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Surface Organometallic Chemistry: Evidence of Disproportionation of $\text{Co}_2(\text{CO})_8$ to $\text{Co}^{2+}[\text{Co}(\text{CO})_4]^-_2$ at the Surface of Partially Hydroxylated Magnesia

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Chemisorption of $\text{Co}_2(\text{CO})_8$ on a partially hydroxylated magnesia surface has been followed by in situ IR and UV spectroscopies and gas-phase analysis. The complex is quickly disproportionated at room temperature into Co^{2+} and $[\text{Co}(\text{CO})_4]^-$ with evolution of ca. 3 mol of CO/mol of $\text{Co}_2(\text{CO})_8$. On the surface, $[\text{Co}(\text{CO})_4]^-$ has been characterized mainly by IR spectroscopy and Co^{2+} by UV spectroscopy. Both Co^{2+} and $[\text{Co}(\text{CO})_4]^-$ could be quantitatively extracted from the surface by $[\text{PPN}]\text{Cl}$ as $[\text{PPN}][\text{Co}(\text{CO})_4]$ and $[\text{PPN}]_2[\text{CoCl}_4]$, respectively. Chemisorption of $[\text{PPN}][\text{Co}(\text{CO})_4]$ on magnesia suggests that $[\text{Co}(\text{CO})_4]^-$ is coordinated to Mg^{2+} surface sites rather than Co^{2+} via heteronuclear metal-metal ion pairing.

Introduction

As part of a general approach of surface organometallic chemistry,¹ the reactivity of transition-metal carbonyls with the surface of magnesia has been studied in a systematic way. As a result, a comprehensive understanding of some elementary steps of this chemistry is now emerging. For example, the formation of $[\text{HM}_3(\text{CO})_{11}]^-$ by adsorption of $\text{M}_3(\text{CO})_{12}$ ($\text{M} = \text{Fe}, \text{Ru}^3$) is unambiguously due to a nucleophilic attack of a surface OH group on a coordinated CO, followed by β -H elimination. For hydrido carbonyl complexes such as $\text{H}_2\text{Fe}_2\text{M}_3(\text{CO})_{13}$ ($\text{M} = \text{Ru}, \text{Os}$),⁴ $\text{HFeCo}_3(\text{CO})_{12}$,⁴ $\text{H}_4\text{Os}_4(\text{CO})_{12}$,⁵ and $\text{H}_2\text{Os}(\text{CO})_4$,⁶ proton abstraction by the OH groups of magnesia leads also to the formation of anionic complexes. These two reaction pathways are well documented in solution chemistry.⁷

We now wish to report the disproportionation of $\text{Co}_2(\text{CO})_8$ into Co^{2+} and $[\text{Co}(\text{CO})_4]^-$ on magnesia, which corresponds to an electron-transfer mechanism also well-known in solution chemistry.⁸⁻¹⁰ Previous reports on the chemistry of cobalt carbonyls on magnesia,¹¹ silica,^{12,13} alumina,^{12,13} and zeolites¹⁴⁻¹⁶ are available; nevertheless, the experimental conditions used in those publications apparently led to a complex set of reactions yielding mixtures that could not be unambiguously characterized.

Experimental Section

Materials. Solvents and gases were dried and deoxygenated by standard procedures. $\text{Co}_2(\text{CO})_8$ (Strem Chemicals Inc.) was stored under dry argon and kept refrigerated; the purity was checked, prior to use, by IR spectroscopy. $\text{Co}_4(\text{CO})_{12}$ was prepared by thermal decomposition of a solution of $\text{Co}_2(\text{CO})_8$ in hexane. $[\text{PPN}][\text{Co}(\text{CO})_4]$ has been synthesized by reaction between $\text{Co}_2(\text{CO})_8$ and KOH ,¹⁷ followed by metathetical exchange with $[\text{PPN}]\text{Cl}$ ($\text{PPN} = \text{bis}(\text{triphenylphosphine})\text{nitrogen}(1+)$). The resultant compound has been purified by recrystallization from $\text{Et}_2\text{O}/\text{CH}_2\text{Cl}_2$ and characterized by its IR spectrum. $\text{MgO}(200)$ was prepared by dehydration of $\text{Mg}(\text{OH})_2$ (obtained by reaction of MgCl_2 with KOH) followed by pretreatment at 200 °C as previously described;² physically adsorbed water is thus removed, and according to the literature, approximately 8-9 OH/nm² are present on the surface. Surface Mg^{2+} density is low.

Instrumentation. IR spectra were recorded on a Nicolet 10-MX FT instrument. DR-UV-vis spectra were obtained on a Perkin-Elmer Lambda 9 spectrophotometer; the design of the cell has been described elsewhere,²⁷ and samples prepared in situ. GC analyses were performed on INTERSMAT IGC 112 G and 120 MB chromatographs.

Procedures. The techniques used for the impregnation of MgO with metal complexes, for spectroscopic and gas evolution measurements, and for extraction of surface species by $[\text{PPN}]\text{Cl}$, were essentially identical with those previously reported by us.²

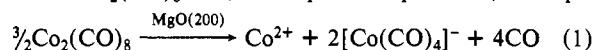
Results

Adsorption of $\text{Co}_2(\text{CO})_8$ and $\text{Co}_4(\text{CO})_{12}$ on $\text{MgO}(200)$ and Extraction of Surface Species. When $\text{MgO}(200)$ (in the form of a pressed disk) is impregnated with a hexane solution of

$\text{Co}_2(\text{CO})_8$ and the solvent evacuated at room temperature, the in situ FTIR spectrum of the resulting solid (type 1) shows broad absorptions corresponding to terminal $\nu(\text{CO})$ modes with maxima at approximately 2027, 1927, and 1869 cm^{-1} (Figure 1b). This spectrum differs considerably from that of the starting complex (Figure 1a), indicating the formation of new surface carbonyl species. An identical $\nu(\text{CO})$ pattern results from the impregnation of $\text{MgO}(200)$ with a hexane solution of $\text{Co}_4(\text{CO})_{12}$ under the same experimental conditions.

The diffuse-reflectance spectrum of 1 shows a broad band at 580 nm, typical of Co^{2+} in an octahedral environment.¹⁸ Simultaneously, the intensity of the absorption peak at 1360 nm (first overtone of $\nu(\text{OH})$) diminishes and a shoulder appears at lower energies (1380 nm) (Figure 2), suggesting a weakening of the O-H bond of some of the surface hydroxyl groups of magnesia upon chemisorption of $\text{Co}_2(\text{CO})_8$.

Volumetric measurements indicate that about 3 mol of CO/mol of $\text{Co}_2(\text{CO})_8$ is evolved during the impregnation process; no other gaseous products are detected. This is in agreement with the reaction shown in eq 1, whose stoichiometry requires 2.7 mol of CO/mol of $\text{Co}_2(\text{CO})_8$. If, in a separate experiment, a sample



of 1 is washed with hexane, only traces of the starting complexes ($\text{Co}_2(\text{CO})_8$ or $\text{Co}_4(\text{CO})_{12}$) are removed, showing that both the

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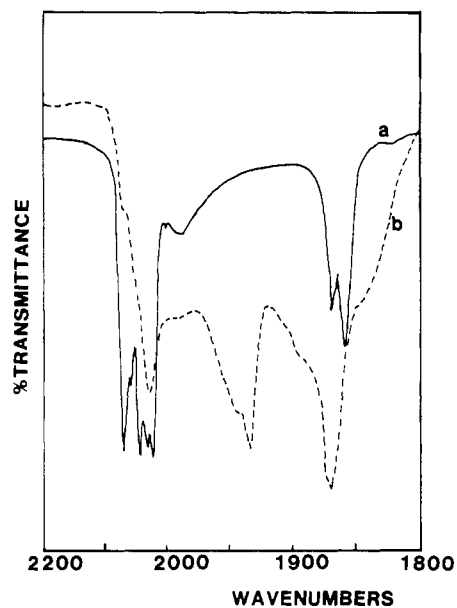


Figure 1. IR spectra in the $\nu(\text{CO})$ region: (a) $\text{Co}_2(\text{CO})_8/\text{hexane}$; (b) $\text{Co}_2(\text{CO})_8/\text{MgO}(200)$, evacuated 1 h.

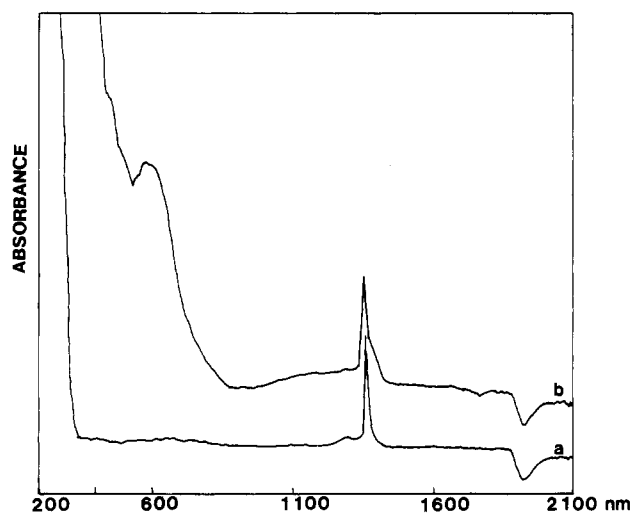


Figure 2. Diffuse-reflectance spectra of $\text{MgO}(200)$: (a) sample after treatment with O_2 for 3 h at 400°C ; (b) sample in (a) impregnated with $\text{Co}_2(\text{CO})_8/\text{hexane}$ and then evacuated 3 h at room temperature.

dicobalt and the tetracobalt carbonyls are totally and immediately converted into the same surface carbonyl species upon interaction with $\text{MgO}(200)$. On the other hand, treatment of **1** with a CH_2Cl_2 solution of $[(\text{Ph}_3\text{P})_2\text{N}]\text{Cl}$ ($[\text{PPN}]\text{Cl}$), at room temperature, results in the extraction of $[\text{PPN}][\text{Co}(\text{CO})_4]$ as the only carbonyl-containing product, characterized by a single $\nu(\text{CO})$ band at 1887 cm^{-1} in the IR spectrum.⁸ The solution also contains the $[\text{CoCl}_4]^{2-}$ ion, identified by its UV-vis spectrum (λ_{max} 632, 667, 692 nm).¹⁸ A blank reaction shows that $\text{Co}_2(\text{CO})_8$ in *n*-hexane is unreactive toward $[\text{PPN}]\text{Cl}$ under the same conditions and in the absence of other reactants. Co analysis of the sample before (1.27 wt % Co) and after (0.20 wt % Co) treatment with $[\text{PPN}]\text{Cl}$ indicates that at least 80% of the cobalt present on the surface is extracted as $[\text{PPN}][\text{Co}(\text{CO})_4]$ plus $[\text{PPN}]_2[\text{CoCl}_4]$.

At higher metal loadings the IR spectrum becomes more complicated in the $1600\text{--}2200\text{-cm}^{-1}$ region (Figure 3). In addition to the bands observed for **1**, new absorption bands at ca. 2050, 2025, 1977, 1936, 1840, and 1743 cm^{-1} appear; a simultaneous color change to green is noticed. Apparently, at least a second independent reaction takes place at these higher metal loadings, which might correspond to the formation of $[\text{Co}_6(\text{CO})_{15}]^{2-}$.¹⁹

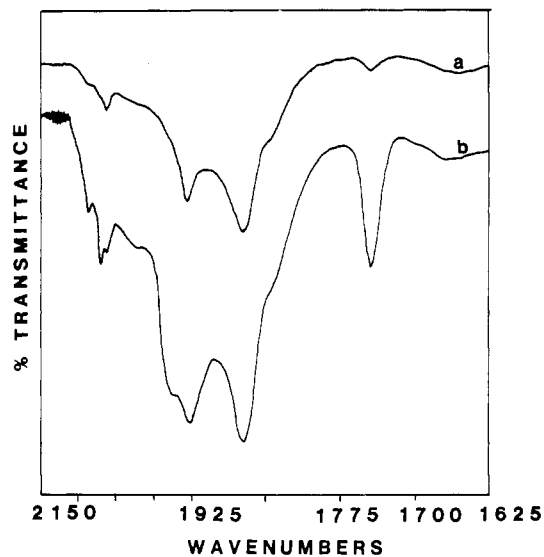


Figure 3. Evolution of the $\nu(\text{CO})$ spectrum of $\text{Co}_2(\text{CO})_8/\text{MgO}(200)$ with Co loading: (a) low loading; (b) higher loading.

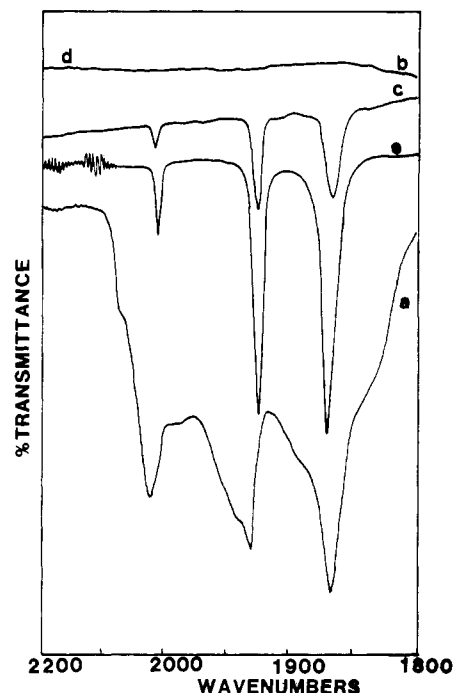


Figure 4. IR spectra in the $\nu(\text{CO})$ region: (a) $\text{Co}_2(\text{CO})_8/\text{MgO}(200)$; (b) sample in (a) under vacuum 200°C , 16 h; (c) sample in (b) under CO (300 Torr), 25°C , 12 h; (d) sample in (c) under vacuum, then under H_2 (300 Torr), 16 h, 400°C ; (e) sample in (d) under CO (300 Torr), 48 h, 25°C .

However, this reaction was not further studied in view of its complexity.

Decarbonylation and Recarbonylation of 1. The IR and DR spectra of **1** remain unchanged upon evacuation of the solid for 24 h at room temperature. When the sample is heated under vacuum for 16 h, a progressive decarbonylation process takes place that is complete at about 200°C , as evidenced by the disappearance of all the $\nu(\text{CO})$ bands in the IR spectrum of **1** (Figure 4b).

Gas chromatographic analysis of the gaseous phase during thermal decomposition at various temperatures confirms the evolution of only CO up to 200°C (4.5 mol/mol of $\text{Co}_2(\text{CO})_8$); between 200 and 300°C , CO is consumed to yield mainly CO_2 and small amounts of CH_4 .

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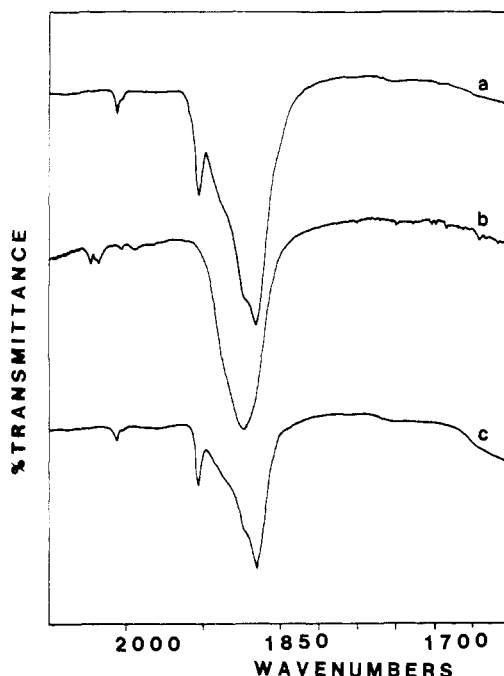


Figure 5. IR spectra in the $\nu(\text{CO})$ region of $[\text{PPN}][\text{Co}(\text{CO})_4]/\text{MgO}(200)$: (a) sample under vacuum 1 h, 25 °C; (b) sample in (a) in the presence of CH_2Cl_2 ; (c) sample in (b) after evacuation of CH_2Cl_2 , 1 h, 25 °C.

When a sample of **1** is decarbonylated at 200 °C as described above and subsequently treated with CO (300 Torr) at ambient temperature, the new carbonyl species **2** is generated, whose IR spectrum in the $\nu(\text{CO})$ region is very well resolved and shows only three sharp bands at 2015 (m), 1927 (s), and 1873 (s) cm^{-1} (Figure 4c). Reduction of this recarbonylated species **2** with H_2 at 400 °C, followed by evacuation at the same temperature for 2 h, also results in the expected total disappearance of all the $\nu(\text{CO})$ absorptions in the IR spectrum (Figure 4d); exposure of this reduced sample to CO (300 Torr) at room temperature again regenerates species **2**, as evidenced by IR spectroscopy (Figure 4e). The results suggest that very small particles of Co obtained under H_2 at 400 °C react with CO to give $\text{Co}_2(\text{CO})_8$, which disproportionates quickly to $\text{Co}(\text{CO})_4^-$ and Co^{2+} .

In any case, the spectrum of **2** is less intense than that of **1**, indicating that only part of the cobalt deposited on the surface undergoes recarbonylation.

When a sample of **1** is decarbonylated at 200 °C under vacuum, and then treated under O_2 at 400 °C, subsequent generation of **2** under CO is no more observed; in agreement with this observation, the DRS spectrum evidences the formation of Co^{2+} and Co^{3+} species on the surface of magnesia. Here the Co^{2+} or Co^{3+} would not be easily reduced by CO.

Impregnation of $[\text{PPN}][\text{Co}(\text{CO})_4]$ on $\text{MgO}(200)$. If a MgO disk is impregnated with a CH_2Cl_2 solution of $[\text{PPN}][\text{Co}(\text{CO})_4]$ and the solvent is removed under vacuum, the in situ FTIR spectrum of the dry solid shows the three bands at 2015, 1927, and 1873 cm^{-1} corresponding to the same species **2**, plus a shoulder at 1885 cm^{-1} due to $[\text{PPN}][\text{Co}(\text{CO})_4]$ (Figure 5a). If this solid is put into contact with CH_2Cl_2 vapor at room temperature, the spectrum of **2** disappears and only the band of $[\text{PPN}][\text{Co}(\text{CO})_4]$ is observed (Figure 5b); these changes are completely reversible under vacuum (Figure 5c).

Discussion

Nature of the Surface Carbonyl Species **1 and **2**.** Early studies by Hieber showed that $\text{Co}_2(\text{CO})_8$ disproportionates in solution by the action of Lewis bases (e.g. pyridine) to yield $[(\text{py})_6\text{Co}][\text{Co}(\text{CO})_4]_2$, which may be isolated as a stable solid.⁸ More recent studies by Fachinetti and co-workers have established that this reaction proceeds in solution through a series of homonuclear ion pairs in various degrees of association.⁹

Table I. IR Spectral Characteristics of **1**, **2**, and Related Complexes

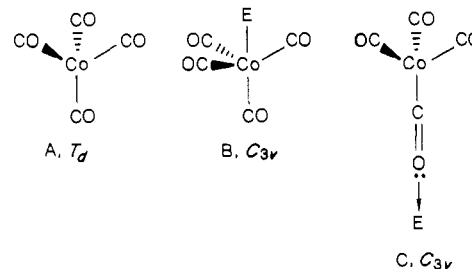
complex	$\nu(\text{CO})$, cm^{-1}	ref
1	2027 m, 1927 m, br, 1869 s, br ^a	this work
2	2014 w, 1927 s, 1873 s ^b	this work
$[\text{PPN}][\text{Co}(\text{CO})_4]$	1890 ^c	8
$\text{HCo}(\text{CO})_4$	2116 w, 2053 s, 2030 vs ^d	20
$[\text{Co}(\text{CO})_4]_2\text{Mg}(\text{py})_4$	2008 w, 1978 sh, 1925 vs, br, 1785 vs ^e	21
$[(\text{py})_3\text{Co}\cdots\text{Co}(\text{CO})_4]^+[\text{Co}(\text{CO})_4]^-$	2050 m, 1992 m, 1947 s, 1933 s, 1887 m, 1867 s ^f	9d
$[(\text{py})_5\text{Co}\cdots\text{OC}-\text{Co}(\text{CO})_3]^+ \text{ } ^\text{g}$	2018 w, 1918 m, 1798 m ^f	9c
$[(\text{py})_5\text{Co}-\text{Co}(\text{CO})_4]^+ \text{ } ^\text{g}$	2059 m, 1986 m, 1947 s ^f	9c
$[\text{Co}(\text{CO})_4]_2\text{Co}(\text{py})_4 \text{ } ^\text{f}$	2040 m, 1963 s, 1929 m, 1903 w ^f	9c

^a From $\text{Co}_2(\text{CO})_8$ on $\text{MgO}(200)$. ^b From $[\text{PPN}]\text{Co}(\text{CO})_4$ on $\text{MgO}(200)$. ^c In THF. ^d In hexane. ^e Nujol mull. ^f In THF. ^g Suggested structure.

Our results on the interaction of $\text{Co}_2(\text{CO})_8$ or $\text{Co}_4(\text{CO})_{12}$ with $\text{MgO}(200)$ are also consistent with a disproportionation reaction promoted by the basic support to yield $[\text{Co}(\text{CO})_4]^-$ anions in association with Co^{2+} and/or Mg^{2+} cations on the surface.

The presence of $[\text{Co}(\text{CO})_4]^-$ on the surface is clearly established by its extraction with $[\text{PPN}]\text{Cl}$, together with IR data for **1** and **2**, which show bands attributable to this anion in interaction with the support (vide infra). Also, diffuse-reflectance results combined with extraction results confirm the presence of Co^{2+} ions on the MgO surface.

In order to propose a structure for the surface species **1** and **2**, the IR spectra of $[\text{Co}(\text{CO})_4]^-$ in various environments must be considered. Free $[\text{Co}(\text{CO})_4]^-$ is a tetrahedral molecule (T_d , structure A) whose IR spectrum is characterized by a single $\nu(\text{CO})$

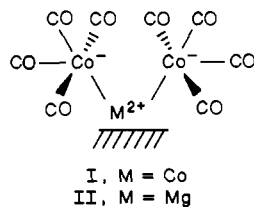


band at 1887 cm^{-1} .⁸ Introduction of a fifth ligand as in structure B lowers the molecular symmetry to C_{3v} , and consequently, the $\nu(\text{CO})$ pattern in this case is expected to be dominated by the presence of three active modes at frequencies characteristic of terminal CO ligands.¹⁹ This is the case, for instance, for the protonated form $\text{HCo}(\text{CO})_4$, which shows bands at 2100 (w), 2040 (s), and 2010 (vs) cm^{-1} (Table I).²¹ If, on the other hand, the fifth ligand is introduced via interaction with a carbonyl oxygen as in structure C, the resulting symmetry is also C_{3v} , and thus the same number of CO bands are to be expected in the IR spectrum. However, the interaction of the oxygen electrons with an electropositive center (as in structure C) causes a weakening of the C–O bond and consequently one of the active modes should be found at low frequencies.²²

The FTIR spectrum of **1** (Figure 1b) shows broad absorptions with maxima at approximately 2027, 1927, and 1869 cm^{-1} assigned to terminal CO modes of $[\text{Co}(\text{CO})_4]^-$ in an environment of symmetry lower than that of the free anion. Structures containing $\text{M} \leftarrow \text{OC}-\text{Co}$ interactions need not be considered, since no low-frequency $\nu(\text{CO})$ bands were observed (at least at low metal loadings). Several species may be envisaged that are in agreement with lower symmetry and/or with known structures. Among them, surface species such as I and II, involving homonuclear ($\text{M} = \text{Co}$) or heteronuclear ($\text{M} = \text{Mg}$) ion pairing are reasonable candidates. Such species have their parallel in molecular chemistry.

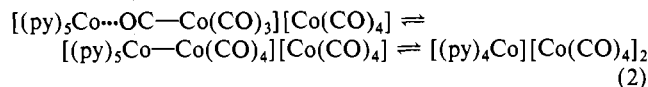
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A comparison of the spectral properties of these molecules with those of the supported complexes ought to be made. The carbonyl stretching frequencies of **1**, **2**, and related species are collected in Table I.

Fachinetti and co-workers have reported the IR spectra of the $\text{Co}^{2+}/\text{py}/[\text{Co}(\text{CO})_4]^{-}$ system in THF solution and interpreted it in terms of an equilibrium between three homonuclear ion pairs (eq 2).^{9c}



The IR spectrum assigned to each homonuclear ion pair (Table I) consists of three bands in accord with structures of type B or C. Very recently, the *metal-metal-bonded* cation $[(\text{py})_3\text{Co}-\text{Co}(\text{CO})_4]^{+}$ was isolated from such solutions and characterized crystallographically.^{9d} Its IR spectrum in the solid state is rather complex (Table I), probably due to the presence of $[\text{Co}(\text{CO})_4]^{-}$ as the counterion.

The heteronuclear complex $[(\text{py})_4\text{Mg}][\text{Co}(\text{CO})_4]_2$ has also been synthesized and characterized by IR (table I) and other pertinent data.²³ The observation of three $\nu(\text{CO})$ bands, one of which appears at low frequency (1785 cm^{-1}), is in accord with a structure containing two $\text{Mg} \leftarrow \text{OC}-\text{Co}$ bonds. Metal-metal-bonded complexes analogous to the surface species II are known for $\text{L}_2\text{Mg}[\text{Co}(\text{CO})_3(\text{PR}_3)]_2$ ²³ and other heteronuclear systems $\text{M}[\text{Co}(\text{CO})_4]_x$, where $\text{M} = \text{Na},^{24} \text{Tl},^{25}$ or $\text{In}.$ ²⁶

When the IR spectrum of **1** is compared with those reported for the molecular complexes (Table I), it is clear that a definitive structural assignment is not possible with the data available. The broadness of the bands corresponding to **1** may be taken as an

indication that both the species I and II are present on the MgO surface after impregnation.

Interestingly, thermal decarbonylation of **1** produces a solid that can be partially recarbonylated at room temperature to yield the new species **2**, which shows a well-defined $\nu(\text{CO})$ pattern consisting of three sharp, medium to strong bands (Figure 4, Table I). This spectrum can be attributed to $[\text{Co}(\text{CO})_4]^{-}$ in a single well-defined environment of approximately C_{3v} symmetry. This implies that during the decarbonylation process the system undergoes an important modification leading to the preferential formation of a single supported metal carbonyl complex.

None of the known molecular complexes present an IR spectrum very similar to that of **2** (Table I), but we note further that the frequencies and relative intensities of the IR bands of $[\text{Co}(\text{CO})_4]^{-}$ are highly sensitive to the environment and the solvent in such discrete complexes or ion pairs.

Some insight into the possible structure of **2** comes from the impregnation of a CH_2Cl_2 solution of $[\text{PPN}][\text{Co}(\text{CO})_4]$ on MgO(200). In this case, the formation of Co^{2+} ions on the surface is not very likely, and therefore the interaction of the carbonylate anion is most probably with surface Mg^{2+} ions. The resulting IR spectrum is identical with that of **2**, and thus we conclude that the same species is obtained by impregnation of $[\text{PPN}][\text{Co}(\text{CO})_4]$ and by decarbonylation-recarbonylation of **1**, i.e. the heteronuclear metal-metal-bonded ion pair II.

Previous reports on the interaction of cobalt carbonyls with SiO_2 ,^{12,13} Al_2O_3 ,^{12,13} zeolites,¹⁴⁻¹⁶ and MgO ¹¹ are available. In all these reports rather complex $\nu(\text{CO})$ patterns have been observed after impregnation. These results have been interpreted in terms of (i) a conversion of $\text{Co}_2(\text{CO})_8$ into $\text{Co}_4(\text{CO})_{12}$ on the surface and strong adsorption of both complexes and (ii) a disproportionation reaction leading to $[\text{Co}(\text{CO})_4]^{-}$ and unidentified surface cobalt subcarbonyls.

In the present work we conclude that under our reaction conditions conversion of $\text{Co}_2(\text{CO})_8$ into $\text{Co}_4(\text{CO})_{12}$ does not represent a major pathway; furthermore, adsorption of either of these complexes on MgO does not take place to any important extent. The main process that occurs upon interaction of $\text{Co}_2(\text{CO})_8$ or $\text{Co}_4(\text{CO})_{12}$ with MgO is the disproportionation into $[\text{Co}(\text{CO})_4]^{-}$ and Co^{2+} , whose presence has been established by a combination of IR and extraction methods.

Two types of ion pairs seem to be formed, corresponding to homonuclear (structure I) and heteronuclear (structure II) metal-metal bonds.

Thermal treatment of the solids thus formed (**1**) and subsequent recarbonylation result in the better defined surface species **2**, for which the heteronuclear metal-metal-bonded structure II is proposed. The same species may be obtained by direct interaction of $[\text{PPN}][\text{Co}(\text{CO})_4]$ with the MgO surface.

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