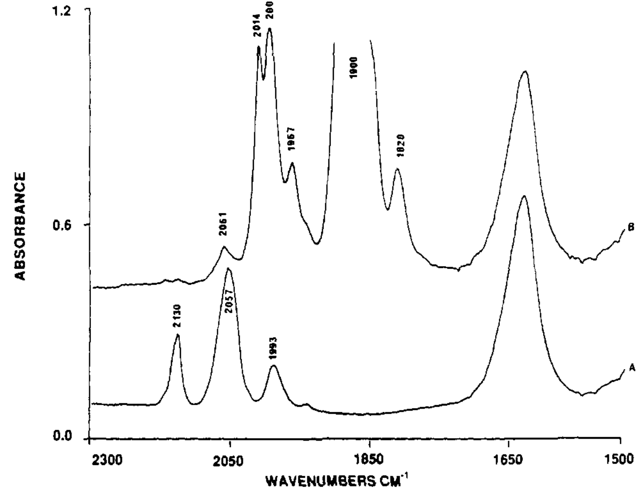


Figure 5. Infrared spectra obtained during the reaction of $[Co(CO)_4]^-$ with **2a** on NaY zeolite. The bottom spectrum was recorded prior to the addition of $[Co(CO)_4]^-$; the top spectrum was recorded immediately after the addition of tetracarbonylcobaltate(1−) to the pellet. The broad peak at 1640 cm^{-1} is due to water adsorbed on the zeolite.

Discussion

Observation of the spontaneous adsorption of **1** combined with the fact that very little CO is evolved suggests that adsorption proceeds with the loss of THF and/or Cl^- from **1**. Thus, either $Ru(CO)_3$(ads) (**2a**) or $Ru(CO)_3Cl_2$(ads) (**2b**) is formed on the surface.

Infrared spectroscopy gives some insight into the number of species present on each support. The spectra shown in Figures 1 and 2 were obtained within 2 min of the immersion of the supports into a solution of **1**; in all cases the spectrum obtained remained unchanged as long as the sample was kept under helium. The infrared spectra for **1** on SiO_2 and NaY are virtually identical with that obtained for **1** in solution, while on Al_2O_3 and MgO the relative intensities of the major bands are different and the positions of the bands are shifted slightly.

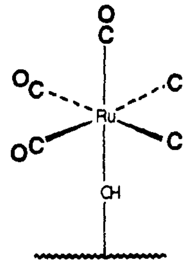
The similarity of the spectra for **1** on SiO_2 and NaY with **1** in solution suggests, but does not prove, that the adsorbed carbonyl has the composition $Ru(CO)_3Cl_2$(ads) on these supports. Previously, we have suggested that **1** adsorbed on alumina is best described as $Ru^{II}(CO)_3(ads)$.[11] The osmium analogue has been postulated to form on MgO by a similar reaction.[13] On the basis of infrared spectroscopy, the compositions of **1** on Al_2O_3 and MgO are nearly identical and most likely $Ru^{II}(CO)_3(ads)$. Thus, the reactions shown as follows may represent the adsorption process on the supports investigated.

$$Ru(CO)_3Cl_2(THF) \xrightarrow{SiO_2} \underset{\textbf{2a}}{Ru(CO)_3Cl_2(HO^-)} \qquad (1)$$

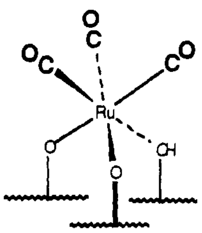
$$Ru(CO)_3Cl_2(THF) \xrightarrow{MgO} \underset{\textbf{2b}}{[Ru(CO)_3(HO-)(O-)_2]} + 2HCl(ads) \qquad (2)$$

The species HO– and O– represent surface hyrdoxyl and oxy groups, respectively.

Although it it not known what combination of oxy or hydroxy species on the surface serve as ligands, the combination shown is consistent with the formation of a neutral complex on the surface. The basic oxides may accept chloride in the form of HCl to allow adsorbed carbonyl complex to be formally neutral rather than cationic. Although the infrared spectra are consistent with these assignments, this does not constitute a proof of the surface composition. Schematic representations of the proposed surface species are as follows:



2a



2b

Chemical Reactions of 2. The chemical reactivity of the adsorbed carbonyls **2** can, in principle, distinguish between the two postulated surface compositions shown. For example, if chloride is lost upon formation of the adsorbed ruthenium carbonyl, it is unlikely that chloride will then displace surface oxide to reform a chloro complex in a subsequent reaction unless a large excess of chloride is added to the surface. Thus, the formation of derivatives that contain chloride would indicate that **2a** best describes the surface species.

Bipyridine is known to react with $Ru(CO)_3Cl_2(THF)$ in solution to yield $Ru(CO)_2Cl_2(bpy)$.[16] When **2**, on the various supports investigated, is treated with bipyridine, one of two reactions is observed. These correlate with the type of infrared spectrum observed for **2**.

Addition of pipyridine as a solution in CH_2Cl_2 to **2a** on either silica or NaY zeolite results in the loss of 1 equiv of CO/ruthenium atom. The color of the support changes immediately from pale yellow to light pink. This color is consistent with the formation of $Ru(CO)_2Cl_2(bpy)$. If this compound is indeed formed on the surface, then it must be simply physisorbed, since all the coordination sites on ruthenium are occupied. Extraction of these supports with CH_2Cl_2 yields a light pink solid after removal of solvent. The solid is identical, as determined by infrared spectroscopy, with an authentic sample of $Ru(CO)_2Cl_2(bpy)$. In situ infrared spectroscopy shows that the bipyridine complex is formed immediately upon addition of bipyridine to **2a**. A comparison of the infrared spectrum of **2a** on silica (Figure 3) shows that it is similar to the spectrum of pure $Ru(CO)_2Cl_2(bpy)$.

In contrast the reaction of **2b** on either Al_2O_3 or MgO with bipyridine proceeds without the evolution of CO while a dramatic change in color from pale yellow to purple-black occurs. The infrared spectrum, as obtained through an in situ experiment, is shown in Figure 4. This bears no resemblance to $Ru(CO)_2Cl_2(bpy)$, nor does it match the infrared spectrum of $Ru_3(CO)_{10}(bpy)$,[23] $[Ru(CO)Cl(bpy)_2]^+$,[24] or $[Ru(CO)_2(bpy)_2]^{2+}$.[24] Interestingly, there is some similarity with the species generated in these reactions with that observed by Pakkanen et al. from the reaction of $Ru_3(CO)_{12}$ and bipyridine on silica, which yields an active water gas shift reaction catalyst.[25] All attempts to extract ruthenium complexes from these surfaces failed. Among the solvents used for the attempted extractions were neat CH_2Cl_2, THF and CH_2Cl_2, and THF solutions of the salts (PPN)Cl and KPF_6.

The reactions of bipyridine with adsorbed ruthenium tricarbonyls are consistent with the surface structures postulated above, $Ru(CO)_3Cl_2(HO-)$ on SiO_2 and NaY, **2a**, and $[Ru(CO)_3(HO-)(O-)_2]$ on Al_2O_3 and MgO, **2b**.

Complex **1** reacts with tetracarbonylcobaltate(1–) in THF to yield $[RuCo_3(CO)_{12}]^-$,[26] while the reaction of $[Ru(CO)_3Cl_2]_2$ with tetracarbonylcobaltate(1–) in water yields $RuCo_2(CO)_{11}$.[27] The reactions of **2** with $[Co(CO)_4]^-$ were monitored by in situ infrared spectroscopy, and as in the case of the reactions with bipyridine, the results correlate with the infrared spectrum observed for **2**.

The infrared spectra from a typical experiment with **2a** on NaY and $[Co(CO)_4]^-$ are shown in Figure 5. Trace A is the spectrum of **2a** alone, and trace B is the spectrum after the addition of $[Co(CO)_4]^-$. In addition to an intense band at 1900 cm^{-1} due to an excess of tetracarbonylcobaltate(1–) new bands are seen at 2061, 2014, 2000, 1967, and 1820 cm^{-1}. Comparison with the spectrum of an authentic sample of $[RuCo_3(CO)_{12}]^-$ suggests that this cluster anion is formed in situ on the zeolite. A similar result is obtained on silica. The cluster anion, along with excess $[Co(CO)_4]^-$, is readily extracted as the PPN^+ salt. Protonation of the extracted anions allows the analysis of the resulting hydrides by mass spectroscopy. After removal of $HCo(CO)_4$ under vacuum the remaining solid shows the molecular ion expected for $HRuCo_3(CO)_{12}$ in the mass spectrum. The ease of extraction of the cluster anion suggests that it is synthesized on the external surface of the NaY zeolite and not within the large supercages of the faujasite structure.

When **2b** on either Al_2O_3 or MgO is treated with $[Co(CO)_4]^-$ in a similar fashion, no new bands are seen in the infrared spectrum; at room temperature one sees only the characteristic 1890-cm^{-1} band of $[Co(CO)_4]^-$ superimposed on the spectrum of **2b**. This persists for up to 8 h, after which no further spectra were recorded. The identical result, i.e. no reaction, is obtained when the order of addition of the reactants is reversed.

It is not surprising that **2a** on silica and zeolite reacts in the same manner as $Ru(CO)_3Cl_2(THF)$ in solution; chloride is still present as a leaving group, and a surface hydroxyl group occupies the coordination site vacated by THF. The lack of reactivity on alumina and MgO is more interesting. If the structure of the adsorbed ruthenium tricarbonyl on these oxides was identical with that on silica, then the reaction with $[Co(CO)_4]^-$ should proceed to yield the cluster anion. The fact that no reaction takes place suggests that **2b** is more strongly bound to Al_2O_3 and MgO than **2a** to SiO_2 or NaY zeolite. This is consistent with structure **2b** on Al_2O_3 and MgO as suggested above. Surface oxide may be proposed to be a poorer leaving group than chloride in this type of displacement reaction.

Previously, we showed that when ruthenium tricarbonyl is generated on alumina, it reacts rapidly with CO under very mild conditions to yield $[HRu_3(CO)_{11}]^-(ads)$ under very mild conditions.[11] The ease of reaction was attributed to the potential of alumina to act as a chloride acceptor. In solution cluster synthesis at room temperature starting from **1** requires the presence of a

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reducing agent other than CO, e.g. Zn, which can also serve as a chloride acceptor.

If structure **2a** is correct for the adsorbed tricarbonyl on SiO_2 and NaY, then there should be no reaction between the adsorbed carbonyl chloride and CO at room temperature, since there is nothing that can serve as a chloride acceptor. This is indeed the case; no reaction is observed between **2a** and CO (25 °C, 1 atm) after 24 h.

Similarly, a reaction is to be expected between **2b** on MgO and CO at room temperature. Although a reaction does occur, it is unfortunately not nearly as clean as previously observed on Al_2O_3. Thus, when **2b** on MgO is treated with CO, a very complicated infrared spectrum is obtained. Some of the bands may be due to $[HRu_3(CO)_{11}]^-$(ads), but if this anion is present, it is not the major product. That a reaction takes place at all however is consistent with MgO acting as a chloride acceptor.

Conclusion

Although $Ru(CO)_3Cl_2(THF)$ is spontaneously adsorbed by a number of oxides, it is impossible to determine the surface structure of the adsorbed species simply by the infrared spectrum. Thus, a previous study on silica assigned the surface structure as $Ru^{II}(CO)_3$(ads), a structure that does not contain coordinated chloride. It is apparent from the present study that a better description of the surface carbonyl on SiO_2 and NaY zeolite is $Ru(CO)_3Cl_2$(ads). Only on the more basic oxides, Al_2O_3 and MgO, is chloride lost to yield the surface species $Ru^{II}(CO)_3$(ads). It is further proposed that the surface ligands include two oxides, O–Al, so that the adsorbed tricarbonyl is not a formally cationic complex. Importantly, the distinction between the two surface structures is not readily made simply from the infrared spectra. The basic chemical reactions of the adsorbed carbonyls are required to confirm the proposed structures.

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Synthesis, Structure, and Properties of a New Ternary Metal Nitride, Ca_3CrN_3

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We have synthesized a new ternary nitride, Ca_3CrN_3, from the binary nitrides at high temperature. The refined structure was solved in the *Cmcm* space group, $Z = 4$, with lattice constants (Å) $a = 8.503$ (2), $b = 10.284$ (2), and $c = 5.032$ (1) and with $R = 3.9\%$ and $R_w = 3.9\%$. This new structure type consists of sheets of $[CrN_3]^{6-}$ planar triangular units and calcium ions. Ca_3CrN_3 is insulating and paramagnetic with Cr^{3+} in the low-spin state. This is the first unambiguous example of low-spin Cr^{3+}. Larger than expected antiferromagnetic interactions produce a maximum in the magnetic susceptibility at 240 K, even though the shortest Cr–Cr distance is 4.73 Å.

Introduction

Although the chemistry of binary nitrides has been explored in detail, comparatively little work on ternary and quaternary nitrides has been reported. Preliminary work has shown that, in addition to the facile formation and stability of ternary nitrides containing electropositive elements, these phases exhibit a variety of novel properties. Examples include the Ni d^9 configuration in CaNiN,[1] the layered structures of $MTaN_2$[2] (M = alkali metal), and the unique structure types found in $Ca_{21}Fe_3N_{17}$,[3] Li_3AlN_2,[4] and CaGaN.[5] These few examples suggest that ternary nitrides will display an extensive assortment of new compounds and structure types. We therefore undertook a large-scale investigation of alkaline-earth-metal- and transition-metal-containing nitrides.

Herein, we report a new compound and structure type, Ca_3CrN_3, discovered initially as an impurity phase in reactions of Ca_3N_2 in stainless steel containers.

Experimental Section

Starting Materials. Chromium nitride was prepared by heating Cr powder (−100 mesh, 3N) in flowing nitrogen (prepurified by passing through finely divided copper at 150 °C and then activated alumina) at 800 °C for 1 day. The product was ground and reheated several times, yielding a mixture of CrN and Cr_2N (approximately 50:50). Granules of calcium (2N) were reacted at 1000 °C for 3 days in flowing nitrogen (prepurified as above) to yield pure Ca_3N_2. The binary products were identified by X-ray powder diffraction methods. Since both Ca_3N_2 and Ca_3CrN_3 are air sensitive, all manipulations were carried out in an argon-filled glovebox.

Synthesis of Ca_3CrN_3. The title compound was first discovered as a minority crystalline phase in a reaction of Ca_3N_2 and tin in a stainless steel tube. The bulk phase consisted of a gray powder, Ca_3SnN,[6] with a minority phase consisting of needle crystals distributed throughout. Microprobe analysis of the crystals indicated the presence of calcium and chromium (a component in the stainless steel) at a Ca:Cr molar ratio of 3:1.

The compound was then prepared as a majority phase by heating 0.2048 g of the CrN/Cr_2N mixture (1.11 mmol of the hypothetical Cr_3N_2) and 0.6011 g of Ca_3N_2 (4.06 mmol) in a sealed stainless steel tube under an argon atmosphere at 1350 °C for 4 days, followed by cooling to 1050 °C in 5 h and finally cooling to room temperature in 12 h. There was no evidence of Ca_3N_2 remaining in the product mixture; however, the brittle nature of the once malleable tube indicated that the excess Ca_3N_2 was consumed by a reaction with the stainless steel. The product contained air-sensitive, burgundy needle crystals up to 1 mm in length, which were used for the structure determination. X-ray powder diffraction indicated a nearly pure Ca_3CrN_3 powder with a small unidentified impurity phase. The intensity of the strongest impurity diffraction peak was 6% as intense as the strongest peak of the majority phase.

The material used for susceptibility measurements was prepared by heating a pressed pellet of an intimate mixture of 0.3103 g of CrN/Cr_2N (1.69 mmol of Cr_3N_2) and 0.5070 g of Ca_3N_2 (3.43 mmol) powders in a sealed molybdenum crucible under argon at the heating schedule mentioned above. The only impurity observable in the product by powder X-ray diffraction was Cr metal. The most intense Cr peak was only 6%

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