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Intrazeolite Chemistry of Cobalt Carbonyls

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The adsorption of $Co_2(CO)_8$ onto Na–X and Na–Y from pentane solution yields $Co(CO)_4^-$ and species assigned as $Co_4(CO)_{12}$, $Co(CO)_3L_2^+$, and $Co_x(CO)_y$. These are identified by in situ infrared spectroscopy and chemical reactivity. On Na–X the tetracarbonylcobaltate ion is the predominant species while on Na–Y the cluster $Co_4(CO)_{12}$ is the most abundant. The infrared spectrum of the species assigned to $Co_4(CO)_{12}$ on Na–Y is shifted significantly from that observed in solution for this cluster. An identical set of bands for the cluster is obtained from both $Co_2(CO)_8$ and $Co_4(CO)_{12}$ adsorbed on Na–Y. The adsorbed cluster reacts via disproportionation with the phosphines PEt_3 and $P(t-Bu)_3$ to yield $Co(CO)_4^-$. When $Co_4(CO)_{12}$ is adsorbed on Na–X zeolite, an infrared spectrum identical with the solution spectrum is obtained.

Introduction

A great deal of effort has recently been directed toward the synthesis of metal complexes within the pore structure of zeolites.[1-12] The chemistry has extended from the synthesis of coordination compounds[7-10] to metal carbonyl[1,2,4-6] and organometallic chemistry.[3,11,12] Much of this chemistry has been developed with the goal of creating shape-selective transition-metal catalysts. In this regard the principal role of the zeolite is to immobilize the metal within the pores and to impart selectivity to a catalytic reaction by forcing the substrate molecule to pass through the zeolite channels to find the metal. Thus only molecules of a certain size and shape will be able to participate in the catalytic reaction.

At this time the selectivity enhancement obtained by bifunctional catalysts of this type is modest at best.[2-4,12] To obtain good selectivity it is necessary to poison complexes on the surface of the catalysts.[3] Furthermore, in solution these materials are highly susceptible to loss of metal so that it is difficult to distinguish heterogeneous from homogeneous catalysis.[4,13]

A variety of techniques are avialable for the study of metal complexes that are directly supported on metal oxides; these include magic-angle-spinning NMR,[14-16] in situ infrared spectroscopy,[17-19] temperature-programmed decomposition,[20] and catalytic activity.[21] In the use of spectroscopic techniques to identify surface species, a great deal of reliance is placed upon analogies with known model complexes. A well-documented example is the subcarbonyl, $Mo(CO)_3$, which is postulated to form on alumina surfaces. Many spectroscopic and analytical techniques have been used to establish this composition. The variety of complexes containing the $Mo(CO)_3$ group have provided the necessary model compounds to help confirm the structure.[22] In another case, the cluster $Rh_6(CO)_{16}$ is assigned to a species observed on zeolites by comparison of the infrared spectrum of the complex formed on the zeolite with that of $Rh_6(CO)_{16}$ in solution.[2,4]

In some cases the chemistry of the surface species is unexpected or unprecedented and lacks a good analogy to the chemistry in homogeneous solution. For example the organothorium complex $(\eta^5-C_5H_5)_2Th(CH_3)_2$ reacts with partially dehydroxylated aluminas to transfer a methyl group to the alumina surface.[15]

It has recently been shown that dicobalt octacarbonyl reacts with a variety of surfaces in the gas phase to yield $Co_4(CO)_{12}$ and/or $Co(CO)_4^-$ adsorbed on the support.[23,24] At the time this report appeared, work was in progress in our laboratory on similar experiments from pentane solution. In this paper we discuss the chemistry of $Co_2(CO)_8$ and $Co_4(CO)_{12}$ adsorbed onto Na–X and Na–Y zeolites from solution; in many respects this is complementary to the work reported by Watters et al.[23] Furthermore the species assigned to $Co_4(CO)_{12}$(ads) is shown to react with phosphines in an unusual fashion for this cluster. The location of the cluster on the zeolite is established from considerations of its reactivity toward phosphines.

Experimental Section

General Data. Dicobalt octacarbonyl, obtained from Pressure Chemical Co., Inc., was sublimed under vacuum at ambient temperature and stored under nitrogen. Tetracobalt dodecacarbonyl was synthesized by literature methods.[25] The black crystals were repeatedly washed with dry, oxygen-free pentane, vacuum-dried, and stored under nitrogen. The $Co_4(CO)_{12}$ was determined to be free of impurities by its infrared spectrum.

Pentane and THF (Fisher Scientific) were distilled from Na–K alloy/benzophenone under a nitrogen atmosphere immediately prior to use. All phosphines were obtained from Strem Chemicals, Inc., and stored under nitrogen.

The zeolites used were powdered Na–X and Na–Y purchased from Strem Chemicals, Inc. The zeolites were slurried in 1 M NaCl for several hours, filtered, washed with distilled water until the wash was free of chloride, and stored in air at 110 °C. Self-supporting wafers were formed by compressing 10–20 mg of powder at 1500 psi in a standard infrared pellet die. The pellets were 8 mm in diameter and approximately 0.1 mm thick; they transmitted from 50 to 60% of the IR beam intensity.

In Situ Infrared Spectroscopy. All in situ infrared spectra were recorded on a Nicolet 5DX Fourier transform spectrometer in the cell illustrated in Figure 1. A typical experiment was performed in the following manner. The zeolite pellet was mounted in the cell, calcined in flowing oxygen at 375 °C for 30 min and allowed to cool to room temperature in a helium flow. A pentane solution of cobalt carbonyl was then added by syringe to the well at the bottom of the apparatus. The

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Table I

| system	carbonyl stretching frequencies, cm⁻¹											
					Solution							
Co₂(CO)₈/pentane	2112 w	2071 s	2045 s	2031 s	2024 s	2001 w			1867 m	1858 m		
Co₄(CO)₁₂/pentane		2064 s	2056 s	2036 w	2025 w				1867 m			
[Co(CO)₃(PEt₃)₂][Co(CO)₄]/THF						2008 s	1995 s		1885 s, br			
Co₂(CO)₈/Na–Y batch (Nujol mull)	2122 w	2078 s	2050 m	2030 m		2007 m	1940 m	1913 m	1893 m	1860 w		1817 m
					In Situ							
Co₂(CO)₈/Na–Y	2122 w	2079	2062	2029		2010	1943	1914	1885			1809 m
Co₂(CO)₈/Na–X	2127 w	2090	2069	2042	2026		1934		1894	1870		1805
PEt₃/Na–Y, Co₂(CO)₈						2003	1989		1884	1869		
PEt₃/Na–X, Co₂(CO)₈						2003	1989		1884	1869		
Co₂(CO)₈/Na–Y, PEt₃		2080 sh	2060 w		2012 m	1995 m	1966 m	1912 sh	1890 s	1876 sh		
Co₂(CO)₈/Na–X, PEt₃	2127 w	2090 w	2069 w		2026 w			1920 sh	1894 s			
Co₄(CO)₁₂/Na–Y	2121 w	2115 w	i078 s	2056 sh	2030 sh		1997 w		1899 w	1870 w	1811 m	1804 m
Co₄(CO)₁₂/Na–X	2108 w	2064 s	2055 s	2040 m	2029 m		1989 w		1902 s, br	1868 s	1833 w	
Co₄(CO)₁₂/Na–Y, PEt₃			2070 w	1980 m	1964 m	1944	1925 sh	1918 sh	1905 s	1870 m	1846 w	
Co₄(CO)₁₂/Na–Y, P(t-Bu)₃									1902 s, br			
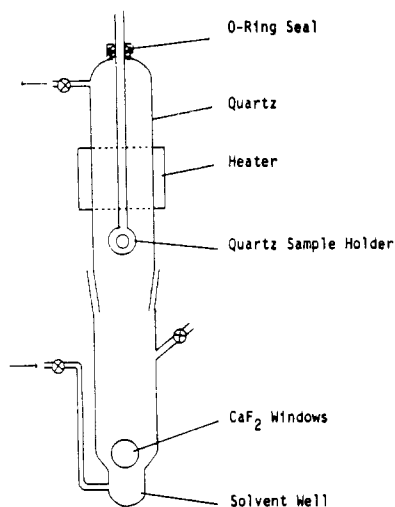
Figure 1. Schematic representation of the IR cell.

pellet was loaded with cobalt carbonyl by immersion into the pentane solution. The first infrared spectrum in a series was recorded immediately after lifting the pellet into the IR beam. The pellet could be reimmersed until the desired loading of cobalt carbonyl was achieved as judged by the intensity of the infrared absorbance in the carbonyl region.

Carbon Monoxide Evolution. The carbon monoxide evolved during adsorption of Co₂(CO)₈ and Co₄(CO)₁₂ onto the zeolite was quantitated by using larger zeolite samples in an apparatus similar in design to that of Burwell and Brenner.[26,27]

Results and Discussion

Adsorption of Co₂(CO)₈ and Co₄(CO)₁₂ on Faujasites. The cation-exchange capacity of zeolites is well established.[28] Cobalt(II), for example, will readily replace 77% of the sodium ions in Na–Y zeolite.[7] Modified ZSM-5 materials may exchange cations beyond the value calculated from elemental analysis.[29] The added capacity is associated with silicate sites within the structure. Other complexes may react directly with protons on the zeolite. Thus, Rh(allyl)₃ reacts with protonated faujasites to yield a supported rhodium complex.[11,12]

Dicobalt octacarbonyl is also adsorbed onto faujasites by chemical reaction although protons are not required for the reaction. Thus dry Na–X and Na–Y zeolites react directly with pentane solutions of Co₂(CO)₈ to completely remove the cobalt

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Table II. Assignment of Carbonyl Stretching Frequencies (cm⁻¹)[a]

support	complex	assigned frequencies
Na–Y	Co₂(CO)₈	2062, 2030, 1846, 1802
	Co₄(CO)₁₂	2121, 2079, 2054, 1812
	Co(CO)₃L₂⁺	2008
	Co(CO)₄⁻	1902, 1885
	Coₓ(CO)ᵧ	1943
Na–X[a]	Co₄(CO)₁₂ (surface)	2108, 2064, 2055, 2040, 2029, 1989, 1869, 1833
	Co(CO)₃L₂⁺	2026
	Co(CO)₄⁻	1902, 1894

[a] Many of the carbonyl bands observed upon adsorption of Co₂(CO)₈ and NaX are left unassigned at this time. These may be due to species Coₓ(CO)ᵧ.

complex from solution with concomitant evolution of carbon monoxide. Extremely high-weight-percent loadings of cobalt may be achieved in this fashion without precipitation of the complex onto the zeolite. In one experiment a 4.8 wt % loading of cobalt metal was obtained in which all of the Co₂(CO)₈ was removed spontaneously from solution. This corresponds to approximately 1.5 cobalt atoms per supercage. Unless otherwise indicated the loadings for all the materials generated from Co₂(CO)₈ were from 0.6 to 0.8 wt % of cobalt. At low cobalt loadings the zeolite powder is reddish brown in color.

Many experiments were performed to quantitate the evolution of carbon monoxide during the adsoprtion of Co₂(CO)₈. It was found that the quantity of CO evolved is very sensitive to the reaction conditions. Up to 2 equiv of CO/Co₂(CO)₈ are observed if the adsorption is performed in a closed vessel. If however a continuous flow of helium is purged through the reaction vessel up to 4 equiv of CO/Co₂(CO)₈ are evolved at 25 °C. Thermolysis of adsorbed Co₂(CO)₈ on Na–Y zeolite at 150 °C for 1 h yields a total of 6 equiv of CO/Co₂(CO)₈. Obviously Co₂(CO)₈ is very reactive toward faujasitic zeolites. Also it is apparent from the infrared spectrum of the resulting zeolite powders that the reaction of Co₂(CO)₈ with the zeolite does not proceed by a single pathway (See Table I).

The tetramer, Co₄(CO)₁₂, reacts in a very different fashion with faujasites. Only very small quantities of Co₄(CO)₁₂ are spontaneously extracted from pentane solution. The maximum weight-percent loading obtained from the spontaneous extraction of Co₄(CO)₁₂ from pentane was 0.08 wt % of cobalt. This is approximately 2 orders of magnitude less than the quantity of Co₂(CO)₈ adsorbed under similar conditions. Furthermore, virtually no carbon monoxide is evolved during the adsorption process. In several experiments the quantity of CO evolved was always <0.2 equiv ov CO/Co₄(CO)₁₂. Thus Co₄(CO)₁₂ appears to be simply physisorbed onto NaY zeolite.

These results are consistent with the fact that Co₄(CO)₁₂ is too large to penetrate the channels of the faujasite and therefore must
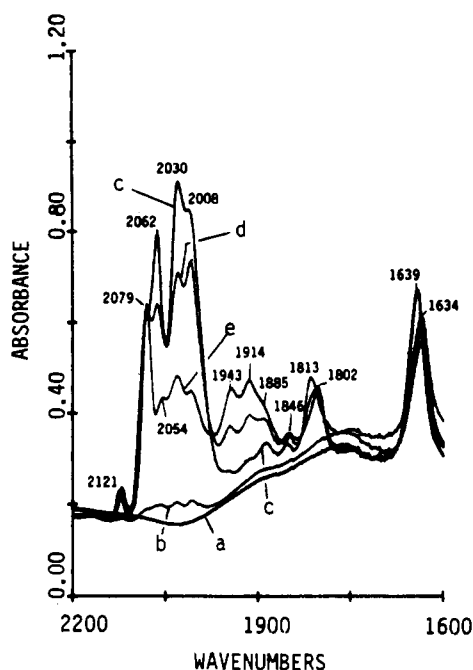
Figure 2. Infrared spectra obtained upon adsorption of $Co_2(CO)_8$ on Na–Y zeolite: a, of the clean pellet; b, after addition of a pentane solution of $Co_2(CO)_8$; c, immediately after immersion in the pentane solution; d, after 2.5 min; e, after 15 min.

Figure 3. Infrared spectra obtained upon adsorption of $Co_2(CO)_8$ on Na–X zeolite. Traces a, b, and c were recorded immediately after immersion and after 2.5 and 5 min, respectively.

be located on the surface. On the other hand the dimer, $Co_2(CO)_8$, is small enough to penetrate the channels. This may account for the large capacity of faujasites for this molecule.

In Situ Infrared Spectroscopy: Binary Cobalt Carbonyls. A typical set of infrared spectra resulting from the adsorption of $Co_2(CO)_8$ on Na–Y are shown in Figure 2. Table I summarizes the results of this experiment and others to be discussed later. Table II shows the proposed assignments.

Trace a shown in Figure 2 is of the clean Na–Y wafer immediately prior to addition of the pentane solution. The second trace is of the pellet after addition of the solution but before immersion. It can be seen that minimal quantities of cobalt carbonyl are adsorbed from the gas phase over the solution. The intense band at 1639 cm^{-1} on the blank zeolite is assigned to the bending mode of residual water strongly bound to the zeolite. Upon addition of the pentane solution the water bending mode is shifted slightly to lower wavenumber. The OH stretching bands at 3697 and 3247 cm^{-1} are shifted to 3678 and 3200 cm^{-1}, respectively, upon addition of pentane vapor.

Trace c was recorded immediately after a 30-s immersion of the wafer in the pentane solution. A complex series of absorption bands is generated as this spectrum is followed with time. Most changes occur in the first 15 min after immersion and after 60 min no further changes in the spectrum are observed. The most intense bands in the terminal region of trace c, i.e. 2062 and 2030 cm^{-1} are assignable to $Co_2(CO)_8$. In the bridging region there is a band of medium intensity at 1802 cm^{-1} and a weak bank at 1846 cm^{-1}. The intensity of these correlate with the terminal bands at 2062 and 2030 and are thus assigned to $Co_2(CO)_8$.

The bands assigned to $Co_2(CO)_8$ diminish fairly rapidly with time and after 15 min (trace e) have virtually disappeared from the spectrum. In the terminal region the most intense band is at 2079 cm^{-1}, and in the bridging region the band at 1802 cm^{-1} is replaced by a new peak at 1813 cm^{-1}. Collectively the bands at 2121, 2079, 2054, and 1813 cm^{-1} are assigned to $Co_4(CO)_{12}$. This is consistent with the assignment made by Watters et al. However the shifts observed between the spectra for Co_4-$(CO)_{12}$(ads) and $Co_4(CO)_{12}$(solution) should not be interpreted as evidence for the cluster residing within the zeolite (vide infra).

There are several places in the spectrum where near isosbestic behavior is observed, for example at ca. 1980 cm^{-1}. However the match is not exact. This is consistent with some loss of carbon
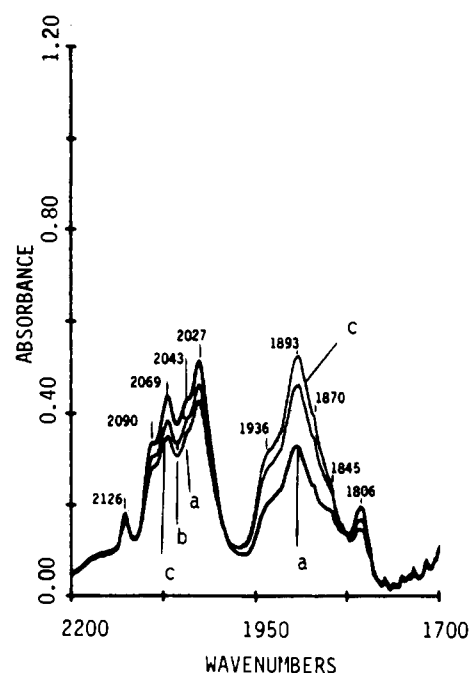
monoxide during the experiments. As the terminal bands decrease in intensity, three peaks are seen to grow in intensity at 1943, 1914, and 1885 cm^{-1}. One of these, 1885 cm^{-1}, may be assigned directly to $Co(CO)_4^-$ (vide infra). The others may be attributed to as yet unidentified cobalt carbonyls. In the terminal region two remaining bands are unassigned in spectrum e, i.e., those at 2030 and 2008 cm^{-1}. These may, in part, be due to species of the type $Co(CO)_3L_2^+$ where L is a framework oxide (vide infra).

Figure 3 shows the infrared spectra obtained upon adsorption of $Co_2(CO)_8$ on Na–X zeolite. Qualitatively the results are similar to those observed on Na–Y zeolite. Spectrum c shows the spectrum 5 min after immersion of the wafer. The band at 1893 cm^{-1} continues to grow slowly after this time. The most intense band is seen at 1893 cm^{-1}; as on Na–Y, this is assigned to Co-$(CO)_4^-$. Thus Na–X zeolite favors formation of $Co(CO)_4^-$ compared to Na–Y zeolite. A similar result was observed by Watters et al.

In the terminal region of the infrared spectrum bands are seen at 2126, 2090, 2045, and 2027 cm^{-1}. These are shifted to higher wavenumber compared to those for Na–Y zeolite. Also, these decrease in intensity as the 1893-cm^{-1} band increases. A bridging band is observed at 1806 cm^{-1}. By analogy with the results on Na–Y zeolite the bridging band at 1806 cm^{-1} is assigned to $Co_4(CO)_{12}$(ads); however, the corresponding terminal bands cannot be clearly assigned.

Confirmation of the bands at 2121, 2079, 2054, and 1813 cm^{-1} assigned to $Co_4(CO)_{12}$ on Na–Y zeolite is obtained by direct adsorption of this cluster onto Na–Y zeolite. The results of this experiment are shown in Figure 4A. Traces 1–4 in Figure 4A represent four successive immersions of the Na–Y wafer into a pentane solution of $Co_4(CO)_{12}$. The spectra do not change with time. With each immersion all infrared adsorptions simply increase in intensity. At heavy loadings (traces 3 and 4) a bridging carbonyl band appears at 1870 cm^{-1}, which is assigned to physisorbed $Co_4(CO)_{12}$. This band however is extremely weak; the principal bands are observed at 2121, 2078, 2056, and 1811 cm^{-1}. These are extremely close to bands in the spectrum of $Co_2(CO)_8$ on Na–Y and are assigned to $Co_4(CO)_{12}$ strongly physisorbed.

From Table I it can be seen that these bands are shifted significantly from $Co_4(CO)_{12}$ in solution. The terminal bands move to higher wavenumber while the bridging band is shifted to lower wavenumber. This has previously been taken as evidence for the cluster to reside within the zeolite structure. This cannot be the
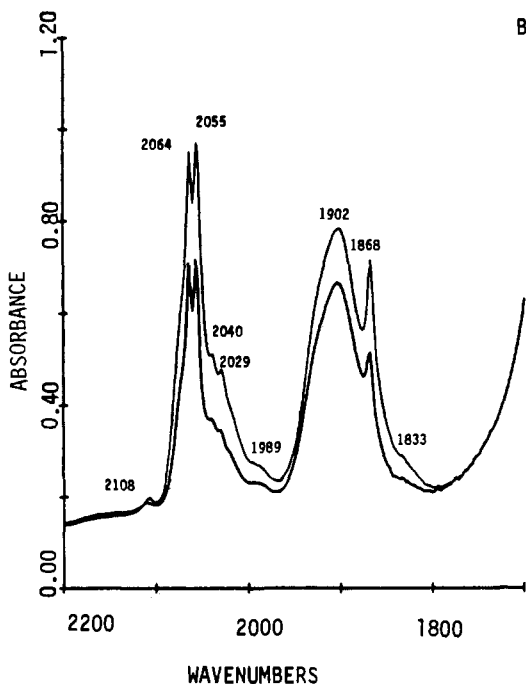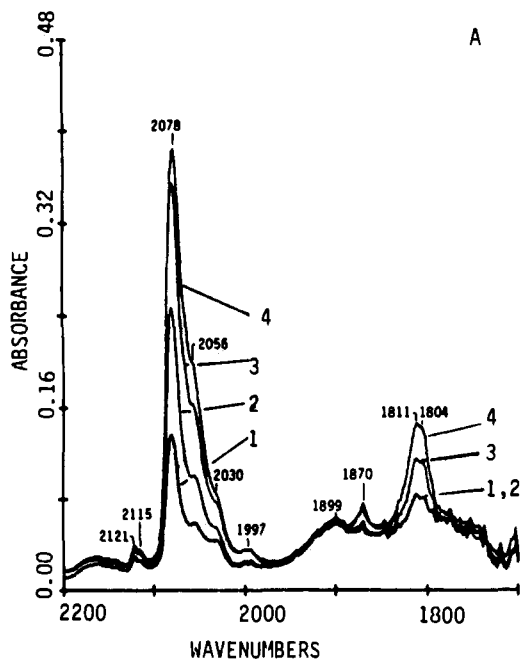
Figure 5. Infrared spectrum of $[Co(CO)_3(PEt_3)_2][Co(CO)_4]$ generated on a Na–Y wafer by preadsorption of PEt_3 followed by addition of $Co_2(CO)_8$.

In Situ Infrared Spectroscopy: Reactions with Phosphines. The identity of the adsorbed cobalt carbonyls may be assigned, in principle, on the basis of their reactivity with phosphines. Since it is well-known that basic phosphines like PEt_3 disproportionate $Co_2(CO)_8$[30] to yield complexes such as $[Co(CO)_3(PEt_3)_2][Co-(CO)_4]$, this phosphine was chosen to probe the surface chemistry of cobalt carbonyls. Also the tetramer $Co_4(CO)_{12}$ is well-known to react with simple phosphines to yield neutral substituted clusters of the type $Co_4(CO)_{12-x}(PR_3)_x$.[25,31]

In two experiments PEt_3 was preadsorbed onto a wafer of Na–X or Na–Y zeolite. A solution of $Co_2(CO)_8$ was then syringed onto the wafer and the infrared spectrum recorded. The resulting spectrum on Na–Y zeolite is shown in Figure 5; the spectrum on Na–X is identical. The spectrum is completely consistent with $[Co(CO)_3(PEt_3)_2][Co(CO)_4]$ as expected. The anion gives a strong absorption at 1885 cm^{-1}, confirming the previous assignment of this species. The cation bands are seen at 2003 and 1990 cm^{-1}. If, as suggested earlier, the terminal bands observed at 2030 and 2008 cm^{-1} are due to a complex of the type $[Co(CO)_3L_2]^+$ when L = framework oxide, then the bands are shifted to higher wavenumber compared to the present example when L = PEt_3.

Figure 6 shows the infrared spectra obtained upon addition of PEt_3 onto a Na–Y wafer that had already been reacted with $Co_2(CO)_8$. (The spectra shown in Figures 6 and 2 are of similarly prepared samples.) The spectrum shown in 6B is after addition of PEt_3. The most obvious feature of this spectrum is that the most intense band occurs at 1891 cm^{-1}. Thus nearly all of the supported cobalt carbonyl reacts with PEt_3 to yield $Co(CO)_4^-$, including adsorbed $Co_4(CO)_{12}$ since the bands assigned to this species nearly disappear. No evidence is observed for phosphine-substituted tetracobalt clusters except for a very weak bridging band at 1756 cm^{-1}. All other terminal bands also diminish in intensity as the 1891-cm^{-1} band increases. Thus PEt_3 reacts with the adsorbed cobalt carbonyls by further disproportionation. Bands assigned to $Co(CO)_3(PEt_3)_2^+$ in Figure 6B, i.e. 2012 and 1995 cm^{-1}, are relatively weak. It is possible that the cation formed is $Co(PEt_3)_6^{2+}$, which obviously will not give a carbonyl stretch in the infrared spectrum. When the same experiment is performed on Na–X zeolite, a similar infrared

Figure 4. (A) Infrared spectra obtained after immersion of an Na–Y zeolite pellet into a pentane solution of $Co_4(CO)_{12}$. Traces 1–4 are of consecutive immersions of 30 s each. Spectrum 4 did not change with time over a period of 15 min. (B) Infrared spectra obtained after immersion of an Na–X zeolite pellet into a pentane solution of $Co_4(CO)_{12}$. Trace a is the spectrum obtained immediately after immersion. Trace b is the spectrum obtained after 3 min.

case for adsorption of $Co_4(CO)_{12}$, however, since this cluster is too large to pass through the 7.4-Å channels of Na–Y zeolite. Reaction with large and small phosphines confirms this expectation.

Adsorption of $Co_4(CO)_{12}$ on Na–X gives a distinctly different infrared spectrum, as seen in Figure 4B. One set of bands at 2064 s, 2055 s, 2040 w, 2029 w, and 1868 cm^{-1} is nearly superimposable on the spectrum of $Co_4(CO)_{12}$ in pentane. The only other infrared band resulting from adsorption of $Co_4(CO)_{12}$ on Na–X is a broad absorption at 1902 cm^{-1}, which may be due to $Co(CO)_4^-$ from disproportionation of the cluster. Thus the surfaces of faujasites Na–X and Na–Y appear to have different types of sites for adsorption of $Co_4(CO)_{12}$.
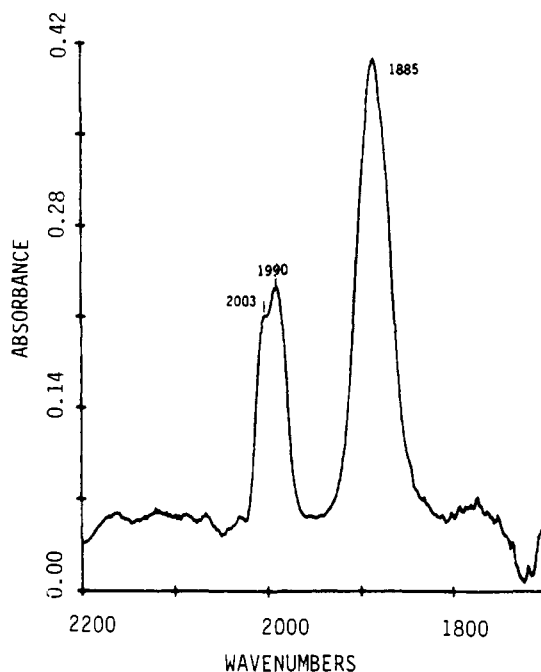
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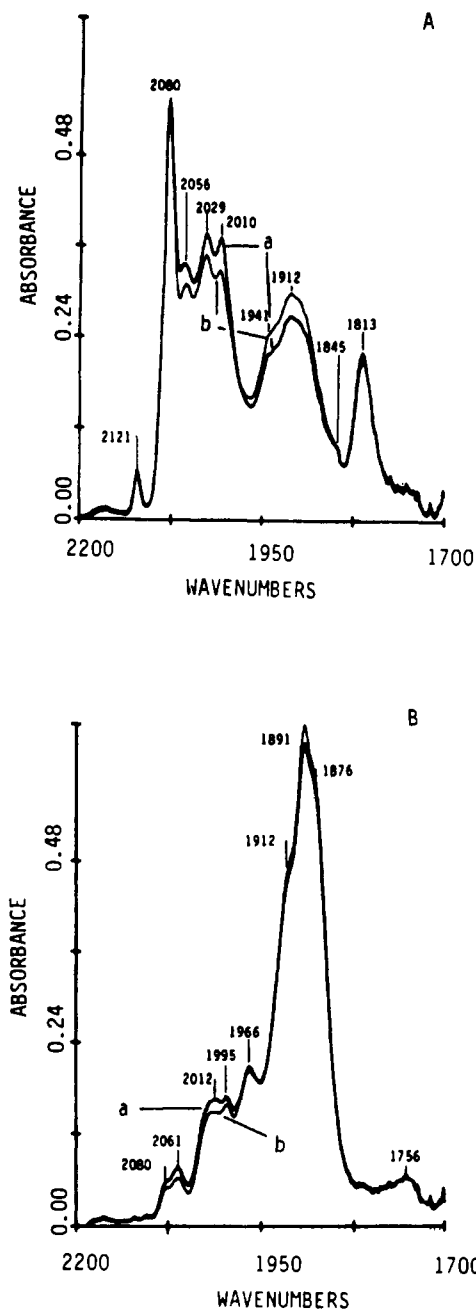(31) Darensbourg, D. J.; Incorvia, M. J. *Inorg. Chem.* **1981**, *20*, 1911.

Figure 6. (A) Spectra obtained upon immersion of an Na–Y wafer into a pentane solution of $Co_2(CO)_8$. Trace b is the spectrum after 2.5 min. (B) Spectra obtained from the same sample in part A immediately after addition of PEt_3.

spectrum is generated; i.e., nearly all of the carbonyl intensity is in the 1890-cm^{-1} peak.

The adsorbed tetracarbonyl cluster formed directly from $Co_4(CO)_{12}$ also reacts with PEt_3 to yield an intense band at ~ 1900 cm^{-1}. Disproportionation of $Co_4(CO)_{12}$ in solution has previously been observed upon reaction with nitrogen- or oxygen-containing bases, such as pyridine.[32] With phosphines, simple ligand substitution reactions are observed with $Co_4(CO)_{12}$.[31] Thus this cluster is activated toward disproportionation when adsorbed onto a faujasite.

Figure 7 compares the reactions of supported cobalt carbonyls from $Co_2(CO)_8$ and $Co_4(CO)_{12}$ with the large phosphine $P(t\text{-Bu})_3$.

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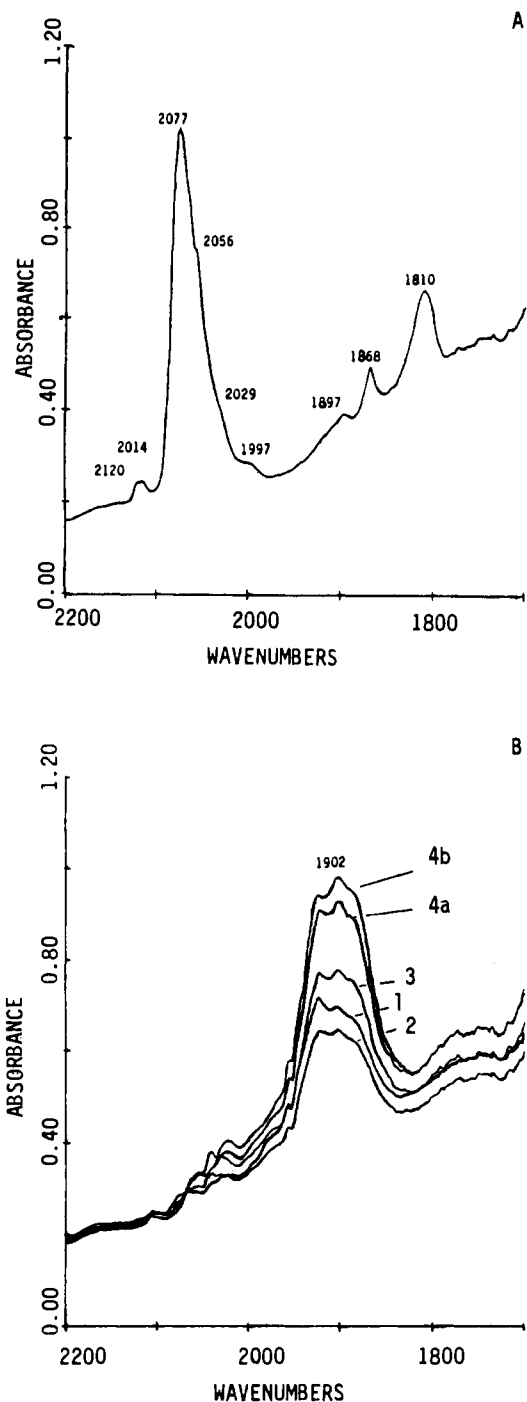
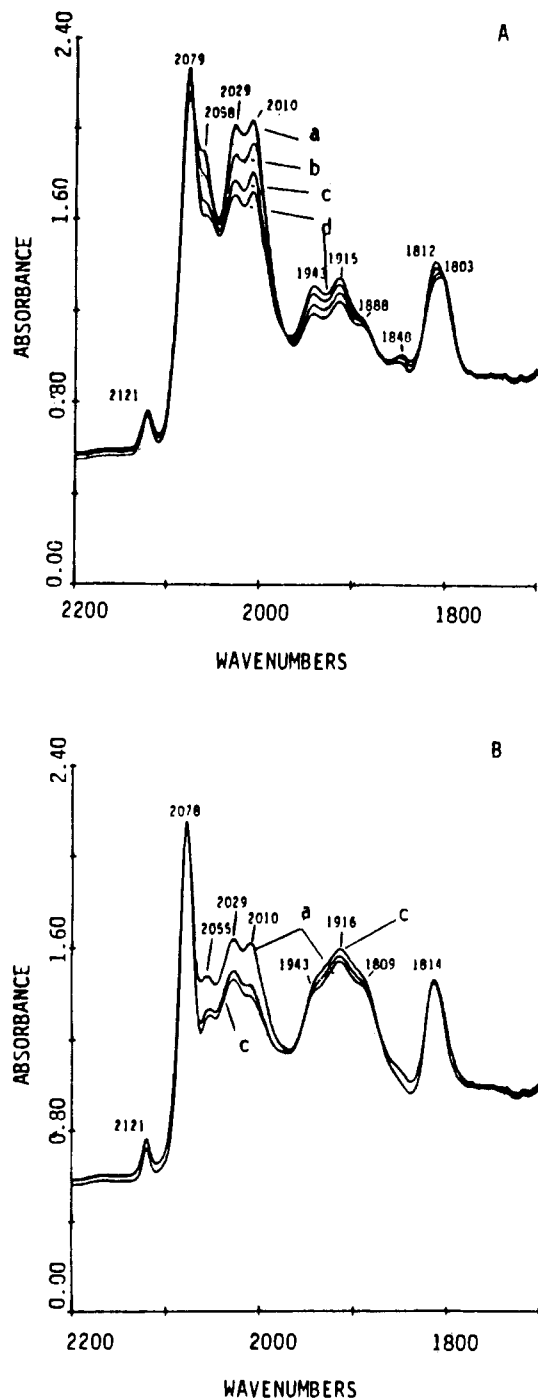(34) Cotton, F. A. *Inorg. Chem.* **1966**, *5*, 1083.

Figure 7. Spectra of $Co_4(CO)_{12}$ adsorbed on Na–Y zeolite (A) before the addition of $P(t\text{-Bu})_3$ and (B) after $P(t\text{-Bu})_3$, respectively. In part B trace 1 is the spectrum immediately after addition of $P(t\text{-Bu})_3$ while traces 2 and 3 represent the spectra after additional immersions into $Co_4(CO)_{12}$ solution. Traces 4a and 4b represent the spectra after addition of $Co_4(CO)_{12}$ from a syringe and 5 min after the addition, respectively.

From molecular models it is estimated that $P(t\text{-Bu})_3$ has a cross sectional diameter of ca. 8.3 Å. This is only slightly larger than the kinetic pore diameter of Na–Y zeolite, ca. 8.1 Å.[28] Thus this phosphine is too large to penetrate the pores of the zeolite at a reasonable rate at room temperature and so can only react with surface carbonyls.

In the set of spectra labeled A and B in Figure 7, the reaction of $Co_4(CO)_{12}(ads)$, generated from $Co_4(CO)_{12}$, with $P(t\text{-Bu})_3$ is shown. Clearly all the bands associated with the adsorbed carbonyl cluster (vide supra) disappear when $P(t\text{-Bu})_3$ is added. These are replaced by a set of three bands centered at $1902\ cm^{-1}$. The reaction therefore appears to yield $Co(CO)_4^-$. This reaction

Recent results by Herron et al.[35] for $Ni(CO)_4$ on Na–X zeolite show that, at high metal loadings in which at least 75% of all the supercages contain a nickel atom, a phosphite that is small enough to enter the zeolite pores will not find all of the nickel carbonyl due to pore blockage near the surface by the complexes formed with the phosphite. In the experiments reported here, the cobalt loading from $Co_2(CO)_8$ is approximately 0.6 wt % cobalt metal, corresponding to a 16% occupancy of supercages by one cobalt atom, given a random distribution. In fact, many cages appear to contain four cobalts as $Co_4(CO)_{12}$ clusters. Thus, if a phosphine is small enough to enter the zeolite pores, it will be able to diffuse through the zeolite until it finds all of the cobalt carbonyl.

Thermal Decomposition of Adsorbed $Co_2(CO)_8$. As mentioned previously pyrolysis of $Co_2(CO)_8$ adsorbed on Na–Y zeolite yields a total of 6 CO per 1 equiv of $Co_2(CO)_8$. The infrared spectrum of this sample shows carbonyl stretches at 2029 and 1948 cm^{-1}.

The infrared spectrum of adsorbed $Co_2(CO)_8$ on Na–Y zeolite was monitored as a function of temperature. The starting point for this experiment was the steady state spectrum after adsorption of $Co_2(CO)_8$ that is a spectrum like those shown in Figures 2, 6A, and 8A.

Heating slowly to 60 °C causes the bands at 2028 and 2008 cm^{-1} to decrease in intensity while the bands at 1941, 1910, and 1890 cm^{-1} increase slightly. Thus additional disproportionation may take place. The bands assigned to $Co_4(CO)_{12}$ are unaffected at 60 °C. When the temperature is raised to 80 °C, the $Co_4(CO)_{12}$ bands disappear rapidly. New bands appear and disappear at 2052 and 2025 cm^{-1} during the course of this experiment. At 80 °C the most intense peak is a broad adsorption centered at 1918 cm^{-1}. Also there are at least 5 overlapping bands between 1786 and 1701 cm^{-1}. Further heating to 100 °C decreases the overall intensity of the spectrum; two broad bands remain at 1918 and 1740 cm^{-1}. It is not clear what these bands are due to at this time. The samples turn black during heat treatment so it is possible that larger clusters or even cobalt metal is formed during thermolysis.

Proposed Reactions of $Co_2(CO)_8$ on Faujasites. Two independent reaction pathways appear to function for $Co_2(CO)_8$ as it is adsorbed on faujasites. These are shown in eq 1 and 2 (the

$$2Co_2(CO)_8 \rightarrow Co_4(CO)_{12} + 4CO \qquad (1)$$

$$Co_2(CO)_8 + 2L \rightarrow Co(CO)_3L_2^+ + Co(CO)_4^- + CO \quad (2)$$
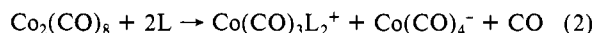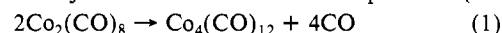
symbol L is used to refer to framework oxygen of the zeolite). At least one additional pathway is required to generate the species, giving rise to the 1941-cm^{-1} band. This species is assigned as $Co_x(CO)_y$ in Table II. Further disproportionation may take place to yield cobalt(II) salts according to eq 3.

$$Co_2(CO)_8 + 2Co(CO)_3L_2^+ + 8L \rightarrow$$
$$2Co(L)_6^{2+} + 2Co(CO)_4^- + 6CO \quad (3)$$
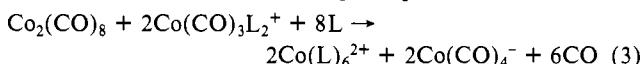
Equations 1 and 2 are sufficient to explain most of the infrared spectrum obtained for $Co_2(CO)_8$ adsorbed on Na–Y. Additionally, a combination of pathways 1 and 2 yields an average stoichiometry for CO evolved during adsorption that approaches 2CO's per $Co_2(CO)_8$. This is consistent with the observed result under static conditions for CO evolution. On Na–X the infrared adsorption due to the anion is far more intense than the terminal bands in the region 2100–2000 cm^{-1}; thus, it is likely that reaction 3 is an important pathway on Na–X zeolite.

The observations for the reaction with phosphine may be explained by eq 4–7. Reactions 4 and 5 show the formation of

$$3Co_4(CO)_{12} + 24PR_3 \rightarrow 4Co(PR_3)_6^{2+} + 8Co(CO)_4^- + 4CO \qquad (4)$$

$$Co_4(CO)_{12} + Co(CO)_3L_2^+ + 12PR_3 \rightarrow$$
$$2Co(PR_3)_6^{2+} + 3Co(CO)_4^- + 3CO \quad (5)$$

$$Co(CO)_3L_2^+ + 2PR_3 \rightarrow Co(CO)_3(PR_3)_2^+ \qquad (6)$$

$$Co_4(CO)_{12} + xPR_3 \rightarrow Co_4(CO)_{12-x}(PR_3)_x + xCO \quad x = 1-4 \qquad (7)$$

Figure 8. Spectra of $Co_2(CO)_8$ adsorbed on Na–Y zeolite (A) before and (B) after the addition of $P(t\text{-Bu})_3$, respectively. In part A, spectrum a was obtained immediately after immersion into $Co_2(CO)_8$ solution, while spectra b–d were obtained at 2.5-m intervals. In part B, spectrum a is that prior to addition of $P(t\text{-Bu})_3$. Spectra b and c were obtained immediately following addition of $P(t\text{-Bu})_3$ (approximately 30 s) and 5 min after addition, respectively.

confirms that $Co_4(CO)_{12}$(ads) generated from $Co_4(CO)_{12}$ in solution lies on the surface.

The set of spectra labeled A and B in Figure 8 represents the results from the same experiment with the adsorbed carbonyls generated from $Co_2(CO)_8$ on Na–Y. (The spectra shown in Figure 8A thus are from a sample prepared similarly to the compounds whose spectra are shown in Figures 6A and 2. The spectra shown in Figures 2, 6A, and 8A give an indication of the reproducibility of the infrared experiment.) The spectra shown in Figure 8B were run after addition of $P(t\text{-Bu})_3$. Clearly very little of the adsorbed carbonyls react with this phosphine. Thus the majority of the chemistry with $Co_2(CO)_8$ takes place within the faujasite.
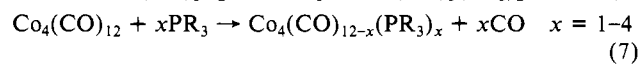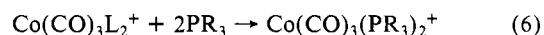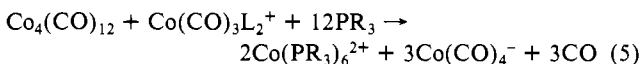
(35) Herron, N.; Stucky, G. D.; Tolman, C. A. *Inorg. Chim. Acta* **1985**, *100*, 135.

six-coordinate cobalt(II) complexes. It is possible that one or more of the phosphines should be replaced with zeolitic oxygens.

The disproportionation of $Co_4(CO)_{12}$ appears to take place for the cluster both inside and on the surface of the zeolite as judged by its reactions with phosphines. The disproportionation of adsorbed $Co_4(CO)_{12}$ with phosphines represents a departure from the expected chemistry of this cluster. It is apparent that the adsorbed species is somehow activated for disproportionation.

Location and Structure of $Co_4(CO)_{12}$(ads). In addition to the unique chemistry for adsorbed $Co_4(CO)_{12}$ the infrared spectrum for the adsorbed species on Na–Y zeolite is unusual. This has been noted by Watters et al.,[23] and their conclusion was that the cluster must reside within the supercage of the zeolite. Briefly the assignment is that the bridging carbonyl is shifted to lower wavenumber by interaction with a Lewis acid site on the zeolite. There is then a corresponding shift to higher wavenumber for the terminal carbonyls. This, in fact, is well established for carbonyl clusters adsorbed on alumina surfaces.[17] It was argued that this type of interaction for $Co_4(CO)_{12}$ could best be achieved in the supercage. We have shown here that the identical spectrum can be achieved for $Co_4(CO)_{12}$ adsorbed directly on the surface of NaY zeolite (vide supra). Thus the infrared spectrum alone is not sufficient to locate the cobalt carbonyl cluster.

The observation of identical spectra for $Co_4(CO)_{12}$ adsorbed on the surface and on the interior of Na–Y zeolite is unexpected. For $Rh_6(CO)_{16}$ adsorbed on the surface of a zeolite a different infrared spectrum is observed compared to that for $Rh_6(CO)_{16}$ that is postulated to occur within the zeolite.[4,33] In the case of $Co_4(CO)_{12}$ similar sites for adsorption must exist on the surface and in the interior of Na–Y zeolite. It was postulated that a site of 3-fold symmetry could be found in the supercage.[23] This allows the C_{3v} structure of $Co_4(CO)_{12}$ to retain its symmetry upon adsorption. Certainly sites of 3-fold symmetry will also exist on the surface of the zeolite particle. This is easily seen from models of the faujasite structure; the α-cage may be terminated in such

a fashion to give 6 β-cages in a chair conformation that has 3-fold symmetry.

It should be noted that Watters et al.[23] observe that when $Co_4(CO)_{12}$ is added to Na–Y zeolite by sublimation overnight, a spectrum consistent with crystalline $Co_4(CO)_{12}$ is obtained. The cluster in this case lies on the surface of the zeolite.

The argument above does not address the fact that the spectrum for $Co_4(CO)_{12}$ adsorbed on Na–Y is significantly simpler than that observed in solution. As indication of this is given in Table I. In solution, three intense adsorptions are seen for $Co_4(CO)_{12}$ at 2062 s, 2054 s and 1868 m cm^{-1}. The adsorbed species gives only one intense band at ~2080 cm^{-1} and a weak band at 2056 cm^{-1}. An intriguing possibility is that the adsorbed cluster adopts a structure different from the C_{3v} structure observed in solution. One possibility is the D_{2d} structure with four bridging carbonyls first suggested by Cotton.[34] Raman studies are underway in an attempt to further elucidate the structure for the adsorbed cluster.

Furthermore it is clear that Na–X and Na–Y zeolite stabilize different cobalt carbonyl species. On the Na–X zeolite the dimer, $Co_2(CO)_8$, is observed to give substantially more disproportionation to $Co(CO)_4^-$. Also the cluster $Co_4(CO)_{12}$ when adsorbed on the surface of Na–X gives a spectrum that is identical with the solution spectrum. Then there must be different sites for $Co_4(CO)_{12}$ adsoprtion on Na–X and Na–Y zeolite, or the structure for the adsorbed cluster is different on the two supports.

Chemistry and Stereochemistry of Reactions of Organophosphorus Ligands in Chiral Mo(CO)₅L Complexes[1]

Louis P. Reiff,* David I. Rossman,* Leonard J. Szafraniec,* and Herbert S. Aaron*

[Me(EtO)(HO)P]Mo(CO)₅ (3), a coordination complex with a chiral organophosphorus ligand, was synthesized and resolved. The OH group on the ligand of the (–) complex was esterified to give (+)-[Me(EtO)(*i*-Pr₂NCH₂CH₂O)P]Mo(CO)₅ (7), which was then converted into its *N*-methiodide derivative, (+)-**8**, with retention of configuration at the phosphorus atom in each step. Compound (+)-**8**, when treated with sodium methoxide in methanol, gave a nearly equal mixture of (–)-[Me(EtO)(MeO)P]-Mo(CO)₅ (9) and the original (–)-**3**. Since (+)-**9** was obtained directly with retention of configuration from the reaction of (–)-**3** and diazomethane, the formation of (–)-**9** by the reaction of methoxide ion with (+)-**8** must occur with inversion of the phosphorus configuration. This reaction is highly if not completely stereospecific, but some racemization of the (–)-**9** product does occur under the experimental conditions. The unexpected formation of the (–)-**3** byproduct is due to a competing elimination reaction, which apparently occurs via the formation of a nitrogen ylide intermediate under the basic reaction conditions.

While an extensive literature exists on metal coordination compounds that contain one or more phosphorus ligands,[2] the chemistry and especially the stereochemistry of reactions of these species from the standpoint of the complexed ligand has received rather limited attention.[3] Kraihanzel and his students recently

studied phosphorus ligand chemistry using species mainly of the general formula Mo(CO)₅L and Mo(CO)₄L₂.[4] Here,[5] the syn-

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(1) Presented in part at the 189th National Meeting of the American Chemical Society, Miami, FL, April 1985, and the 19th Middle-Atlantic Regional Meeting, West Long Branch, NJ, May 1985.

(2) (a) Verkade, J. G.; Coskran, K. J. *Organic Phosphorus Compounds*; Kosolopoff, G. M., Maier, L., Eds.; Wiley-Interscience: New York, 1972; Vol. 2, p 1. (b) Booth, G. *Ibid.*; Vol 1, p 443. (c) Stelza, O. *Top. Phosphorus Chem.* **1977**, *9*, 1.

(3) Optically active organometallic species in which the metal is the center of chirality are well-known, and the stereochemistry of their reactions has been reviewed, e.g.: (a) Basolo, F.; Pearson, R. G. *Mechanisms of Inorganic Reactions*; Wiley: New York, 1967; p 302. (b) Brunner, H. *Top. Curr. Chem.* **1975**, *56*, 67. (c) Brunner, H. *Adv. Organomet. Chem.* **1980**, *18*, 151. In addition, numerous catalytic studies of organometallic species containing a chiral organophosphorus ligand have also been reported, e.g.: (d) Capler, V.; Comisso, G.; Sunjic, V. *Synthesis* **1981**, 85. (e) Brunner, H. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 249. (f) Bogdanovic, B. *Ibid.* **1973**, *12*, 954. (g) Knowles, W. S. *Acc. Chem. Res.* **1983**, *16*, 106.