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Matrix Isolation Spectra of the Thermal and Photochemical Decomposition Products of Dicobalt Octacarbonyl[1]

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The infrared spectrum of the product of photochemical decomposition of $Co_2(CO)_8$ in argon matrices is reported. Evidence is presented that the major product is $Co_2(CO)_7$, and that this species has no bridging CO groups. Irradiation of matrix-isolated $Co_2(CO)_8$ in argon at 350 nm results in no appparance of $Co(CO)_4$ radicals. However, irradiation of $Co_2(CO)_8$ in CO matrices at 254 nm causes formation of $Co(CO)_4$ as well as $Co_2(CO)_7$. Passage of $Co_2(CO)_8$ over an active cobalt metal surface before matrix isolation causes complete decomposition, so that no matrix spectra are seen. On less active cobalt surfaces some decomposition occurs, and $Co(CO)_4$ is seen in the matrices. An absorption due to a second decomposition species, possibly $Co_2(CO)_6$, is also seen.

In the previous article we have presented evidence for the existence of three isomeric structural forms for dicobalt octacarbonyl in matrix isolation spectra.[2] In this paper we discuss the infrared spectra of cobalt carbonyl species produced as a result of thermal or photochemical decomposition of $Co_2(CO)_8$.

The most likely pathways for decomposition of $Co_2(CO)_8$ are homolysis of the Co–Co bond, to produce $Co(CO)_4$, or dissociative loss of CO, to produce $Co_2(CO)_7$. Presumably, metal–metal bond cleavage would occur from one of the nonbridged isomeric forms of $Co_2(CO)_8$. This mode of decomposition is rendered likely by estimates of a low metal–metal bond energy in $Co_2(CO)_8$.[3,4] The mass spectrum of $Co_2(CO)_8$[3] and ESR spectra of deposits of $Co_2(CO)_8$ in glasses at low temperature provide evidence for the presence of $Co(CO)_4$.

Dissociative loss of CO has been invoked to account for the kinetics of several reactions of $Co_2(CO)_8$, e.g., with acetylenes[6] and with H_2.[7] In fact, the equilibrium constant for the reaction

$$Co_2(CO)_8 \; \rightleftarrows \; Co_2(CO)_7 + CO \qquad (1)$$

has been estimated by Ungvary and Marko to be on the order of 10^{-5} atm at room temperature.[8]

Experimental Section

Most of the relevant experimental details appear in the previous paper.[2] The pyrolysis experiment reported here was conducted by modifying the apparatus shown in Figure 1 of ref 2. The 100 × 18 mm Pyrex tube leading into the vacuum shroud of the cryostat was wound with resistance wire secured in place with glass fiber tape. The heater was insulated with spun-glass insulation. A thermocouple was inserted beneath the insulation in the middle of the heated region to provide a crude estimate of temperature. The electronic spectrum of $Co_2(CO)_8$ was obtained using a Cary Model 14.

Results and Discussion

Photolysis of $Co_2(CO)_8$. When a matrix of $Co_2(CO)_8$ is photolyzed with ultraviolet light, bands due to $Co_2(CO)_8$

decline in intensity as new bands appear. When a photolyzed matrix is subsequently exposed to visible radiation, e.g., the Nernst glower source of the spectrometer, the changes caused by photolysis are reversed. In the previous paper[2] we employed the decline and reappearance of the bands of $Co_2(CO)_8$ to demonstrate the existence of three isomers.

Among the new bands produced by photolysis of $Co_2(CO)_8$, a band at 2139 cm^{-1} can be assigned to free CO. The infrared spectrum of a deposit of $Co_2(CO)_8$ in argon which has been subjected to extensive photolysis is shown in Figure 1. New bands occur at 2123.0, 2066.0, 2062.5, 2053.2, 1967, 1955, and 1947 cm^{-1}. In addition, a band which does not correlate in terms of its intensity variations with the seven bands also appears at 2046.0 cm^{-1}. The bands at 1967, 1955, and 1947 cm^{-1} are quite broad relative to the bands at higher energy. In neon matrices only two bands are observed in this lower frequency region; possibly the bands at 1955 and 1947 cm^{-1} in Ar are due to solid-state splittings of a single normal mode.

Assignment of the new bands to $Co_2(CO)_7$ is based on the following considerations.

(1) The new bands do not correspond to any of the mononuclear cobalt carbonyl species reported by Hanlan and co-workers;[9] thus the new bands must be due to dinuclear species. (CoCO is reported to have infrared bands at 1956.0 and 1949.0 cm^{-1}, frequencies close to two of those observed in our matrices. However, the presence of this species is highly unlikely in light of the fact that none of the other mononuclear cobalt carbonyls are observed either upon initial photolysis or subsequent visible light irradiation.)

(2) When the photolyzed matrix is exposed to the radiation of the Nernst glower, the extent of recovery of the $Co_2(CO)_8$ spectrum and the rate at which recovery occurs are directly related to the amount of CO in the matrix. In argon matrices the bands assigned to $Co_2(CO)_7$ decline by about 60% of their maximum intensity, after which the rate of decline becomes

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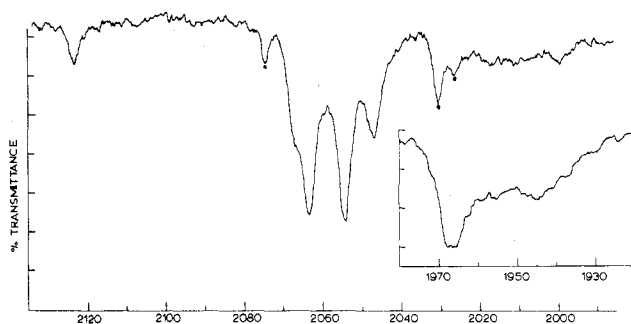
Figure 1. IR spectrum of $Co_2(CO)_8$ matrix in argon, extensively photolyzed. Bands marked are due to residual $Co_2(CO)_8$.

very slow. In argon matrices that have been doped with CO, bands assigned to $Co_2(CO)_7$ decline on glower irradiation more rapidly and more nearly completely. These results and the observation of free CO in photolyzed matrices of $Co_2(CO)_8$ suggest that the new bands are due to a species deficient in CO. It is noteworthy that in the course of recovery of the $Co_2(CO)_8$ spectrum upon visible radiation no set of bands appears which belongs to some intermediate species. This suggests that the species resulting from photolysis is deficient in only one CO and that recovery of the $Co_2(CO)_8$ proceeds in a single step.

(3) There is considerable precedent for photochemically induced recombination of CO with coordinately unsaturated metal carbonyl fragments produced in matrices upon photolysis.[10] This recombination has been ascribed to electronic excitation of the coordinatively unsaturated carbonyl, with resultant rearrangements within the matrix cage which reexpose the carbonyl fragment to the CO in the near environment and make possible a facile recombination. Unfortunately, our attempts to obtain the UV–visible spectrum of the photolysis product were not successful. It does not possess any outstanding spectral features that were clearly visible above the absorptions due to remaining $Co_2(CO)_8$.

The IR spectrum of $Co_2(CO)_7$ contains no absorptions characteristic of bridging carbonyl groups. The structure can thus be written as $(CO)_4Co–Co(CO)_3$. The CO stretching frequencies in the mononuclear cobalt carbonyls decline steadily with decreasing number of CO groups attached to cobalt.[9] Assuming that an analogous behavior applies to the CO groups attached to cobalt atoms of a dinuclear, nonbridged species, $(CO)_4Co–Co(CO)_3$, the barycenter of the absorption frequencies associated with the CO groups of the coordinatively saturated portion of the molecule should be higher than for the CO groups of the coordinatively unsaturated $–Co(CO)_3$ portion. However, there is undoubtedly some coupling between the two ends of the molecule, and a more detailed assignment to normal modes is not possible without additional isotopic substitution data. The structure of $Co_2(CO)_7$ is probably similar to that shown as **1**. It is reasonable to expect that the


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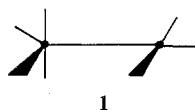
four-coordinate cobalt center, with 16 electrons in its valence orbitals, will adopt a planar environment. The choice of local geometry about the five-coordinate cobalt is uncertain; it is of interest, however, that isomer III is the predominant product of recombination of $Co_2(CO)_7$ with CO. For this reason, we have assigned the local structure at the five-coordinate cobalt to be the same as that which we have previously assigned for isomer III, structure **3**.[2]

Figure 2 shows the UV–visible spectra of $Co_2(CO)_8$ matrix-isolated in Ar at 12 K and in hexane at 77 K. As shown
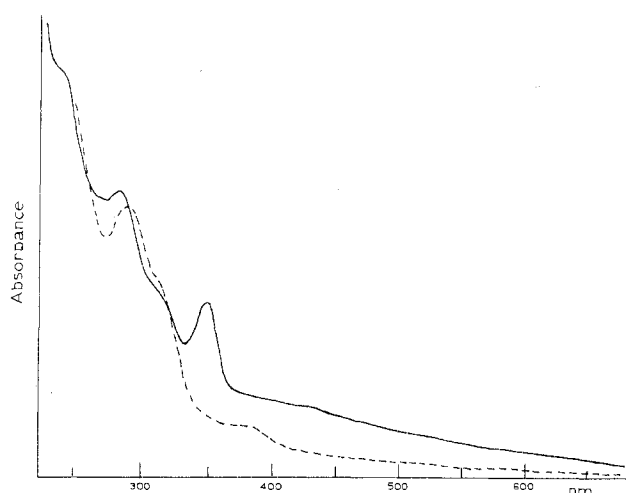
Figure 2. Electronic spectrum of $Co_2(CO)_8$ matrix-isolated in Ar at 12 K (solid line) and in hexane at 77 K (dotted line).

Scheme I
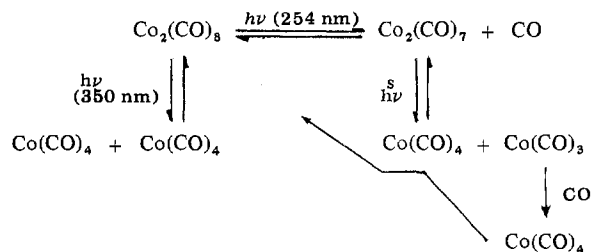
previously, the former sample contains considerable quantities of the two nonbridged forms, whereas the latter sample does not. On this basis it is clearly possible to associate the 290-nm absorption with the bridged form of $Co_2(CO)_8$, and the 347-nm absorption with the nonbridged form. The 347-nm band is similar in position and prominence to bands in the spectra of other dinuclear carbonyls, e.g., $Mn_2(CO)_{10}$[11,12a] or $Co_2(CO)_6L_2$.[12b] The band has been assigned to a $\sigma-\sigma^*$ transition associated with the metal–metal bond.[11] Irradiation of $Co_2(CO)_8$ at the wavelength corresponding to this transition should result in homolysis of the metal–metal bond, producing metal carbonyl radicals. However, in argon, photolysis of $Co_2(CO)_8$ at 350 nm for periods of 30 min produced no visible effects. These results suggest that recombination of $Co(CO)_4$ radicals in the argon matrix cage to re-form $Co_2(CO)_8$ occurs with relatively high efficiency. Similarly, while irradiation in various matrices using 254-nm radiation produces substantial quantities of $Co_2(CO)_7$, no $Co(CO)_4$ is seen. The sole exception was found to be irradiation of CO matrices with the low-pressure mercury lamp (254 nm), which did produce absorptions at 2029 and 2011.2 cm^{-1} in addition to those assigned to $Co_2(CO)_7$. These bands can be assigned to $Co(CO)_4$.[9,13] The peculiar appearance of $Co(CO)_4$ radicals only in CO matrices is not easily accounted for. It does, however, suggest that more than one pathway for photodecomposition may be involved.

In addition to photodissociation of CO, homolysis of the Co–Co bond may occur. The relative importances of these processes differ between isomers, and for a given isomer, they differ with wavelength of irradiation. Recent experimental work strongly suggests that some carbonyl radical species are susceptible to very facile loss of CO.[10,12a,14,15] Obversely, a coordinatively unsaturated species such as $Co(CO)_3$ would be expected to react with CO with a very low or zero free energy of activation. Scheme I accounts for our observations. The relative importances of CO dissociation and metal–metal bond cleavage are wavelength dependent. Irradiation at 350 nm
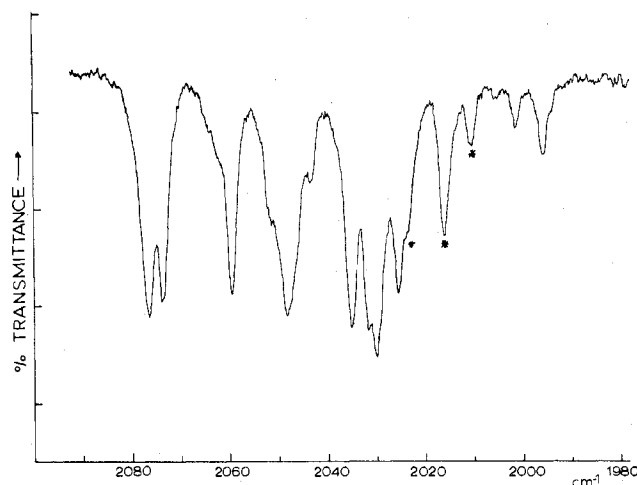
Figure 3. IR spectrum of Co₂(CO)₈ matrix-isolated in Ar following exposure to a partially active Co metal surface at 35 °C.

produces only $Co(CO)_4$ radical species which recombine with high efficiency. Shorter wavelength irradiation produces $Co_2(CO)_7$, which itself should be susceptible to metal–metal bond rupture. If the matrix cage consists only of inert atoms, $Co(CO)_4$ and $Co(CO)_3$ should recombine with high efficiency to re-form $Co_2(CO)_7$. On the other hand, when the CO concentration in the environment is high, it may happen that the $Co(CO)_3$ formed via photolysis of $Co_2(CO)_7$ captures a CO to form $Co(CO)_4$. The two $Co(CO)_4$ radicals should ordinarily combine to form $Co_2(CO)_8$, but there may be some displacement of matrix molecules or an orientational effect that prevents recombination in the CO matrices.

Deposits of $Co_2(CO)_8$ in argon exhibit weak features in the curve-resolved spectra that are ascribable to $Co_2(CO)_7$, even before photolysis. The most apparent features of $Co_2(CO)_7$ in matrices of $Co_2(CO)_8$ are shoulders on the high-energy side of the band at 2059 cm⁻¹ and, in thick matrices, the band at 2122 cm⁻¹. By using curve-fitting routines, bands can be located at 2063.7 and 2061.0 cm⁻¹. These frequencies do not precisely match the bands observed for $Co_2(CO)_7$ generated photolytically. Presumably the environment in the matrix is slightly different in the two cases. In a variation of the deposit procedure, the tube through which $Co_2(CO)_8$ passes prior to deposit was heated. The relative intensity of these peaks assigned to $Co_2(CO)_7$ increased as the temperature of the tube was raised. It appears that the origin of the heptacarbonyl is dissociation of CO from $Co_2(CO)_8$, possibly in the course of a reaction at the wall. We cannot assume from these results that dissociative loss of CO occurs in the gas phase.

Catalytic Decomposition of Co₂(CO)₈. We have already noted that the bands assigned to $Co_2(CO)_7$ increase in relative intensity in deposits of $Co_2(CO)_8$ formed by passage of $Co_2(CO)_8$ through a heated tube. A clean tube can be heated to about 65 °C without an especially large change in the resulting spectra. However, at about 65 °C, decomposition of $Co_2(CO)_8$ is extensive. The tube becomes coated with a metallic mirror and the resulting matrices show evidence of only CO. Following deposition of a metal mirror, the tube was cooled to below 65 °C. However, in the presence of a freshly deposited mirror, no $Co_2(CO)_8$ is observed in argon matrices, even when the tube wall is at 30 °C. The metal mirror evidently catalyzes decomposition of $Co_2(CO)_8$. Exposure to low pressures of CO or to air greatly attenuates the activity of the metal mirror toward decomposition of $Co_2(CO)_8$. Figure 3 shows a spectrum obtained by depositing $Co_2(CO)_8$ through a tube at a temperature of 35 °C, following formation of the metal mirror and subsequent exposure of the tube to small quantities of CO. Notable features in the

spectrum are the appearance of new bands at 2023.7, 2016.6, and 2011.2 cm⁻¹. In addition, free CO is noted in the matrix. On annealing the matrix at 24 K while exposing it to the radiation of the Nernst glower, the band at 2011 cm⁻¹ declines in intensity. The bands at 2024 and 2017 cm⁻¹ remain nearly unchanged. These bands are assigned to $Co(CO)_4$. Bands at 2024.0 and 2014.4 cm⁻¹ have previously been assigned[9] to $Co(CO)_4$. In that work, $Co(CO)_4$ was formed by deposition of Co in 10% CO in argon. Slight differences in reported frequencies apparently reflect the different manner in which $Co(CO)_4$ was produced and possibly also the amount of free CO in the matrix. In any case, we cannot be sure of the precise frequency of the higher frequency band at about 2024 cm⁻¹; it occurs as a shoulder on the much more intense features due to $Co_2(CO)_8$ and is difficult to resolve.

The band at 2011 cm⁻¹, which declines in intensity upon annealing, is not assignable to any mononuclear species of cobalt. The most likely candidate is $Co_2(CO)_6$, a likely intermediate in the thermal decomposition of $Co_2(CO)_8$ to form $Co_4(CO)_{12}$. Formation of a metal–metal triple bond following photolysis of a metal–metal bonded dimer species is known, e.g., for $(\eta^5-C_5H_5)_2Mo_2(CO)_4$.[16] We might speculate that $Co_2(CO)_6$, as a product of $Co_2(CO)_8$ photolysis, possesses a Co–Co triple bond. The molecule should possess D_{3d} point group symmetry and thus should exhibit only two infrared-active modes in the CO stretching frequency region.

The results relating to the decomposition of $Co_2(CO)_8$ on a cobalt surface, while fragmentary, are interesting for two reasons. In the first place, they suggest that it should be possible to employ matrix isolation spectroscopy to examine the products of interaction of gas-phase species with solid surfaces. Second, they provide some insights into the mode of interaction of $Co_2(CO)_8$ with the cobalt metal surface.[17] It is especially interesting that one of the products of such an interaction is $Co(CO)_4$, which suggests that adsorption of $Co_2(CO)_8$ on the metal surface may result in rupture of the metal–metal bond, with subsequent desorption of $Co(CO)_4$. Alternatively, a loss of CO from each cobalt atom of adsorbed $Co_2(CO)_8$, followed by desorption, would lead to $Co_2(CO)_6$. Such a decomposition is along the pathway leading to complete decomposition of $Co_2(CO)_8$ at the metal surface. Extensive additional experimentation will be required to more fully characterize the properties of the surface, the competitive influence of CO, and so forth.

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Carbon-13 Nuclear Magnetic Resonance Studies on Cobaloximes

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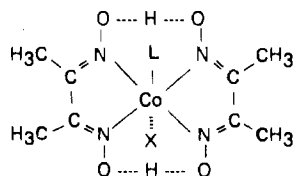
The ^{13}C NMR spectra of 51 cobaloxime complexes were measured and interpreted. Cobaloximes contain the moiety bis(dimethylglyoximato)cobalt(III), $Co(DH)_2$, and, in this study, one of the two remaining coordination positions contained a neutral ligand L (either 4-*tert*-butylpyridine (Bupy), series I; trimethyl phosphite, series II; or tri-*n*-butylphosphine (Bu$_3$P), series III) and the remaining position contained a negative ligand X. For all three ligands L, X = NO$_3$, Br, Cl, N$_3$, NO$_2$, CN, SO$_2$C$_6$H$_4$CH$_3$, P(O)(OCH$_3$)$_2$, CH$_2$Br, C$_6$H$_5$, and CH$_3$. For some of the L ligands, X = SCN, NCS, I, NCO, S$_2$CO-*i*-C$_3$H$_7$, S-*t*-C$_4$H$_9$, CHBr$_2$, C$_6$H$_4$Br, CH$_2$Si(CH$_3$)$_3$, CH$_2$C$_6$H$_4$CN, P(O)(C$_6$H$_5$)$_2$, C$_2$H$_5$, and CH$_2$C$_6$H$_5$. Two hundred and thirty-one linear least-squares comparisons were made to determine the relationship between all the ^{13}C shifts and ^{31}P–^{13}C coupling constants. Both cis and trans ^{13}C NMR shifts were influenced similarly by X in all three series with the exception of the ^{13}C NMR shifts of the α C of Bupy in series I and C(1) of Bu$_3$P in series III. However, these shifts correlated well with each other. With the exception of these α-C and C(1) shifts and the C(2) and C(3) shifts of Bu$_3$P, the dependence on X of the ^{13}C NMR of axial ligands L is almost exactly opposite in order to the ^1H NMR shifts of coordinated Bupy. The ^{13}C NMR and ^1H NMR shifts of the equatorial ligand follow essentially the same dependence on X and this dependence is similar to that for the ^{13}C NMR shifts of the axial ligands. This pattern of shifts can be understood if the ^{13}C NMR shifts are influenced primarily by through-bond effects of X and the ^1H NMR shifts are influenced primarily by through-space effects of the near neighbor cobalt. This through-space effect in turn is influenced by the changes in cobalt magnetic anisotropy induced by the variation of X. The ordering of X generally observed is as follows: oxygen donors < halides or pseudohalides ~ CN ~ sulfur donors ~ phosphorus donors < alkyl or aryl groups. The position of CN in this series is variable and a comparison is made with similar variability observed in studies of organomercurials.

One of the major problems encountered in the understanding of the influence of the metal center on the chemical shifts of carbon atoms in attached ligands (as an aid in structural elucidation,[1] in the evaluation of electronic effects,[2,4] and in the identification of metal binding sites in labile systems[3]) is the assessment of the anisotropic effects of the metal or of other ligands.[2,5]

We have measured the ^{13}C NMR spectra of over 50 different complexes containing the bis(dimethylglyoximato)-cobalt(III) (cobaloxime) moiety. The large number of possible axial groups[4] makes cobaloximes particularly suitable for a detailed study of the influence on ^{13}C spectra of changing the metal coordination environment. These groups range from nitrate to methide and include neutral N donors, phosphines, and phosphites. Three series of cobaloximes, LCo(DH)$_2$X, were chosen for study: (I) L = 4-*tert*-butylpyridine (Bupy),


```
        O ---- H ---- O
        |             |
H3C     N      L      N      CH3
   \  //  \    |    /  \\  /
    C       \  |  /      C
    |        \ | /       |
    |         Co         |
H3C     /   / | \   \     CH3
   \  C    /  |  \    C  /
    \\N       X      N//
      |               |
      O ---- H ---- O
```

I. L = 4-t-Bupy
II. L = (CH3O)3P
III. L = (n-Bu)3P

(II) L = trimethyl phosphite, and (III) L = tri-*n*-butyl-phosphine (Bu$_3$)P [where X is a mononegative ligand and DH = dimethylglyoximato monoanion].

It has been possible to interpret[6] the ^1H NMR shielding trends in these cobaloximes by assuming that, when ligand anisotropic effects are small or absent, the ^1H NMR shifts are dominated by the dipolar field about the cobalt center caused by currents induced in the d orbitals by the applied magnetic field. In such a case, knowing the geometry of the complexes, it is possible to estimate the anisotropic near-neighbor effect of the metal on the shifts ($\Delta\sigma$) of the ligand atoms[4,6,7,8] with McConnell's equation, (1), for an axially symmetric anisotropic

$$\Delta\sigma = \Delta\chi \frac{(1 - 3\cos^2\theta)}{3R^3} \tag{1}$$

dipole.[9] The effect will drop off rapidly with distance, R, of the resonating nucleus from the metal and will depend on θ, the angle between R and the symmetry axis of the dipole. Deviations from this estimate would then arise either from ligand anisotropies or from variations in local (mainly paramagnetic) shielding terms. The relatively large neutral ligands used in this study have carbon atoms which will be sufficiently distant from the metal to exclude any major anisotropic influence from the heavy atom. It should then be possible to determine whether systematic X-ligand-induced electronic changes in the metal center can cause changes in the shifts of ^{13}C resonances in the neutral L and anionic (DH) ligands.

Cobaloximes containing phosphorus donor ligands allow the assessment of P–C coupling constants. Variations in coupling constants can be interpreted as possibly arising from rehybridization of one or both of the coupled nuclei.[10]

Experimental Section

All of the complexes studied here either had been previously isolated and characterized for other studies or were prepared from known, isolated compounds by simple ligand-exchange reactions.[11,12] Spectra were measured in CDCl$_3$ with respect to internal TMS (4%) at a probe temperature of 23 °C. Complex concentrations were 0.1 M or less depending on solubility. Chemical shifts and coupling constants appeared to be concentration independent in this range, although no