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A Combined Electron Paramagnetic Resonance and Fourier Transform Infrared Study of the $Co(C_6H_6)_{1,2}$ Complexes Isolated in Neat Benzene or in Cryogenic Matrixes

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The products obtained in the reaction of cobalt atoms in neat benzene or in a benzene/argon mixture at low temperature have been reinvestigated. At least three cobalt-containing species were detected by IR, namely, $Co(C_6H_6)$, $Co(C_6H_6)_2$, and $Co_x(C_6H_6)$, $x > 1$. The IR bands were assigned to these complexes by monitoring their behavior as a function of (a) Co and C_6H_6 concentration, (b) isotopic substitution, and (c) photoirradiation. We were able to analyze the sample in neat benzene by both electron paramagnetic resonance (EPR) and IR spectroscopy and to determine the magnetic parameters (g tensor and Co hyperfine interaction) for the $Co(C_6H_6)_2$ sandwich compound. The large number of fundamental bands observed in the IR spectrum of $Co(C_6H_6)_2$, the absorption pattern observed in the Co-ring stretching region of the IR spectrum of the mixed complex, $Co(C_6H_6)(C_6D_6)$ and the orthorhombic g-values extracted from the EPR spectrum are most consistent with nonequivalent benzene ligands in $Co(C_6H_6)_2$, i.e., C_s symmetry. A bonding scheme consistent with both the EPR and IR data for $Co(C_6H_6)_2$ is discussed.

Introduction

Bisarene late first-row transition metal complexes share with their better-known metallocene analogues the ability to assume various oxidation states as a result of electron delocalization effects and of steric shielding of the metal center by the sandwich structure. This makes the study of metal−bisarene complexes not obeying the 18-electron rule all the more interesting, despite a likely lower stability.[1]

Unlike the case of Ti and V where the $Ti(C_6H_6)_2$ and $V(C_6H_6)_2$ 16- and 17-electron complexes are relatively well documented, only the methyl-substituted arene-Fe, Co, and Ni analogues have been prepared.[2] For instance, the relative stability of the $Co(C_6Me_6)_2{}^{2+}$, $Co(C_6Me_6)_2{}^{+}$, and $Co(C_6Me_6)_2$ series has been investigated.[3] By consideration that maximum stability is displayed by complexes with 18 electrons, $Co(C_6Me_6)_2$, with 21 electrons, is the least stable of the Co-arene sandwich complexes. As a result, $Co(C_6Me_6)_2$ is a precursor of the more stable oxidized forms and easily undergoes ligand displacement to yield a number of arene−diolefin or arene−alkyne mixed complexes.[4] Besides having shown that $Co(C_6Me_6)_2$ is a paramagnetic species ($\mu = 1.86\ \mu_B$), likely having a doublet ground state, not much is known about its structure or the hapticity of the arene ligand.

The relative instability of the cobalt−arene complexes might make their synthesis problematic in solution, but Kurikawa and co-workers showed, using direct gas-phase synthesis and mass spectrometry, that a whole range of $Co_n(C_6H_6)_m$ species can be formed by reacting laser-ablated Co atoms with benzene in the gas phase.[5] The $m = n + 1$ magic-number behavior and ionization energies determined for the clusters were explained by assuming sandwich and multiple-decker structures. In a negative ion photoelectron spectroscopic study, Gerhards et al.[6] determined the electron affinity of $Co(C_6H_6)_2$ and based their interpretation of the photodetachment spectrum on the assumption of a symmetrical sandwich structure. Such a model is also assumed in various ab initio calculations,[7,8] but the more recent electric deflection study of Rayane et al. has shown unambiguously that the $Co(C_6H_6)_2$ complex has a permanent electrical dipole and therefore does *not* have a symmetrical sandwich structure.[9] The exact nature of the distortion is, however, not known.

The $Co(C_6H_6)_2$ species produced by the co-condensation of atomic metal vapor with the arene ligand[10] has been the subject of two spectroscopic studies.[11,12] In the first study, Efner and co-workers deposited a number of different metal atoms (among which were Cr and Co) with benzene or in benzene/argon matrixes at low temperature.[11] In the case of Cr, the product was easily identified as the well-known $Cr(C_6H_6)_2$ sandwich complex from its IR absorption spectrum.[13,14] However, for the reaction of Co atoms with benzene, they observed a product which presented an IR spectrum different enough from that of $Cr(C_6H_6)_2$ to be thought to originate from a qualitatively different chemical entity. The lack of resolvable IR features in $Co + C_6H_6/C_6D_6$ isotopic mixtures, distinct from those observed with either of the two isotopic precursors taken separately, lead the authors to conclude that the half-sandwich, CoC_6H_6 species, rather than the dibenzene complex formed under these conditions. In a second study, Shobert et al.[12] reinvestigated the Co atom reactions in neat benzene and toluene matrixes. By evaporating the excess unreacted arene at higher temperature, additional IR absorptions as well as shifts in the positions of the previously reported bands were observed. These findings were attributed to the presence of two species of different stoichiometry, i.e., CoC_6H_6 and $Co(C_6H_6)_2$. Unfortunately, the absence of isotopic data rendered the proposed vibrational

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assignments tentative. The coexistence of both the 1:1 and 1:2 Co:benzene complexes in neat benzene is an intriguing proposition as it would thus imply the existence of a notable reaction barrier.

The goal of the present study is 2-fold, first to assess the nature of the coordination of a cobalt atom to the simplest arene, benzene, and second to determine spectroscopic properties which can be of use (a) in ascertaining the geometrical or electronic structure of Co−arene complexes or (b) as a benchmark in quantum chemical calculations.[7,8,15,16] As is the case for Co-$(C_6Me_6)_2$, a dibenzene sandwich complex, if formed, ought to be paramagnetic and electron paramagnetic resonance (EPR) spectroscopy can be used to characterize the overall molecular symmetry of the singly occupied molecular orbital (SOMO) via analysis of hyperfine and superhyperfine interactions (Co, $I = {}^{7}/_{2}$, H or ^{13}C, $I = {}^{1}/_{2}$).[4] On the other hand, with modern IR interferometric techniques that have superior photometric accuracy and resolving power, a thorough re-evaluation of the vibrational spectrum of the cobalt complex appears possible, even in the presence of strong background absorptions due to the unreacted arene. To complete this study, we also present an IR rare gas matrix isolation study of the Co + C_6H_6 reaction. The very weak interactions of the matrix medium (solid argon) with the encaged species causes the IR absorptions to be much sharper,[14] and both the increased resolution and optical transparency are useful for the vibrational study of large organometallic molecules. The technique also enables the investigation of intermediate steps of coordination, by kinetic stabilization of the less stable coordinatively unsaturated species.

Experimental Section

The reactions of Co atoms with benzene were investigated in Sudbury by co-condensing cobalt vapor in neat benzene onto the cold surface of a 77-K rotating cryostat, described elsewhere.[17] IR spectra were collected in situ in the transmission−reflection mode using a Mattson Sirius 100 FTIR spectrometer equipped with a narrow-band HgCdTe detector in the 4000−750-cm^{-1} region. EPR spectra of the reaction products were recorded in the 77−300-K range on a Varian E-109 spectrometer operating at X-band after collection and storage in sealed quartz tubes using cryogenic procedures already described. The spectra were calibrated with the aid of a Systron Donner frequency counter and a Varian magnetometer. Powder spectra were simulated using computer programs provided by Dr. L. Belford.[18]

Experiments carried out in Paris used standard rare gas matrix-isolation procedures in which both the cobalt and dilute benzene−Ar mixtures (0.5 to 4.5 % benzene in Ar) were co-condensed onto a flat, highly polished, Ni-plated copper mirror maintained at ca. 10 K using a closed-cycle cryogenerator. IR spectra of the resulting sample were recorded in the transmission-reflection mode between 5000 and 70 cm^{-1} using a Bruker 120 FTIR spectrometer and suitable combinations of CaF_2/Si, KBr/Ge, or 6-μm Mylar beam splitters with either liquid N_2-cooled InSb or narrow-band HgCdTe photodiodes or a liquid He-cooled Si−B bolometer, fitted with cooled band-pass filters.

For both IR spectrometers, the resolution was maintained at 0.5 cm^{-1} and bare mirror backgrounds, recorded prior to sample deposition, were used as references in processing the sample spectra. The spectra were subsequently subjected to baseline correction to compensate for IR light scattering.

UV−visible absorption spectra were recorded in situ between 260 and 750 nm at 0.5-nm resolution using optical fibers, a combined D_2−W lamp (DH 2000-Sensor system) and an ORIEL MS125 monochromator fitted with a 1024-element diode array. Narrow band photolysis was performed using a high-pressure HgXe lamp and 20-nm bandwidth interference filters centered at Hg atomic line position.

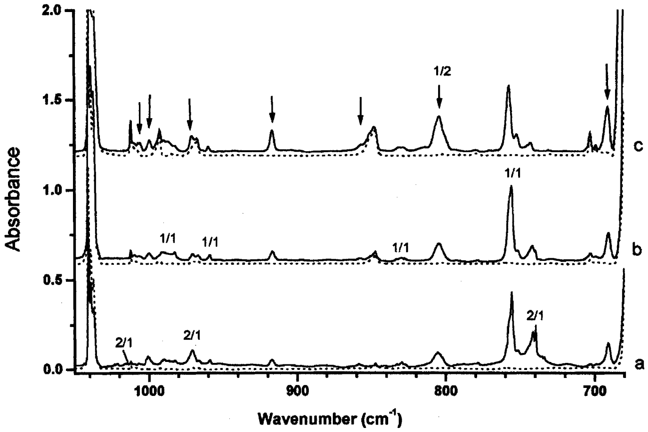


Figure 1. IR spectra of C_6H_6/Ar deposits with Cobalt atoms (solid line) or without (dotted line) recorded between 1550 and 670 cm^{-1}: (a) Co/C_6H_6/Ar = 0.8/0.5/100; (b) Co/C_6H_6/Ar = 0.4/1.5/100, absorbance scale × 0.66; (c) Co/C_6H_6/Ar = 0.3/4/100, absorbance scale × 0.33. The deposits contain CoC_6H_6 (1/1), $Co_2C_6H_6$ (2/1), and $Co(C_6H_6)_2$ (1/2). The absorptions of the 1/2 complex are designated by bold arrows.

In both experimental setups, a tungsten filament, mounted in a furnace assembly and wetted with cobalt (Alpha Inorganics, 99.9965%), was heated from 1200 to 1400 °C to generate the Co vapor. The metal deposition rates were carefully monitored with the aid of quartz microbalances and were typically of the order of about 0.2−1.2 μg/min. Spectrum-grade benzene (Caledon or Fluka, dried over potassium), high purity argon (Prodair; 99.995%), C_6D_6 (Eurisotope-CEA, Saclay, France, 99.95% D or Merck, 99.6% D), and $^{13}C_6H_6$ (Eurisotope-CEA, Saclay, France or Cambridge Isotope Laboratories, 99% ^{13}C) were used without further purification to prepare the samples after thorough freeze-and-thaw outgassing under vacuum.

Results

IR Data.

Co/Benzene/Argon. In rare gas matrixes, three species with different Co−benzene stoichiometries were detected. These were differentiated by their relative dependencies on either the cobalt or benzene concentration. The IR spectra for three experiments differing in the [Co]/[C_6H_6] ratio are presented in Figure 1. To enhance the relative variations in the spectra as a function of [Co]/[C_6H_6] ratio, the absorptions due to benzene were normalized. This concentration study clearly shows the existence of three different products, labeled 2/1, 1/1, and 1/2 in Figure 1. The stoichiometry of each product is based on the results of several experiments in which the concentration of Co and benzene were changed systematically. Product 2/1 is prominent when the [Co]/[C_6H_6] ratio is greater than one and gradually disappears as the benzene concentration is increased indicating the species contains more than one Co atom, most likely two, and a single benzene molecule. A second product, labeled 1/1, is present in all three samples, but is less prominent when the [Co]/[C_6H_6] ratio is smaller than one. This product disappears completely after prolonged annealing (promoting diffusion and thus the formation of large aggregates) and is not seen in neat benzene (*vide infra*). Finally, the species labeled 1/2 is the only one remaining in samples with high benzene and low cobalt concentrations. From the first- and second-order C_6H_6 concentration dependencies, it appears that these two products (1/1

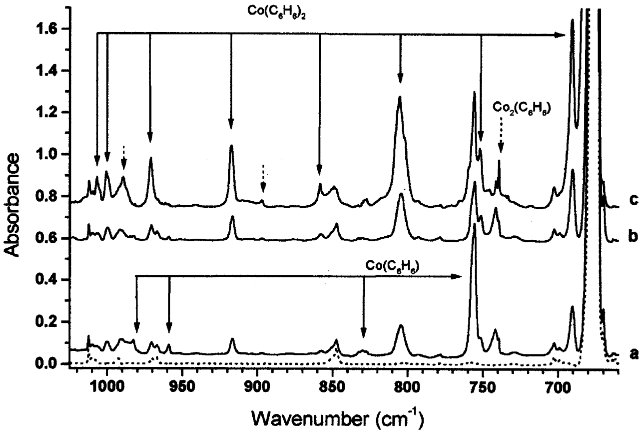


Figure 2. IR spectra of a $Co/C_6H_6/Ar = 0.3/1.5/100$ sample in the 1050−670-cm^{-1} region. (a) After deposition (without Co, dotted line), (b) after photolysis ($\lambda = 580$ nm), (c) after annealing to 35 K to promote diffusion.

TABLE 1: Frequencies (cm^{-1}) and Relative Intensities (in Parentheses) for the IR Absorptions of the Monobenzene−Cobalt Complexes in Solid Argon at 10 K

$Co(C_6H_6)$	$Co(C_6D_6)$	$Co(^{13}C_6H_6)$	$Co_x(C_6H_6)$	$Co_x(C_6D_6)$
4140 (4)[a]	4140[a]	4140[a]		
~3055 (0.02)	[b]	~3048		
1424 (0.03)	[b]	1400.5	1440	1305
982.5 (0.15)	788.0	962.0	971	
958.9 (0.05)	917.8	925.4		
829.5 (0.08)	646.0	821.0		
755.6 (1)	576.5	751.1	739	565
~278 (0.07)	~265	~273		

[a] Broad (50 cm^{-1} bandwidth), structureless absorption. [b] Too weak to be detected or obscured due to overlapping with bands from other species formed in the present experimental conditions.

and 1/2) correspond to $Co(C_6H_6)$ and $Co(C_6H_6)_2$, respectively. It should be noted that these concentration studies indicate that the IR absorptions, reported in ref 11 and assigned to the half-sandwich complex, belong in fact either to $Co(C_6H_6)$ or to $Co(C_6H_6)_2$ or one or more species not seen in our experiments, therefore the conclusions of these studies must be revised.

Since the samples presented a rich red-brown color, we also recorded the absorption spectrum of the cobalt/benzene/argon samples. In general, a broad, structureless absorption band centered around 580 nm was observed. Photoexcitation of the samples around this wavelength resulted in a decrease in intensity of the IR bands assigned to $Co(C_6H_6)$, Figure 2, a consequence of partial product decomposition. This greatly helped in assigning weak absorptions belonging to this species as well as those overlapping the $Co(C_6H_6)_2$ absorptions. Thermally cycling the sample up to 35 K partly regenerated the $Co(C_6H_6)$ absorptions, and lead to substantial growth of the $Co(C_6H_6)_2$ species with a concomitant decrease of the unreacted benzene absorptions (Figure 2, traces b and c).

Taking into account the effect of (i) varying the cobalt and benzene concentration, (ii) the selective photodecomposition of the monoligand species, and (iii) the diffusion through thermal annealing favoring the diligand species, the absorption bands of the three products could be assigned and are presented in Tables 1 and 2.

Experiments were repeated using $^{13}C_6H_6$, C_6D_6, and an equimolar mixture of C_6H_6 and C_6D_6 as precursors to assist in the vibrational analysis and to confirm the proposed stoichiometry of the three products. Figure 3 presents the effects of isotopic substitution observed for the C_6H_6, $^{13}C_6H_6$, and C_6D_6 isotopic species of cobalt mono- and dibenzene species. For clarity, the absorption bands due to the unreacted benzene molecules have been subtracted from the spectrum. For most absorptions, the shifts in frequencies observed from one isotopic species to another can be followed fairly reliably using band shapes and relative intensities as guides. However, the tracking of some bands is more difficult, due to overlapping, in the relatively congested 1000−800-cm^{-1} spectral region. For the broad, structureless absorption near 4140 cm^{-1}, *no* isotopic shift is observed. The effect of isotopic mixtures is also very informative. Indeed, the spectrum, Figure 4, obtained with an equimolar mixture of C_6H_6 and C_6D_6 presents four bands for

TABLE 2: Frequencies (cm^{-1}) and Relative IR Intensities (Shown in Parentheses) Observed for Various Isotopic Species of the Dibenzene−Cobalt Complex in Solid Argon at 10 K

$Co(C_6H_6)_2$	$Co(C_6H_6)(C_6D_6)$[a]	$Co(C_6D_6)_2$	$Co(^{13}C_6H_6)_2$
~3060			
1518.5 (0.8)		1471.5	1469.4
1506.7 (0.7)			1458.5
1446 (0.16)			1420
1442.0 (0.8)		1351	1414.2
1436.9 (0.5)		1349.2	1410.1
1423.9 (0.15)			1397.5
1340.8 (0.6)		1255.2	1297.5
1157.9 (0.15)		848.2	1154.4
1121.0 (0.9)		843.2	1111.8
1006.6 (0.3)		799.5	982.7
1000.4 (0.5)		796.2	977.0
990.0 (0.7)		778.7	958.9
971.2 (0.8)		926.7	936.9
916.6 (1.10)		894.6	888.5
858 (0.3)		758.2	844.2
804.5 (4.7)	802.4 + 632.7	633.6	796.8
752 (1.0)	838.7	586.1	748
690.7 (5.0)	691.6 + 514.3	512.8	687.9
615 (0.06)			595
595.4 (0.15)		586.1	574.2
560.5 (0.1)		533.9	540.6
454.8 (0.7)	453 + 423	421.9	441.5
366.1 (0.65)	360.0 + 335.2	330.3	358.6
302.1 (0.24)		286.5	295

[a] In a $Co + C_6H_6 + C_6D_6$ mixture. Only the absorptions distinct from those seen for $Co(C_6H_6)_2$ and $Co(C_6D_6)_2$ are reported.

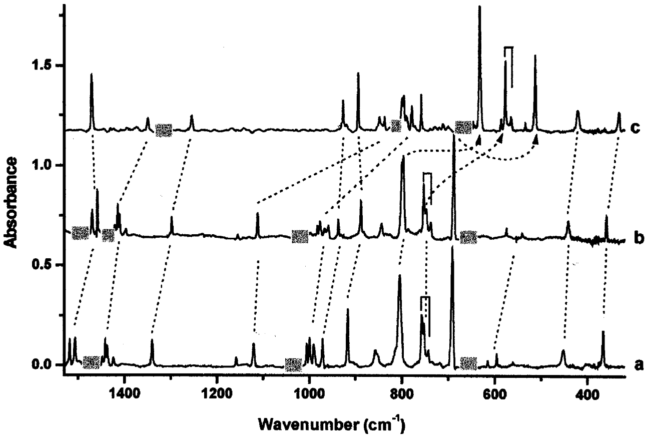


Figure 3. IR difference spectra (with Co minus without Co) in the 1520−320-cm^{-1} region for 35-K-annealed benzene−argon samples for various isotopic precursors: (a) $Co + C_6H_6$, (b) $Co + {}^{13}C_6H_6$, and (c) $Co + C_6D_6$. In all samples the $Co/C_6H_6/Ar$ molar ratios are approximately 0.3/4/100. The cobalt−dibenzene complex absorptions are designated by dotted lines, while bold lines designate some remaining monobenzene complex. The shaded areas mask spectral regions where strong unreacted benzene absorptions might lead to photometric artifacts.

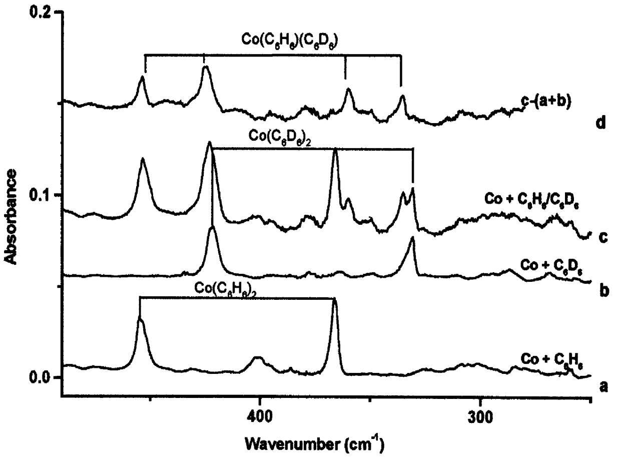


Figure 4. IR spectra in the 520−250-cm^{-1} region for 35-K-annealed benzene−argon samples for various isotopic precursors: (a) Co + C_6H_6, (b) Co + C_6D_6, (c) Co +C_6H_6/C_6D_6, and (d) difference spectrum c − (a + b). In all samples the Co/benzene/Ar molar ratios are approximately 0.3/4/100.

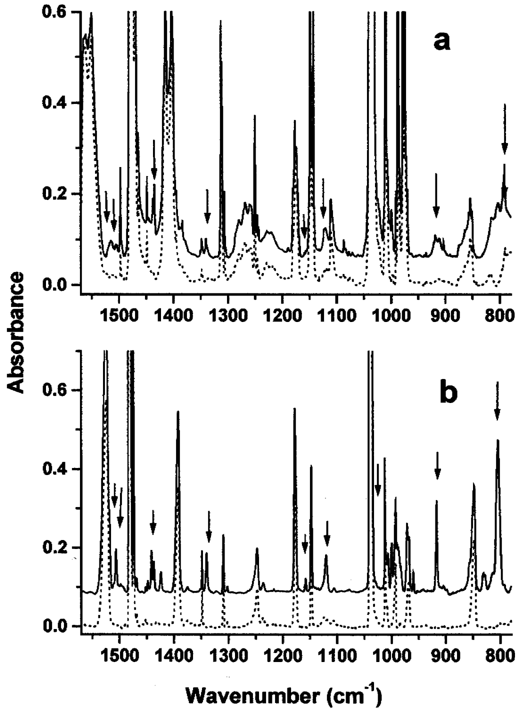


Figure 5. IR spectra in the 1600−780-cm^{-1} range: (a) neat deposits, Co + C_6H_6 (solid line) or C_6H_6 (dotted line); (b) Co/C_6H_6/Ar = 0.3/4/100 (solid line), or C_6H_6/Ar = 4/100 (dotted line).

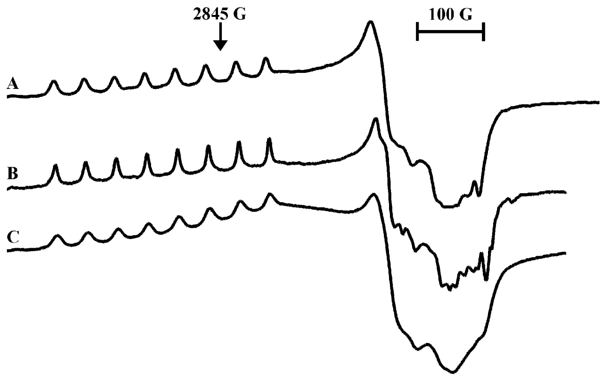


Figure 6. The X-band EPR spectra recorded at 77 K and microwave power (mp) = 2 mW of the products resulting from the reaction of Co atoms and (a) neat C_6H_6 (ν = 9149 MHz), (b) C_6D_6 (ν = 9148 MHz), or (c) $^{13}C_6H_6$ (ν = 9155 MHz).

the cobalt dibenzene species, in the low-frequency, metal−ligand vibration region. This would suggest that the rings in the cobalt dibenzene species are not equivalent and two isotopomers are formed. For example, the isotopomers (η^6-C_6H_6)Co(η^x-C_6D_6) and (η^6-C_6D_6)Co(η^x-C_6H_6), where $x \neq 6$ are then expected to give four IR bands in the metal−ligand vibration region. A triligand species, for instance, would have yielded two sets of extra absorptions, with different dependencies with respect to the [C_6H_6]/[C_6D_6] ratio. Tables 1 and 2 list the frequencies observed for the various isotopomers of Co(C_6H_6) and Co(C_6H_6)$_2$.

Co/Benzene. The spectrum obtained for the reaction of Co atoms in neat benzene, Figure 5, was compared to those recorded for reactions carried out in argon matrixes. In neat benzene, the absorption bands correspond, within a few wavenumbers, to those assigned to Co(C_6H_6)$_2$ in the argon matrixes. Absorption bands were detected in several domains, namely, 1515.5/1505, 1439/1435, 1340, 1119, 917, 910.5, 793, and 766 cm^{-1}. Discrepancies with the result of refs 11 and 12 are many, but mainly (i) the absence of absorption bands at 1175, 860, and 810 cm^{-1}, which must pertain to larger species and (ii) detection of the weaker signals at 1515.5/1505, 917, and 910.5 cm^{-1}.

EPR Data.

Co/Benzene. The X-band EPR spectra recorded at 77 K of the products resulting from the reaction of Co atoms and neat C_6H_6, C_6D_6, or $^{13}C_6H_6$ are shown in parts A−C of Figure 6, respectively. The IR analysis of the reaction of Co with neat C_6H_6 showed that only Co(C_6H_6)$_2$ is formed under these experimental conditions. The EPR spectra can therefore be assigned to the cobalt−dibenzene isotopomers. Upon substituting C_6H_6 by C_6D_6, the EPR spectral line widths decreased. This is particularly evident for the low-field lines. When C_6H_6 is substituted by $^{13}C_6H_6$, the lines appear to have broadened. These changes, although subtle, point to the interaction of the Co nucleus with the ligand and the formation of a Co−benzene complex. It is not possible to obtain much more information from this observation because the isotopic substitution has not resulted in further resolution of the spectral lines.

When the samples were annealed from 100 to 270 K in the cavity of the spectrometer the resolution of the spectra did not improve noticeably. At 270 K, a broad line resulted. This behavior has been previously reported[19] for Co complexes and is thought to be due to rapid relaxation and the large g anisotropy. Recooling the sample to 77 K resulted in the reappearance of the original spectrum.

In the case of the Co−C_6D_6 sample, the annealing process seemed to result in a slight change in the appearance of the spectrum. This may be due to slight changes in the complex's environment upon recrystallization.

Analysis of the EPR Spectrum. The substitution of C_6H_6 by C_6D_6 resulted in a narrowing of the line widths. This aids in the estimation of the Co hyperfine interaction (hfi). We therefore chose to extract the magnetic properties from the EPR spectrum resulting from the reaction of Co atoms and C_6D_6.

The spectrum in Figure 7 may be interpreted in terms of an orthorhombic[20] g and a tensor where $g_1 > g_2 > g_3$ and $a_1 \gg a_3 > a_2$. The complete resolution of the Co hfi would have resulted in a total of 3 × 8 or 24 lines (^{59}Co, 100%, $I = {}^7/_2$), an octet of lines for each of the 3 principal directions of the g tensor. In the low-field region the octet corresponding to g_1 = 2.375 and a_1 = 161 MHz is clearly visible. At least 5 of the 8 lines of the high-field multiplet corresponding to g_3 = 2.023 and a_3 = 30

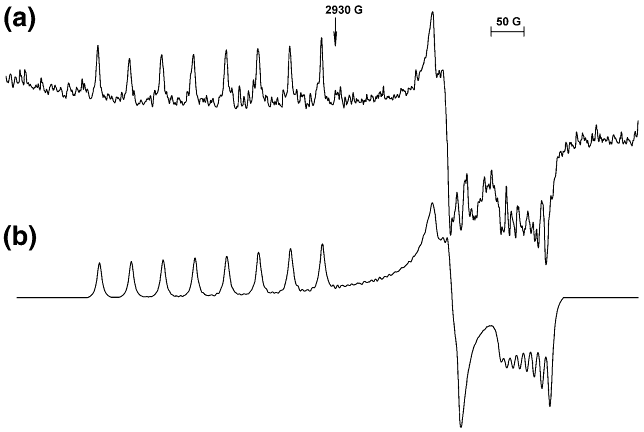


Figure 7. (a) The EPR X-band spectrum ($\nu = 9148$ MHz, mp = 2 mW) of a Co + C_6D_6 reaction mixture recorded at 77 K after being annealed to 270 K. (b) Computer simulation assuming $g_1 = 2.375$, $g_2 = 2.105$, $g_3 = 2.023$, $a_1 = 161$ MHz, $a_2 = 10$ MHz, and $a_3 = 30$ MHz.

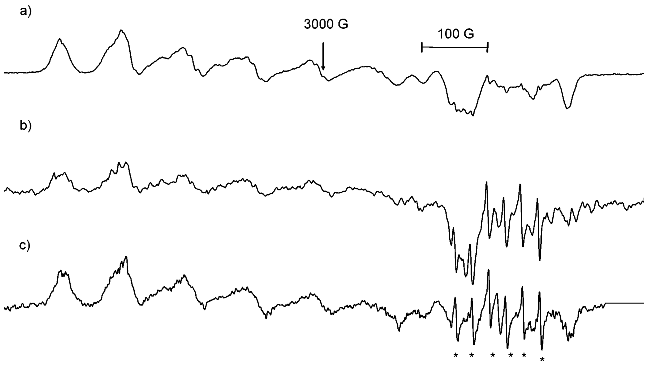


Figure 8. The X-band EPR spectra recorded at 77 K and mp = 2 mW of the products resulting from the reaction of Co atoms and (a) C_6H_6 ($\nu = 9149$ MHz), (b) C_6D_6 ($\nu = 9148$ MHz), or (c) $^{13}C_6H_6$ ($\nu = 9155$ MHz) in adamantane. The six lines in b and c designated by asterisks are due to Mn.

MHz are resolved. The central part of spectrum however is not as well resolved, and a reasonable estimate of $g_2 = 2.105$ and $a_2 = 10$ MHz was obtained by computer simulation, Figure 7b. It is important to note that in carrying out the simulation we assumed that the g and a tensors are coincident. The lines in the g_2 region not simulated were thought to arise from forbidden transitions ($\Delta m \neq 0$).

Co/Benzene/Adamantane. The X-band EPR spectra of the products resulting from the reaction of Co atoms and C_6H_6, C_6D_6, and $^{13}C_6H_6$ in adamantane were recorded at 77 K, Figure 8. An effect due to isotopic substitution was not observed. The samples were annealed in the cavity of the EPR spectrometer. The features broadened as the temperature was raised to 140 K with the exception of the line centered at $g = 2.034$. When the sample was recooled to 77 K the features reappeared. However, the intensity of the lines was significantly weaker than that of the original spectrum with the exception of the feature at 2.034, which was more pronounced, suggesting that two different species are responsible for the spectrum. This change in the spectrum, upon annealing, may be due to diffusion and coalescence of the Co−C_6H_6 species to form $Co_x(C_6H_6)_y$. A six-lined spectrum with $a = 26.9$ G and $g = 2.0014$ due to Mn was also detected at this temperature.[21] The Mn is an impurity in the Co wire as the same six-lined EPR spectrum was found for the deposit consisting of Co vapor in an adamantane matrix.

From the IR analysis of the products of the reaction of Co with C_6H_6 in adamantane, two bands appear to be unique to the Co−benzene−adamantane system. They are 743 and 738 cm^{-1}. In the experiments with argon, there are a number of bands (4140, ~3055, 982.5, 958.9, 829.5, 755.6, and 278 cm^{-1}) that have been attributed to $Co(C_6H_6)$. The most intense is the band at 755.6 cm^{-1}. In adamantane, the band at 743 cm^{-1} is (755.6−743) or 12.6 cm^{-1} lower than that found for the 1:1 complex. The position of the absorption band observed in adamantane is consistent with that assigned to $Co(C_6H_6)$ in Ar, and we conclude that the EPR spectrum observed is due to the 1:1 complex. The band at ~738 cm^{-1} seems to be consistent with that attributed to Co_2Bz in argon.

Analysis of the EPR Spectrum. The spectrum, Figure 9, of one of the species indicates that it contains Co (^{59}Co, 100%, $I = 7/2$) and may be interpreted in terms of axial g and a tensors where $g_1 \cong g_2 > g_3 > 2.0023$ and $a_1 = a_2 > a_3$. At least 12 of the 16 lines of the low field multiplet are visible, while only 2 lines of the high field octet are visible. A reasonable computer simulation was obtained with $g_1 = 2.224 \pm 0.003$, $g_2 = 2.216 \pm 0.003$, $g_3 = 2.030 \pm 0.002$, $a_1 = a_2 = 315 \pm 5$ MHz, and $a_3 = 130 \pm 3$ MHz. The simulation did not take into account the magnetic inequivalency of the hydrogens. It was also assumed that the a and g tensors were coincident. The feature at $g = 2.034$ is not well enough resolved to be of any value in identifying its carrier.

IR Data and Vibrational and Structural Analysis.

Co(C_6H_6). We will restrict the discussion of the unsaturated species to a few remarks because many of the fundamentals were not observed. The broad, structureless absorption above 4100 cm^{-1} does not present an isotopic effect. It thus seems likely to be due to a low-lying electronic transition of the complex. Co itself has a ^4F ($3d^74s^2$) ground state, with the first ^4F and ^2F ($3d^84s^1$ configuration) excited states very close in energy (3483 and 7442 cm^{-1}).[6] The EPR results imply a doublet ground state. From the g-factor analysis, we can say there are occupied low-lying excited states of the proper symmetry to admix with the SOMO. This is based on the fact that g_x, g_y, and g_z are >2.0023. If we use the crystal field approach and just consider the Co d orbitals, we can estimate[22] ΔE from $g_x = 2.0023 + 2\lambda/\Delta E$ where $g_x = 2.224$ and λ is the spin−orbit coupling constant. λ for Co and Co^{2+} is 517 and 515 cm^{-1}, respectively. Substituting these values in the equation gives ΔE = 4664 and 4710 cm^{-1}, respectively, which is in close agreement with the NIR electronic absorption observed near > 4100 cm^{-1}.

From their respective H/D and $^{12}C/^{13}C$ isotopic effects, the 1424- and 982.5-cm^{-1} absorption bands correspond to the coupled C−C stretching and C−H bending motions formerly of E_{1u} symmetry at 1480 and 1036 cm^{-1} in the benzene ligand. These will be IR-active irrespective of the complex's overall symmetry and are likely to be shifted to lower wavenumbers by metal complexation (see for instance 1426 and 999 cm^{-1} in $Cr(C_6H_6)_2$,).[13,23] Although the −39 cm^{-1} red shift predicted for this vibration in the recent ab initio study carried out by Chaquin et al.[7] seems to agree reasonably well with experiment, it must be pointed out that the authors used a spin-restricted method and only considered the doublet configuration. The strong absorption near 755 cm^{-1} has a very small $^{12}C/^{13}C$ shift, while the H/D shift is large, consistent with what is anticipated for an out-of-plane H−C wagging motion. A shift to higher frequency is expected for the IR-active, formerly A_{2u} symmetry motion, at 670 cm^{-1} in free benzene, based on the IR data reported for $Cr(C_6H_6)_2$ (792 cm^{-1}) and $Cr(CO)_3(C_6H_6)$ (750 cm^{-1}). The excellent agreement of the $^{12}C/^{13}C$ and H/D isotopic effects for those observed for this latter motion makes it the most likely possibility. Assignment of the weaker absorption

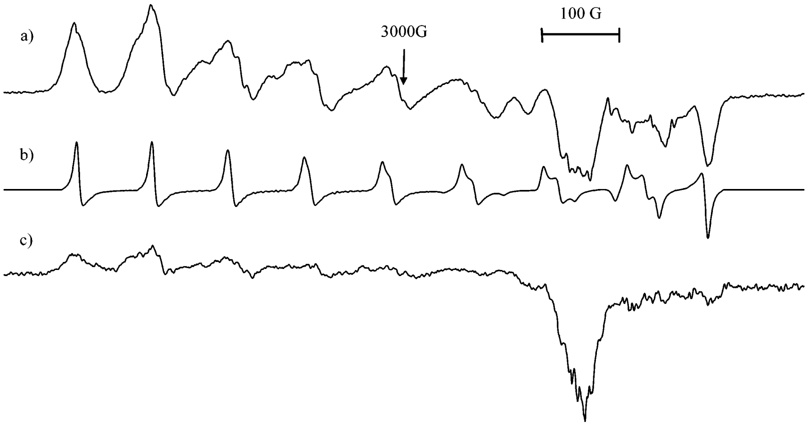


Figure 9. (a) The X-band EPR spectrum recorded at 77 K ($\nu = 9149$ MHz, mp = 2 mW) of the products resulting from the reaction of Co atoms and C_6H_6 in adamantane. (b) Simulation of the EPR spectrum using the magnetic parameters $g_1 = 2.224$, $g_2 = 2.216$, $g_3 = 2.030$, $a_1 = a_2 = 315$ MHz, and $a_3 = 130$ MHz. (c) The X-band EPR spectrum of the Co/C_6H_6/adamantane sample recorded at 77 K after being annealed to 140 K.

near 829 cm^{-1} is less straightforward. The 8.5 cm^{-1} $^{12}C/^{13}C$ shift and 184 cm^{-1} H/D shift indicates that it must be a C−H bending motion. The free ligand has no IR-active fundamental vibration at this wavenumber, and the non-IR-active fundamental which presents the best match to the observed isotopic behavior and energy is the E_{1g} symmetry motion, for which three neighboring C−H bonds move out of the molecular plane, out of phase with the remaining three. To produce an IR activation of a motion of this symmetry, one would have to consider total loss of the symmetry axis perpendicular to the C_6 ring, that is to say a nonaxial position of the Co atom with respect to the benzene ring. The remaining absorption near 280 cm^{-1} is too low to correspond to any benzene fundamental and appears likely to be a metal−ligand vibration. Taking the benzene ligand as a point mass and using the centroïd internal coordinate model as suggested by Berces,[23,24] one would predict a 4.5 cm^{-1} $^{12}C/^{13}C$ shift for a metal-benzene stretching motion, comparable to ~5 cm^{-1} observed here. In this crude approximation, one would compute a 1.4 N/cm bond force constant, indicating a moderate-to-weak interaction (compared to 2.3 found in $Cr(C_6H_6)(CO)_3$ or 3.3 N/cm in $Cr(C_6H_6)_2$). It is to be noted that the larger H/D than $^{12}C/^{13}C$ shift indicates a small coupling with a C−H bending coordinate, which should also warn us of the limitation of this model.

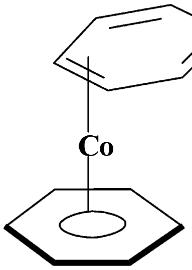
By assumption that the species formed in adamantane is $Co(C_6H_6)$, the magnetic parameters extracted from the EPR spectrum are consistent with a structure whereby Co assumes a non axial position with respect to the benzene ring, i.e., a species with C_s symmetry. The SOMO of the $Co(C_6H_6)$ complex under C_{6v} symmetry is expected to be an e_1 orbital. A Jahn−Teller effect caused by the partial occupation of the antibonding orbital results in a distortion of the $Co(\eta^6\text{-} C_6H_6)$ to $Co(\eta^4\text{-}C_6H_6)$ and the separation of the e_1 orbitals into a′ and a″ orbitals.[25] A simple crystal-field analysis of $Co(C_6H_6)$ predicts that all three g-values are > free spin because the SOMO would be admixing with filled orbitals. $Co(C_6H_6)$ is a d^9 system with the emptying of $4s^2$ electrons into the 3d-orbitals. This is in fact what was observed experimentally. Because the energy of the d_{xz} orbital is close to that of the SOMO, the coupling will be greater than that with the other d orbitals. As a result $g_x \cong g_y > g_z$, and we can assign g_x and g_y to 2.224 and 2.216, respectively, and g_z to 2.030. This would have to be confirmed by a single crystal study. The inability to obtain an isotropic EPR spectrum precludes a detailed analysis of the Co hfi because the sign of a_x, a_y, and a_z cannot be determined. One can obtain possible limits of A_{iso} and A_{dip}, i.e., $A_{iso} = -253$ MHz and $A_{dip} = 62$ MHz if a_x, a_y, and a_z are of the same sign, while $A_{iso} = -167$ MHz and $A_{dip} = 148$ MHz if a_z is opposite in sign to a_x and a_y. These values support the suggestion that the SOMO has a significant amount of d character, i.e., ≥51%.[7]

$Co(C_6H_6)_2$. For the completely saturated species, we were able to detect 25 fundamental vibrations because this product is formed in greater yield. This represents a fraction of the large number of normal modes expected for a 25-atom molecule but is much more than the ten IR-active fundamentals possible for a bisarene sandwich complex of D_{6h} symmetry, as in the case of $Cr(C_6H_6)_2$. Before discussing the effect of symmetry reduction on the total number of observable fundamentals, let us first consider the effect of interligand vibrational coupling. The presence of two equivalent benzene ligands in a complex can cause coupling of intraligand vibrations. For instance, the A_{1g} symmetry "ring-breathing" motion (about 993 cm^{-1} in free C_6H_6[26,27]) will couple into A_{1g} and A_{2u} motions of slightly different energies in a symmetrical sandwich structure (for instance, 970 and 974 cm^{-1} in $Cr(C_6H_6)_2$,[13,23] and 966 and 906 cm^{-1} in $Li(C_6H_6)_2$[28]). For $Cr(C_6H_6)_2$, this effect is small with respect to the perturbation (−23 cm^{-1}) resulting from the coordination of a metal atom and can be neglected, but for $Li(C_6H_6)_2$, this is not the case. One way to detect this effect is to measure IR absorption bands for the mixed $Co(C_6H_6)(C_6D_6)$ species, because nonequivalence in reduced masses causes uncoupling of the ligand molecular vibrations. For this species, only the low-frequency vibrations in the metal−ligand region (below 400 cm^{-1}) show noticeable shifts with respect to the IR bands for $Co(C_6H_6)_2$ or $Co(C_6D_6)_2$ and for the benzene internal modes, only the strong 804.5- and 690.7-cm^{-1} vibrations in $Co(C_6H_6)_2$ show sign of weak molecular coupling (shifting to 802.4 and 691.6 cm^{-1} in $Co(C_6H_6)(C_6D_6)$). This observation indicates that the overall symmetry in cobalt dibenzene is lower than in the chromium or lithium analogues, to the point that the two benzene ligands might already be nonequivalent, even in the absence of partial isotopic substitution. In the absence of interligand vibrational coupling, it is then possible to reason in terms of localized vibrations and to consider a local symmetry for each ligand. A discussion of the assignment of the IR absorption bands of $Co(C_6H_6)_2$, based on $^{12}C/^{13}C$ and H/D shifts with respect to values reported for benzene, follows.[26,27]

The doublet near 1518/1507 cm^{-1} shifts by −47 cm^{-1} and −49 cm^{-1} upon $^{12}C/^{13}C$ and H/D substitution, respectively. This is characteristic of the quinoidlike ring stretching vibration in benzene occurring near 1600 cm^{-1}. This vibration is degenerate (E_{2g}, ν_8) in free benzene and cannot be IR active unless the local symmetry is reduced to at least C_{2v}. In reduction of the symmetry, the degeneracy of the vibration will be lifted and a 2-fold splitting is expected for each ligand. Here only two signals are observed, but overlapping with the strong ν_{19} absorption band of unreacted benzene might preclude observation of other signals. The 1158/1121-cm^{-1} group, which shifts to 1154/1112 and 848/843 cm^{-1} upon $^{12}C/^{13}C$ and H/D substitution, respectively, is likely related to the in-plane-bending motion, $\nu_{9,}$ of benzene (1178 cm^{-1}, also of E_{2g} symmetry). A group of four bands is observed near 1440 cm^{-1}, shifting to 1412 and 1350 cm^{-1} upon $^{12}C/^{13}C$ and H/D substitution, respectively. This isotopic behavior is appropriate for a motion related to the ν_{19} of benzene (1480 cm^{-1}, E_{1u} symmetry); this vibration is already IR-active for unreacted benzene. There are two important points to be made here: (1) the magnitude of the isotopic shift is comparable although slightly weaker than in $Cr(C_6H_6)_2$ and (2) the 4-fold splitting is consistent with removal of the degeneracy of the two benzene ligands. The absorption near 1341 cm^{-1} is in a domain where very few fundamentals of benzene are located and presents $^{12}C/^{13}C$ and H/D effects of −43 and −86 cm^{-1}, respectively. Only the Kekule-like alternating CC bond stretching motion ($\nu_{14,}$ B_{2u} symmetry, 1309 cm^{-1} in C_6H_6) displays a similar isotopic behavior. To obtain IR-activity for this motion, one must consider a benzene local symmetry less than C_{2v}, that is, no symmetry axis perpendicular to the benzene ring, or a nonaxial position of the Co atom. Note that this vibration would be blue shifted with respect to benzene, a situation also occurring in $Cr(C_6H_6)_2$ according to the predictions of Bercès and Ziegler.[23] Two of the absorptions near 1000 cm^{-1}, seem to correspond to C−H in-plane deformation motions as these are expected to exhibit large H/D shifts. More specifically, two of the bands most likely correspond to the red-shifted ν_{18} (E_{1u}) or ν_5 (B_{2g}) of benzene. The absorption bands near 971 and 917 cm^{-1} have distinctly different isotopic behaviors than those mentioned above with larger $^{12}C/^{13}C$ effects and relatively smaller H/D effects. The relative magnitude of the isotopic effects is in strong accord with ν_1 (993 cm^{-1}, A_{1g}) or, less likely, ν_{12} (1008, B_{1u}) of benzene. The presence of several strong IR absorptions between 860 and 700 cm^{-1} with very small $^{12}C/^{13}C$ and large H/D effects is also very informative. These isotope effects suggest that the absorptions can be attributed to the out-of-plane C−H bending vibrations. One of them should correspond to the strong ν_{11} mode at 674 cm^{-1} in benzene, which is IR-active whatever the overall symmetry of the complex. This mode is blue shifted in Cr−arene complexes (790 cm^{-1} in $Cr(C_6H_6)_2$[23] and 751 cm^{-1} in $Cr(CO)_3(C_6H_6)$[29]) and could correspond to either the strong 690.7 or, less likely, the weaker 752 cm^{-1} band. The two strong bands at 858 and 804.5 cm^{-1} must be associated to other wagging motions, and the formerly E_{1g} symmetry doubly degenerate wagging motion (ν_{10}, 849 cm^{-1} in C_6H_6) is the only candidate. Again IR activation implies reduction of symmetry with loss of the symmetry axis for the $Co-C_6H_6$ group, with at most C_s local symmetry.

The weaker signals near 595 and 560 cm^{-1} seem appropriate for motions arising from the formerly doubly degenerate vibration, ν_6 (E_{2g}, 606 cm^{-1}), while the three absorptions bands at 455, 366, and 302 cm^{-1} are in a domain where only the boatlike ring deformation of the ligand (ν_{16}, 404 cm^{-1}) and the metal-ring skeletal vibrations are found.[26] However, none of the isotopic shifts observed for the absorption bands are consistent with the boatlike ring deformation. All the absorption bands present notable $^{12}C/^{13}C$ shifts and the H/D effects are smaller than expected for such a motion. This indicates a strong coupling between ring tilting/wagging and metal-to-ring coordinates. As stated before, the isotopic effects observed in the isotopically mixed species are strongest on the 366-cm^{-1} mode, which should then involve to a larger extent a metal-to-ring stretching motion. In $Cr(C_6H_6)_2$, the skeletal motion frequencies are 490 (E_{1u}), 456 (A_{2u}), 335 (E_{1g}), and 277 cm^{-1} (A_{1g}), the latter two are IR silent. Here the three IR-active modes at 455, 366, and 302 cm^{-1} confirm the loss of symmetry. But, in the absence of further structural data, such as Raman or polarization measurements, firm assignments are not possible. The 366- and 302-cm^{-1} absorptions have isotopic effects close to those observed for the 456 (A_{2u}) and 277 cm^{-1} (A_{1g}) modes of $Cr(C_6H_6)_2$, and IR activity for the related metal-to-ring motions is consistent with the absence of a symmetry axis perpendicular to the arene rings. Finally, the presence of *two* isotopic counterparts in the $C_6H_6 + C_6D_6$ isotopic mixture is consistent with the formation of two isotopomers with the overall composition of $Co(C_6H_6)(C_6D_6)$ and an asymmetrical sandwich structure.

Rayane et al.[9] used density functional theory (DFT) calculations to predict the lowest-energy structure of $Co(C_6H_6)_2$. The geometry optimization was performed using the B3LYP functional and an SDD basis set for the two lowest spin states of the compound. The lowest-energy state, had an asymmetric structure $(\eta^6\text{-}C_6H_6)Co(\eta^x\text{-}C_6H_6)$, (**1**), consistent with the existence of a permanent electric dipole moment as determined experimentally. The predicted value of 1.58 D is, however, larger than the experimental value of 0.7 ± 0.3 D. In this bonding scheme the four last occupied orbitals are d orbitals. The IR data presented above are consistent with the proposed bonding scheme, **1**.



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In recent vibrational studies[30,31] of gas-phase mass-selected $Ni(C_6H_6)_2{}^+$, a complex which is isoelectronic with $Co(C_6H_6)_2$, IR-active vibrations were detected by broad maxima around 732 and 1469 cm^{-1} in multiple-photon IR dissociation processes. This is consistent with some of the normal vibrations observed here, but the proposed structures involved a C_s-symmetry slipped-ring structure with equivalent ligands[30] or a distorted sandwich structure with D_{2h} symmetry,[31] on the basis of DFT calculations.

Finally, in the crude approximation of the "three-mass model" commonly made for bisarene complexes,[27] one would infer a metal-to-ring stretching force constant of approximately 2.6 N/cm for $Co(C_6H_6)_2$. A comparison with values of 2.9 and 2.67 N/cm obtained for $Cr(C_6H_6)_2$ and $V(C_6H_6)_2$, respectively, suggests that $Co(C_6H_6)_2$ is only slightly less stable than the other complexes.

g-Factor Analysis.

One can adapt the simple bonding scheme[25] proposed for $(\eta^6\text{-}C_6H_6)_2Cr$ to accommodate the 21 valence electron $(\eta^6\text{-}C_6H_6)_2$-

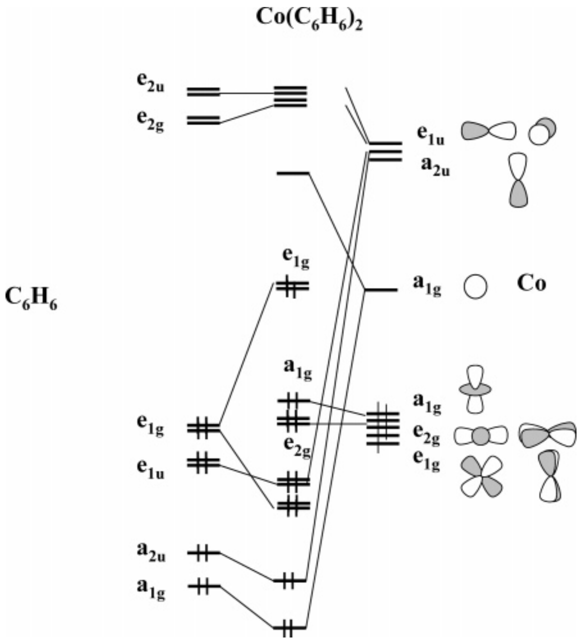

Figure 10. A simple bonding scheme for the 21 valence electron species, (η^6-C_6H_6)$_2$Co.

Co species, Figure 10. The relative energy of the orbitals with a large d contribution is $e_{2g} < a_{1g} < e_{1g}$. When one of the rings slip relative to the other forming (η^6-C_6H_6)Co(η^x-C_6H_6), where $x \neq 6$, the degeneracy of the e_{2g} and e_{1g} levels are lifted. In the case of (η^6-C_6H_6)Co(η^4-C_6H_6) and (η^6-C_6H_6)Co(η^2-C_6H_6), the SOMO has ligand-d_{xz} ($^2A''$) character, while for (η^6-C_6H_6)Co(η^3-C_6H_6), the SOMO has ligand-d_{yz} ($^2A'$) character. The DFT calculations of Rayane et al. predict an (η^6-C_6H_6)Co(η^2-C_6H_6) structure for the dibenzene complex with a d^9 configuration. The three *g*-values extracted from the EPR spectrum of the dibenzene complex are greater than 2.0023, indicating the SOMO admixes with occupied orbitals of proper symmetry, which is consistent with a d^9 configuration.

Often an analysis of the *g* values using a simple crystal field splitting approach is used to predict the electronic nature of organometallic compounds. In this approach one considers the effect of the electrostatic field imposed by the ligands on the relative ordering of the d orbitals of the metal center. By assumption that the ground-state structure of Co(C_6H_6)$_2$ belongs to the $^2A''$ representation in the C_s point group, the excited states which couple to it are $l_x \equiv R_x \equiv {}^2A'$, $l_y \equiv R_y \equiv {}^2A'$, and $l_z \equiv R_z \equiv {}^2A''$. The d_{yz} orbital, the closest in energy to the SOMO, is of the A″ representation. As a result

$$g_z = 2.0023 + 2\lambda/\Delta E(d_{xz} - d_{yz}) \qquad (1)$$

where λ is the spin−orbit coupling constant for Co and ΔE is the difference in energy between d_{xz} and d_{yz}. We can therefore assign g_z to g_1 (2.375), while g_y and g_x correspond to 2.105 and 2.023, respectively.

By use of the *g* factors, the magnetic moment of the compound is estimated as 1.88 μ_B. This can be compared to 1.86 μ_B reported for Co(C_6Me_6)$_2$.[3] This suggests that the two compounds are similar in nature.

A detailed analysis of the electronic structure of Co(C_6H_6)$_2$ based on the Co hfi is not possible because an isotropic spectrum was not attainable. However, the values are similar to those obtained for Co(C_6Me_6)$_2$, i.e., $g_z = 2.290$ and $a_z = 145$ MHz for Co(C_6Me_6)$_2$ vs $g_z = 2.375$ and $a_z = 161$ MHz for Co(C_6H_6)$_2$, indicating that the electronic structure of these two compounds are alike. Values of g_x, g_y, a_x, and a_y were not reported for Co(C_6Me_6)$_2$.[32] This was most likely due to the difficulty in obtaining good estimates of the magnetic parameters. In addition, the magnetic parameters for (η^6-C_6Me_6)Co(η^4-diolefins) are similar to our values for Co(C_6H_6)$_2$, Table 3, affirming the slipped ring bonding scheme for the dibenzene complex. The metal contribution to the SOMO of the (η^6-C_6Me_6)Co(η^4-diolefins) series was estimated[4] to be 60−70%.

TABLE 3: Comparison of the Magnetic Parameters (*a* (MHz) and *g* Values) for Several Zerovalent Co Radicals

radical	g_1	g_2	g_3	a_1	a_2	a_3	ref
(C_6Me_6)Co(C_6H_8)	2.364	2.044	2.026	210	∼15	60	4
(C_6Me_6)Co(C_7H_{10})	2.398	2.088	2.068	222	∼15	52	4
(C_6Me_6)Co(NDB)[a]	2.132	2.043	2.010	444	∼30	∼30	4
(C_6Me_6)Co(COD)[a]	2.122	2.027	2.022	444	99	99	4
Co(C_6Me_6)$_2$	2.290			145			32
Co(C_6H_6)$_2$	2.375	2.105	2.023	161	10	30	this work

[a] NBD and COD are abbreviations for norbornadiene and cyclooctadiene, respectively.

Summary

Cobalt atoms were reacted with benzene under matrix isolation conditions. The 1:1 and 1:2 Co−benzene complexes were characterized using IR and EPR spectroscopy. For Co(C_6H_6), vibrational analysis indicates that the Co assumes a nonaxial position with respect to the benzene ring. This is consistent with the magnetic parameters extracted from the EPR spectrum. Similarly the vibrational data and magnetic parameters for Co(C_6H_6)$_2$ indicate a low symmetry and are consistent with the slipped ring structure suggested by Rayane et al.[9] It is anticipated that the IR and EPR results of the present study will prove important in refining the theoretical methods used to predict the properties of metal−benzene complexes. Finally, it is interesting that the dibenzene complex survives warming to 270 K suggesting a relative stability of 15−20 kcal/mol with respect to Co(C_6H_6). This can be compared to the 30−35 kcal/mol estimate of the dissociation energy obtained for the isoelectronic Ni(C_6H_6)$_2^+$ ion, from modeling of collision-induced dissociation in the gas phase.[33]

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