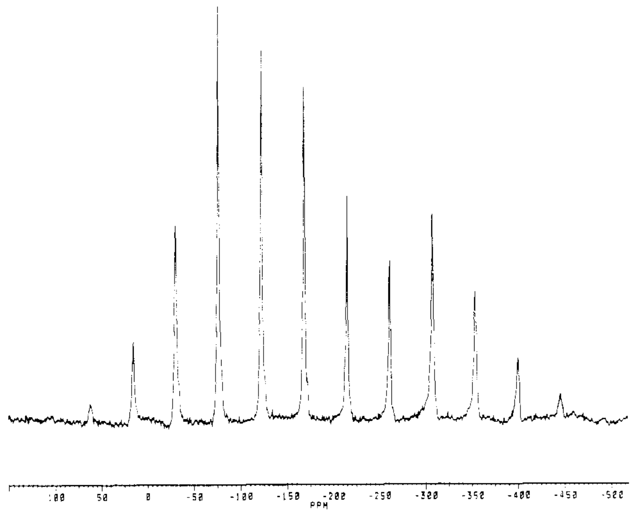

Figure 3. CP/MAS solid-state ^{31}P NMR spectrum of complex **1**.

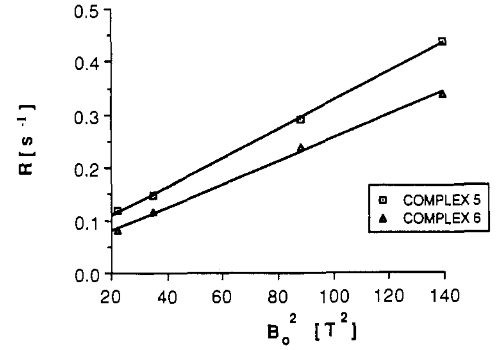

Figure 4. Influence of the external magnetic field, B_0, on the relaxation rate of triphenylphosphine for complexes **5** and **6**.

that coordinated arylphosphines have much larger shielding anisotropies than the free ligands. Thus, for $RhCl(PPh_3)_3$, which has been the subject of a single-crystal solid-state study,[17] the shielding anisotropies of the three phosphorus nuclei are 124, 125, and 222 ppm.[13] A direct result of large CSA values is shorter relaxation times in solution due to the increased efficiency of the CSA mechanism. Our data together with earlier relaxation measurements showing much shorter T_1 values for arylphosphine complexes than for the free ligands[4a] lead us to suggest that ^{31}P chemical shift anisotropy increases upon coordination.

An additional factor governing coordinated phosphine relaxation is the expected increase in τ_c upon complexation due to the reduced mobility and higher molecular weight. Since both the dipolar and the CSA mechanisms are inversely proportional to τ_c (in the extreme narrowing condition), an increase in τ_c will also decrease the observed T_1. The result of these two factors is that the relaxation times for coordinated tertiary phosphines will vary considerably from those of the free phosphines. These differences can be critical in quantitative studies of intermolecular ligand dissociation or phosphine substitution reactions.

It is clear that substantial differences in relaxation behavior exist between coordinated and uncoordinated phosphorus ligands and that the CSA mechanism can play an important role in the relaxation of phosphorus nuclei in transition-metal complexes.

Experimental Section

The ^{31}P NMR spectra were recorded on Bruker AM-500, WH-400, AM-250, AC-200, and WP-80 spectrometers equipped with a standard multinuclear probe head of 10-mm diameter. Temperatures were measured by using the proton shift of methanol or ethylene glycol and were maintained by using the Bruker VT-1000 temperature control unit. The relaxation measurements were performed by using a nonselective inversion-recovery pulse sequence, $(180–\tau–90–T_w)_n$. All solutions were degassed (freeze–thaw cycle) and were measured under dry dinitrogen. Typically 10–15 τ values were employed with a waiting time greater than $5T_1$. The data were analyzed by using a nonlinear least-squares fit to the equation $M(T) = A - Be^{-\tau/T_1}$, and estimated errors are less than 5%. NOE factors were measured by using the gated decoupling technique with a delay of 60 s. To avoid instrumental variations, these measurements were repeated five times and an average value is reported in the tables. Typical concentrations used were 0.1 M solutions. The solution ^{31}P NMR shifts of complexes **1–5** are listed in Table IV. Complexes **1–5** were prepared by literature methods[18-20] and have been characterized by elemental analysis and proton, carbon, and phosphorus NMR spectroscopies. Complex **6** was obtained from Strem Chemicals.

Table IV. ^{31}P Solution Chemical Shifts for Complexes **1–5**

complex	chem shift,[a] ppm	complex	chem shift,[a] ppm
1	−171.5	**4**	148.4
2	125.2	**5** μ-PPh_2	124.7
3	334.3	PPh_3	39.7

[a] Relative to H_3PO_4.

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Registry No. **1**, 118920-01-7; **2**, 82647-83-4; **3**, 77716-69-9; **4**, 59584-68-8; **5**, 118949-35-2; **6**, 15318-31-7.

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High-Field Magic-Angle-Spinning ^{13}C NMR Spectroscopy of $Co_4(CO)_{12}$

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and Brian E. Hanson*[‡]

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The elucidation of the solution and solid-state structures of $Co_4(CO)_{12}$ has attracted the interest of metal carbonyl chemists for over 30 years.[1-12] A representation of the solid-state structure as determined by Wei and Dahl is shown in Figure 1.[10,11] The determination of this structure was complicated by a disorder of the molecule which lies on a special position requiring a 2-fold rotation axis. Redetermination of the structure confirmed the disorder model proposed by Wei and Dahl but was unable to define the separate positions for the overlapping carbonyl ligands.[12] Both orientations of the molecule are represented in Figure 1. The solution structure and has recently been shown to be same as the solid-state structure by high-field ^{13}C NMR[9] and ^{17}O NMR.[5]

Recently one of us reported the low-field (2.1 T, 22.6 MHz) variable-temperature MAS ^{13}C NMR spectra for solid Co_4(C-

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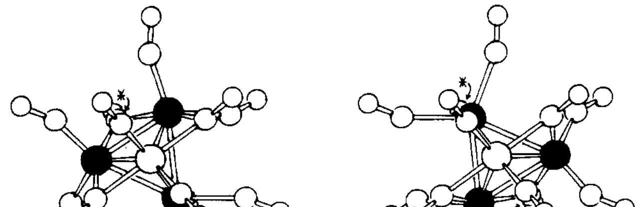

Figure 1. Representation of the solid-state structure of $Co_4(CO)_{12}$ as viewed down the crystallographic 2-fold rotation axis. The two orientations of the Co_4 core, which together satisfy the 2-fold rotational symmetry required by the symmetry of the symmetry of the crystal, are labeled A and B.

$O)_{12}$.[13] It was argued that the observation of one signal at 62 °C is consistent with a dynamic process in the solid state that makes all 12 carbonyls equivalent on the NMR time scale. However, the low-temperature spectrum obtained at 22.6 MHz was not observed to be consistent with the reported isotropic chemical shifts for $Co_4(CO)_{12}$ in solution.[13] In particular, no distinct bridging carbonyl resonances were observed, and resonances significantly upfield from the normal terminal region for cobalt carbonyls were observed.[13]

It has been shown that the lineshape expected for the NMR spectrum of spin-$^1/_2$ nuclei bonded to a quadrupolar nucleus depends on the relative magnitudes of the Zeeman resonance frequency and the quadrupolar resonance frequency for the quadrupolar nucleus.[14,15] Under MAS conditions the effect has been demonstrated for the spin systems $^1/_2 - 1$, $^1/_2 - {}^3/_2$, and $^1/_2 - {}^5/_2$.[15] The combination of a low Zeeman energy and a large quadrupolar coupling constant can lead to very complicated spectra for the spin-$^1/_2$ nucleus.[15] This is the most likely cause for the anamalous chemical shifts reported at 22.6 MHz. The line shapes are simplified as the Zeeman energy is increased relative to the quadrupolar resonance frequency. Experimentally the Zeeman resonance frequency is increased by going to higher field. Since the quadrupolar coupling is not field dependent, the MAS ^{13}C spectra of carbonyl ligands bonded to ^{59}Co ($I = {}^7/_2$) are expected to be simplified at high field.

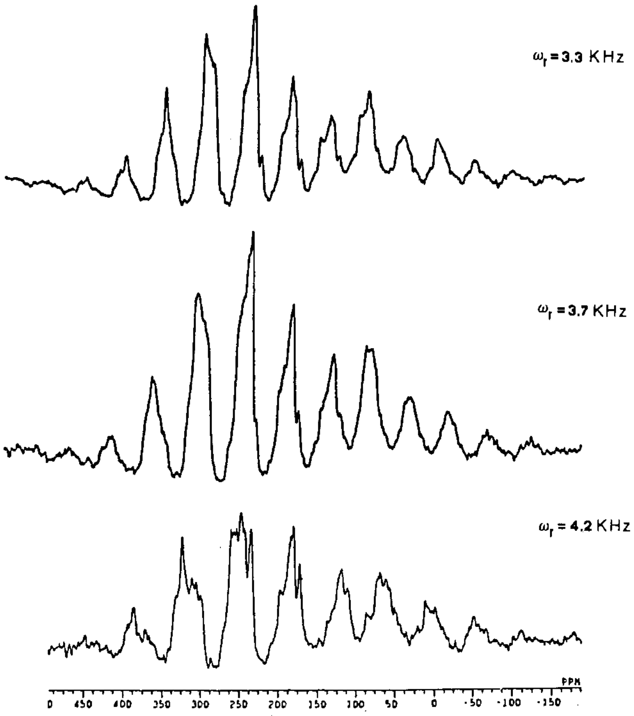

Figure 2. Variable-spinning-rate ^{13}C MAS NMR spectra of $Co_4(CO)_{12}$ at 68 MHz.

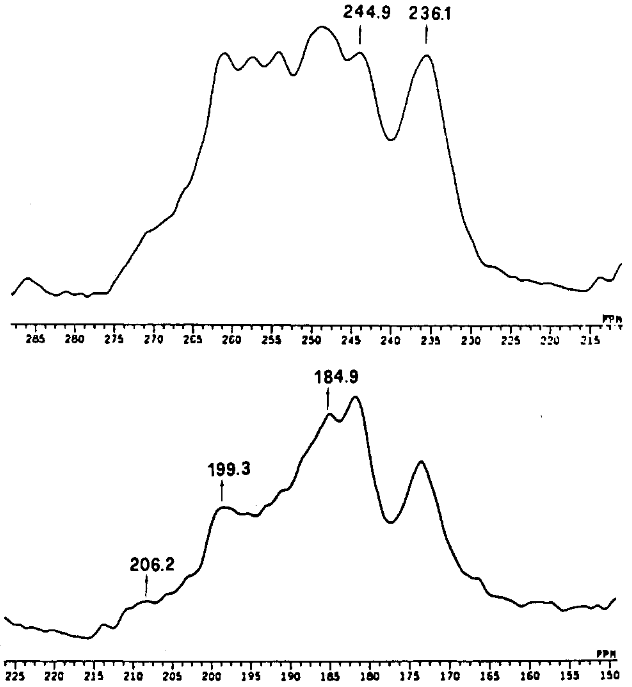

Figure 3. Expansion of the centerband in the bridging carbonyl region (top) and the terminal region (bottom) at a spinning rate of 4.2 kHz. The chemical shifts for the resonances that do not move with changing spinning rate are labeled.

The high-field (68-MHz) ^{13}C MAS NMR spectra for solid $Co_4(CO)_{12}$ are shown in Figure 2 at three different spinning rates. The different spinning rates are required to allow the separation of sidebands from centerbands in the spectrum. The sidebands arise from the fact that the spectra were obtained in the slow-spinning regime for a compound containing carbon environments with a large chemical shift anisotropy. The spectrum recorded at a spinning rate of 4.2 MHz is expanded on the center bands in Figure 3 to show more clearly the bands assignable to bridging carbonyls. Although the resonances are quite broad, there is sufficient resolution to observe at least three peaks in the terminal region and certainly one peak and perhaps two peaks in the bridging region. One of the bridging carbonyl peaks, 236.1 ppm, is clearly resolved from the spinning sidebands while the assignment of the 244.9 ppm peaks to a bridging carbonyl is more tenuous due to overlap with the spinning sidebands of the terminal signals. It is well-known that bridging carbonyls typically have

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a smaller chemical shift anisotropy than terminal carbonyls[16] and thus can aid in the assignment of peaks. The overlap of spinning sidebands at 4.2-kHz spinning rate is such that sidebands due to the bridging carbonyls occur at higher field than those due to terminal carbonyls within a cluster of bands. In the sideband progressions at low field (to the left) in the spectrum at 4.2 kHz, the peaks assigned to bridging carbonyls diminish faster than those for the terminal carbonyls as expected. A more detailed analysis of the sideband unfortunately is not possible due to the broadness of the peaks.

An estimate of the average value for the carbon T_1's in solid $Co_4(CO)_{12}$ by the inversion recovery method gives a value of approximately 500 ms. This is much shorter than typically observed for metal carbonyls[17,18] and is consistent with scalar relaxation of the second kind, through coupling with rapidly relaxing ^{59}Co nuclei, as the dominant relaxation mechanism in the solid state.[4]

The prediction of the expected MAS ^{13}C NMR spectrum for solid $Co_4(CO)_{12}$ for both dynamic and static structures is straightforward:

Case I. The observation of a single line in the MAS ^{13}C NMR spectrum may only be observed when the 12 carbonyls in solid $Co_4(CO)_{12}$ are equivalent on the NMR time scale due to a dynamic process. Such a process can be envisioned by an interconversion of the C_{3v} structure in the solid state and a higher energy T structure. A structure of T symmetry has recently been predicted by Lauher for $M_4(CO)_{12}$ molecules.[19] Since both of these structures are based on an icosahedral arrangement of carbonyl ligands, they may be interconverted by a rotation of the Co_4 core within the icosahedral array of carbonyl ligands. The magnitude of the rotation necessary to interconvert the structures is reported to be 12°.[19]

Case II. A more limited dynamic process may involve the rapid interconversion of the two orientations of the Co_4 core that are present in the crystalline solid. If rotation about the crystallographic 2-fold axis is rapid on the NMR time scale, then a six-line NMR spectrum is expected: four terminal carbonyl signals, one bridging carbonyl signal, and one signal that represents the time average of a bridging and terminal carbonyl. This type of reorientation has been proposed to occur in crystalline $Fe_3(CO)_{12}$.[20,21]

Case III. A static structure would be expected to yield an NMR spectrum containing 12 carbonyl resonances: 9 in the terminal carbonyl region and 3 in the bridging region. Fewer than 12 signals could be obtained through accidental degeneracies. Although 12 distinct terminal carbonyl resonances have been recently observed in solid $Os_3(CO)_{12}$,[22] such resolution cannot be anticipated for cobalt carbonyls due to the influence of the quadrupolar ^{59}Co nuclei.

The experimental spectra for solid $Co_4(CO)_{12}$ at room temperature and 68 MHz cannot conclusively distinguish between cases II and III. For case II to hold, the peak at 244.9 ppm must be due to a true bridging carbonyl and the peak at 236.1 ppm must represent the time average of a bridging and a terminal carbonyl. Although the latter is shifted upfield from the isotropic chemical shift of the bridging carbonyls for $Co_4(CO)_{12}$ (243.1 ppm[4]), this may be due to solid-state effects. For example, the range of chemical shifts for the axial carbonyls in solid osmium carbonyls is 8 ppm.[22]

For case III to hold, there must be degeneracies for both terminal and bridging carbonyl resonances. Without the observation of more than four signals assignable to terminal carbonyls, a definitive argument for a static structure at room temperature cannot be made. (It should be noted that the presence of additional lines due to residual coupling with cobalt, although minimized at high field, is still a possibility; vide supra.)

In conclusion, the use of high-field MAS ^{13}C NMR has allowed the observation of signal(s) due to bridging carbonyls as required by either a dynamic (case II) or static (case III) $Co_4(CO)_{12}$ structure. The failure to observe bridging carbonyl resonances at low field is most likely due to residual coupling to the quadrupolar cobalt nucleus and/or rapid and selective scalar relaxation of the carbonyl ligands by the cobalt.

Experimental Section

The MAS ^{13}C NMR spectra were recorded at 68 MHz on a Varian 270-MHz spectrometer. The rotors were made of Delrin; no decoupling was used since the samples contain no protons. Tetracobalt dodecacarbonyl was prepared from $Co_2(CO)_8$ by refluxing in *n*-octane for 2 h. The sample was enriched in ^{13}CO by stirring under ^{13}CO in hexane at room temperature and recrystallized prior to use.

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Failure To Observe Peroxide in $YBa_2Cu_3O_7$, $La_{1.8}Sr_{0.2}CuO_4$, La_2CuO_4, and La_2NiO_4 by Reaction with Permanganate

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The high-temperature superconductors $YBa_2Cu_3O_7$[1] and $La_{1.8}Sr_{0.2}CuO_4$ behave as oxidizing agents toward I^-, Br^-, Fe^{2+} when dissolved in acidic solution.[2-4] In the absence of a good reducing agent, O_2 (whose atoms are derived from the solid, not the solvent[5]) is evolved.[1,6] Iodometric titrations used to measure the oxygen content of $YBa_2Cu_3O_{7-x}$, can be interpreted in terms of the formula $YBa_2Cu^{II}{}_{2+2x}Cu^{III}{}_{1-2x}O_{7-x}$ $(0 \leq x \leq 0.5)$ (assuming that no O_2 is evolved in the procedure).[1,2] The average copper oxidation state inferred from such titrations is in good agreement[1] with that deduced from the mass lost in the reaction of yttrium barium copper oxide with H_2 at elevated temperature, in which the products are Y_2O_3, BaO, Cu, and H_2O.

It is possible that all copper in $YBa_2Cu_3O_{7-x}$ is Cu^{2+} and that some oxygen is present as peroxide. This gives the formula $YBa_2Cu^{II}{}_3(O^{2-})_{6+x}(O_2{}^{2-})_{0.5-x}$ $(0 \leq x \leq 0.5)$, which is indistinguishable from $YBa_2Cu^{II}{}_{2+2x}Cu^{III}{}_{1-2x}O_{7-x}$ by iodometric titration or by reaction with H_2. On the basis of copper 2p X-ray photoelectron and X-ray absorption spectra, some studies concluded

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[1] The formulas $YBa_2Cu_3O_7$, $La_{1.8}Sr_{0.2}CuO_4$, La_2CuO_4, and La_2NiO_4 are used for convenience in this paper. The oxygen content is actually variable, but close to that of the ideal formula.

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