

# Some Aspects of Metal-Olefin Bonding in Cyclopentadienylcobalt-Cyclic Olefin Complexes As Evidenced by $^{59}\text{Co}$ Nuclear Quadrupole Resonance

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$^{59}\text{Co}$  nuclear quadrupole resonance reflects the extent of electron redistribution in delocalized cyclic olefin complexes containing Co(III).  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}^+$  is compared to  $(\eta^5\text{-C}_5\text{H}_5)[\eta^4\text{-C}_4(\text{C}_6\text{H}_5)_4]\text{Co}$ . In localized cyclic olefins the electron density is significantly asymmetric, and the strength of the bond between the  $(\eta^5\text{-C}_5\text{H}_5)\text{Co}$  unit and the olefin is found to be cyclooctadiene > duroquinone > cyclopentadienone. The origin of this trend is related to the ability of the ligand to distort in order to maximize the overlap between the  $\pi$  system and the  $d_{zz}$  orbital of cobalt. This view is consistent with the EHMO calculations on similar complexes. The NQR data for  $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\eta^4\text{-cyclopentadienone})$  complexes where the cyclopentadienone ring is substituted indicate that the cyclic olefin is a partially localized diene and that little variation in the Co-cyclic olefin bonding occurs as a function of substitution of the cyclopentadienone ring.

## Introduction

The metal-olefin bond is fundamental to organometallic chemistry. Although a great deal is known both experimentally and theoretically about this interaction,<sup>1-3</sup> the individual details from complex to complex continue to be of considerable interest.

An experimental technique that is capable of elucidating the ground-state electron distribution in appropriate transition-metal complexes is nuclear quadrupole resonance spectroscopy. It has been applied on several occasions to the study of metals involved in metal-polyene bonds.<sup>4-6</sup> In this paper we report a  $^{59}\text{Co}$  NQR spectroscopy study of  $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{cyclic olefin})$  complexes in which some of the details of the cobalt-olefin bond are analyzed.

## Experimental Section

**Synthesis.**  $\text{CpCo}(\text{CO})_2$  ( $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ) was obtained from Pressure Chemical. All ligands are available from commercial sources and were used as received. Literature procedures were employed for preparation of the complexes:  $\text{CpCoC}_4\text{Ph}_4$ ,<sup>7</sup> ( $\text{C}_4\text{Ph}_4 = \eta^4\text{-C}_4(\text{C}_6\text{H}_5)_4$ ),  $\text{CpCoC}_5\text{Ph}_4\text{O}$ ,<sup>7</sup>  $\text{CpCoC}_5(\text{CF}_3)_4\text{O}$ ,<sup>8</sup>  $\text{CpCoC}_6(\text{CH}_3)_4\text{O}_2$ ,<sup>9,10</sup>  $\text{CpCoCOD}$ <sup>11</sup> ( $\text{COD} = \eta^4\text{-cyclooctadiene}$ ), and  $[\text{CpCoC}_5\text{H}_4\text{COOH}]\text{PF}_6$ ,<sup>12</sup>  $[\text{C}_5\text{H}_4\text{C}(\text{OH})(\text{C}_6\text{H}_5)_2\text{CoC}_4\text{Ph}_4]$  was obtained from Professor D. Seyferth, MIT.

The products were characterized by accurate correlation of melting points and  $^1\text{H}$  NMR spectra with the literature values.

**NQR Spectroscopy.** The NQR spectra were recorded on polycrystalline samples at room temperature with a spectrometer system described elsewhere.<sup>13</sup> Uncertainty in the measurement

of the center line of the resonance multiplet produced a maximum error of 0.01 MHz in the resonance frequencies. The nuclear quadrupole coupling constant and asymmetry parameter were calculated from the eigenvalue equation<sup>14</sup> for  $I = 7/2$  using a computer program.<sup>15</sup>

We were unable to detect signals in  $\text{CpCoC}_6\text{H}_8$ ,  $[\text{C}_5(\text{CH}_3)_5]\text{-CoC}_6\text{H}_8$ , and a number of substituted  $\text{Cp}_2\text{Co}^+$  salts and  $\text{CpCoC}_4\text{Ph}_4$  complexes. While relaxation times often determine whether or not a signal is detected with a superregenerative oscillator, the number of NQR-active nuclei in the coil (the filling factor) is also important.

## NQR Analysis

$^{59}\text{Co}$  ( $I = 7/2$ ) produces three allowed transitions in NQR spectroscopy. These transitions occur between the  $m_I = \pm 1/2, \pm 3/2, \pm 5/2$ , and  $\pm 7/2$  levels with a selection rule of  $\Delta m_I = \pm 1$ . In practice the  $3/2 \leftrightarrow 1/2$  transition may not be observed unless the higher frequency transitions are intense. Nuclear quadrupole resonances occur in the RF region. Their location depends on the magnitude of the nuclear quadrupole moment,  $Q$ , which is constant, and the electric field gradient (EFG),  $q$ , at the nucleus, which varies in magnitude and symmetry depending on the distribution of charge about the nucleus.  $q$  is a tensor, the largest component of which is chosen by convention to be  $q_{zz}$ . The nuclear quadrupole coupling constant,  $e^2Qq_{zz}/h$ , and the asymmetry parameter of the electric field gradient,  $\eta$ , can be calculated from any two identified nuclear transitions.  $e^2Qq_{zz}/h$  (hereinafter  $e^2Qq/h$ ) measures the magnitude of the EFG sensed by the nucleus while  $\eta = (q_{xx} - q_{yy})/q_{zz}$  measures its deviation from axial symmetry about  $Z$ .  $\eta$  may take on values from 0 to 1 depending on the degree of EFG asymmetry. Values of  $\eta$  in the 0.0-0.15 range can arise from distortions produced by lattice forces and generally are too small to have chemical significance. Values of  $\eta$  greater than 0.15 may be chemically important.

The magnitude of the EFG on the metal in diamagnetic transition-metal complexes is dominated by the distribution of electron density in the valence  $d$  orbitals.<sup>16</sup> If  $d_{zz}$  is chosen to coincide with the  $Z$  axis of the EFG tensor, then the molecular coupling constant is related to the atomic value (a constant) through the combination of orbital populations,  $N_d$ , given in the bracketed quantity

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of eq 1. Although eq 1 is an approximation, it is valuable

$$(e^2Qq/h)_{\text{mol}} = (e^2Qq/h)_{\text{at.}} \left[ N_{d_{z^2}} + \frac{N_{d_{zz}} + N_{d_{yz}}}{2} - N_{d_{xy}} - N_{d_{x^2-y^2}} \right] \quad (1)$$

for relating the trend in the coupling constants over a series of complexes to changes that occur in metal-ligand bonding.

The asymmetry parameter,  $\eta$ , reflects the d orbital populations according to eq 2, assuming the Z axis of the

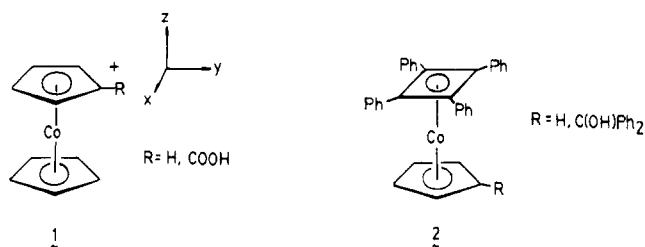
$$\eta = \frac{\frac{3}{2}(N_{d_{zz}} - N_{d_{yz}})(e^2Qq/h)_{\text{at.}}}{(e^2Qq/h)_{\text{mol}}} \quad (2)$$

EFG is the same as that chosen in eq 1.  $\eta$  is very useful because it detects the difference in the electron distribution on perpendicular planes of the molecule containing the Z axis of the EFG.

In addition to the intramolecular EFG, a contribution to the EFG in salts comes from the electrostatics of the lattice. The lattice contribution has been found to be relatively small in organometallic complexes where the metal atom is insulated from the counterions by the ligands.<sup>17</sup> Such is the case in  $\text{Cp}_2\text{Co}^+$  salts. The data in Table I for  $\text{Cp}_2\text{Co}^+$  cover several temperatures and salts. The coupling constant usually increases with a decrease in temperature.<sup>18</sup> The values of  $e^2Qq/h$  at 100 K are slightly larger than those at 298 K. All of the salts will have coupling constants in a narrow range around 166 MHz when the low-temperature values are scaled a few megahertz lower for comparison with the room-temperature values. Consequently there is only a small lattice effect, and no hazard should be encountered in comparing these organometallic salts to neutral complexes.

### Delocalized Cyclic Olefin Bonding

The metal orbital participation in the bonding of  $\text{Cp}_2\text{Co}^+$ , 1, and  $\text{CpCoC}_4\text{Ph}_4$ , 2, is well-known.<sup>19</sup> The Z axis



of the orbitals and the EFG tensor coincides with the metal-ring axis so that the  $d_{z^2}$ ,  $d_{xy}$ , and  $d_{x^2-y^2}$  orbitals are mostly filled and nonbonding while  $d_{zz}$  and  $d_{yz}$  dominate the MO's comprising the metal-ligand bonding.<sup>20,21</sup> The cobalticinium salts are axially symmetric with respect to the orbitals of cobalt and consequently the values of  $\eta$  in Table I are very small. The  $\text{CpCoC}_4\text{Ph}_4$  complexes have at most  $C_s$  in symmetry, but the delocalization of electron density in the occupied MO's of the ring produces effectively axial symmetry at cobalt. Accordingly, the asymmetry parameters for these compounds are observed to be

very small. Ring substitution in these compounds produces a negligible effect on the EFG at cobalt although a larger range of substituents might produce an observable effect such as that found in substituted  $\text{CpMn}(\text{CO})_3$  complexes.<sup>22,23</sup> The presence of phenyl groups on the cyclobutadiene ring in 2 improves the stability of these complexes and will not alter the description of the ring because the substituent effect of  $\text{C}_6\text{H}_5$  is small.<sup>24</sup>

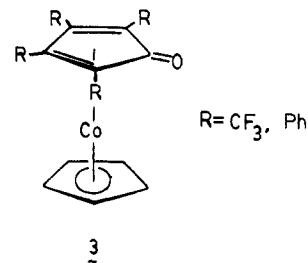
$\text{Co}(\text{III})$  has an initial d electron distribution of  $d_{z^2}(2)$ ,  $d_{x^2-y^2}(2)$ ,  $d_{xy}(2)$ ,  $d_{zz}(0)$ ,  $d_{yz}(0)$ . Significant redistribution of the electron density occurs when the  $\text{Co}(\text{III})$  ion bonds to cyclic olefin ligands to form 1 and 2. An increase in  $N_{d_{xy}}$  and  $N_{d_{yz}}$  will produce a lower value of  $e^2Qq/h$  according to eq 1. The lower value of  $e^2Qq/h$  in 2 compared to that in 1 results from the fact that the six-electron donor  $\text{Cp}^-$  and six-electron donor  $\text{C}_4\text{Ph}_4^{2-}$  ligands in 2 produce higher electron density in the  $d_{zz}$  and  $d_{yz}$  orbitals than do the two six-electron donor  $\text{Cp}^-$  ligands in 1. The magnitude of the bracketed quantity in eq 1 is, therefore, smaller in 2 than 1.

Alternatively, 2 might be considered to have a  $\text{Co}(\text{I})$  atom with an initial d electron distribution of  $d_{z^2}(2)$ ,  $d_{x^2-y^2}(2)$ ,  $d_{xy}(2)$ ,  $d_{zz}(1)$ ,  $d_{yz}(1)$  bonded to  $\text{Co}^-$  and a neutral four-electron donor  $\text{C}_4\text{Ph}_4$  ligand. Comparison of this electron distribution with that given above for  $\text{Co}(\text{III})$  shows by eq 1 that  $e^2Qq/h$  in 1 will be larger than for 2. With either formalism the net electron density on the metal is less for 1 than 2. If only the metal d orbitals are considered, the difference in the electron occupation of the  $m_l = 0, \pm 1$  orbital set and the  $m_l = \pm 2$  orbitals is about 17% greater in 1 compared to that in 2.

### Localized Cyclic Olefin Bonding

Localized dienes yield rather different NQR data (Table II) than the delocalized dienes. The bonding between cyclic olefins and metals partly depends on how readily the olefin can alter its structure and orientation in order to optimize the overlap with the metal orbitals. Inflexible dienes where the metal-ligand bonding is restricted in a preset way are likely to produce overall less bonding MO's than those possible with flexible dienes. An experimental test of this prediction can be made by comparing the orbital populations of a series of  $\text{CpCo}(\text{cyclic olefin})$  complexes where a rigid cyclic diene is compared to a flexible one.

Cyclopentadienone represents a relatively inflexible diene. It is based on butadiene in which the ring is cyclized by a carbonyl. The double bonds are at an angle to one another<sup>25,26</sup> and, therefore, are not optimized for metal-ligand orbital overlap in 3.



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Table I. Cobalt-59 Nuclear Quadrupole Resonance Frequencies for Delocalized Cyclic Olefins at 298 K, Unless Otherwise Indicated<sup>a</sup>

| complex   | $\nu$ , MHz               |                           |                           | $e^2Qq/h$ , MHz | $\eta$ |
|---|---------------------------|---------------------------|---------------------------|-----------------|--------|
|   | $1/2 \leftrightarrow 3/2$ | $3/2 \leftrightarrow 5/2$ | $5/2 \leftrightarrow 7/2$ |                 |        |
| [Cp <sub>2</sub> Co]NO <sub>3</sub> ·H <sub>2</sub> O, <sup>b</sup> 1                     | 11.833                    | 23.678                    | 35.513                    | 165.61          | 0.007  |
| [Cp <sub>2</sub> Co]Br <sub>3</sub> , <sup>c</sup> 1                                      |                           |                           |                           | 168.43          | 0.0    |
| [Cp <sub>2</sub> Co]ClO <sub>4</sub> , <sup>d</sup> 1                                     | 12.250                    | 24.500                    | 36.740                    | 171.43          | 0.0    |
| [CpCoC <sub>5</sub> H <sub>4</sub> COOH]PF <sub>6</sub> , 1                               |                           | 23.635 (20)               | 35.547 (10)               | 165.98          | 0.076  |
| CpCoC <sub>5</sub> Ph <sub>4</sub> , 2  |                           | 20.09 (10)                | 30.17 (15)                | 140.8           | 0.05   |
| [C <sub>5</sub> H <sub>4</sub> C(OH)Ph <sub>2</sub> ]CoC <sub>4</sub> Ph <sub>4</sub> , 2 |                           | 19.770 (3)                | 29.650 (3)                | 138.37          | 0.0    |

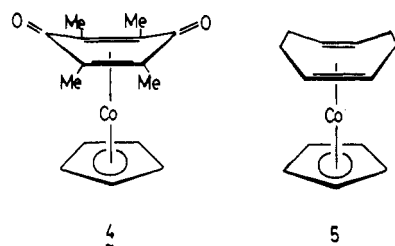
<sup>a</sup> Parenthetical numbers are signal-to-noise ratios. <sup>b</sup> Spiess, H. W.; Hass, H.; Hartmann, H. *J. Chem. Phys.* 1969, 50, 3057. <sup>c</sup> Nesmeyanov, A. N.; Semin, G. K.; Bryukhova, E. V.; Anisimov, K. N.; Kolobova, N. E.; Khandozhko, V. N. *Izv. Akad. Nauk SSSR* 1969, 9, 1936. Data at 77 K. <sup>d</sup> Voitlander, J.; Longino, R. *Naturwissenschaften* 1959, 46, 664. Data at 103 K.

Table II. Cobalt-59 Nuclear Quadrupole Resonance Data for Localized Dienes at 298 K<sup>a</sup>

| complex   | $\nu$ , MHz               |                           |                           | $e^2Qq/h$ , MHz | $\eta$ |
|---|---------------------------|---------------------------|---------------------------|-----------------|--------|
|   | $1/2 \leftrightarrow 3/2$ | $3/2 \leftrightarrow 5/2$ | $5/2 \leftrightarrow 7/2$ |                 |        |
| CpCoC <sub>5</sub> (C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> O, 3 |                           | 20.436 (4)                | 32.091 (4)                | 152.68          | 0.431  |
| CpCoC <sub>5</sub> (CF <sub>3</sub> ) <sub>4</sub> O, 3               |                           | 20.726 (3)                | 32.357 (7)                | 153.11          | 0.367  |
| CpCoC <sub>6</sub> (CH <sub>3</sub> ) <sub>4</sub> O <sub>2</sub> , 4 | 19.765 (2)                | 17.745 (7)                | 27.858 (7)                | 136.70          | 0.680  |
| CpCoC <sub>8</sub> H <sub>12</sub> , 5                                | 12.456 (4)                | 15.701 (20)               | 24.653 (50)               | 117.27          | 0.415  |

<sup>a</sup> Parenthetical numbers are signal-to-noise ratios.

To represent examples of more flexible ligands, cyclooctadiene and duroquinone were selected. Duroquinone is distorted in the CpCo complex 4 such that the ketone



groups bend away from the cobalt atoms while the Me groups move closer.<sup>27</sup> The ring has C<sub>2v</sub> symmetry. Such a distortion appears to occur in order to orient the  $\pi$ -electron density of the diene in the direction of the Co bonding orbitals.<sup>24</sup> Similarly the flexibility of COD permits the diene to position itself for optimum overlap with the metal orbitals in 5. These ligands, represented on one hand by nonparallel dienes with a less flexible five-membered ring, 3, and on the other hand by parallel dienes with flexible six- and eight-membered rings, 4 and 5, should produce alterations in the Co orbital occupation numbers.

The Z axis of the Co EFG tensor is chosen as shown on 1. While this orientation is satisfactory for 4 and 5, it would be fortuitous if the axis system orientation were precisely the same as this in 3. The Z axis in 3 will reside in the molecular mirror plane but may be canted from the Co-Cp axis.<sup>6</sup> Thus the present discussion of 3 will be purposefully subjective.

In these complexes Co(I) has an initial d orbital electron distribution of d<sub>z<sup>2</sup></sub>(2), d<sub>x<sup>2</sup>-y<sup>2</sup></sub>(2), d<sub>xy</sub>(2) with the remaining two electrons largely occupying the d<sub>yz</sub> orbital. Recent EMO calculations of Albright et al.<sup>28</sup> on CpCo(olefin)<sub>2</sub> complexes indicate that the metal MO's involving d<sub>z<sup>2</sup></sub>, d<sub>x<sup>2</sup>-y<sup>2</sup></sub>, and d<sub>xy</sub> are filled and largely nonbonding in the diene complexes of the type 3-5. Consequently, these orbitals will be taken as filled and unchanging. The variations in the metal electron density as reflected by the NQR data

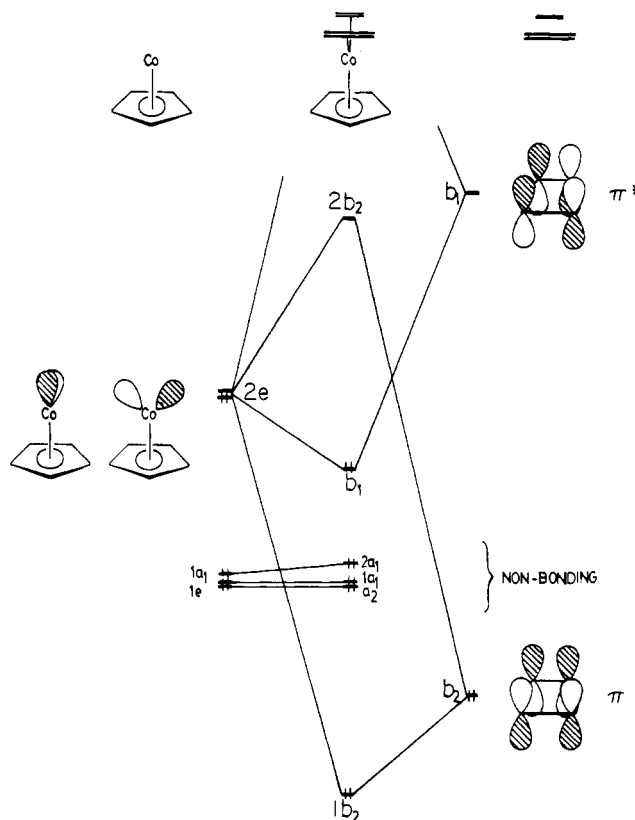


Figure 1. The interaction diagram for a parallel diene and the d<sub>zx</sub> and d<sub>yz</sub> orbitals of cobalt.<sup>28</sup>

take place via the d<sub>zx</sub> and d<sub>yz</sub> orbitals of Co which have the correct symmetry for bonding with the dienes in Table II. Figure 1 illustrates the overlap arrangement. The d<sub>zx</sub>-b<sub>2</sub> overlap is much more strongly bonding than the d<sub>yz</sub>-b<sub>1</sub> overlap which involves the  $\pi^*$  levels of the olefins.<sup>28</sup> It is reasonable, therefore, to expect a greater population for the d<sub>zx</sub> orbital of cobalt than d<sub>yz</sub>. Although the electron density in these orbitals is redistributed to some extent by bonding, the sum of the negative terms in eq 1 will exceed the sum of the positive terms in 3-5. Because the d<sub>zx</sub> and d<sub>yz</sub> orbitals participate to a different extent in bonding, eq 2 predicts a nonzero value of  $\eta$ . The values

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of  $\eta$  will be discussed shortly.

By using the fact that the negative terms are overall larger than the positive terms in eq 1, it is easy to see that an increase in the olefin-to-metal electron transfer through improved orbital overlap with the  $d_{xz}$  orbital will decrease the  $^{59}\text{Co}$  coupling constant. The trend in the coupling constants (Table II) is  $5 < 4 < 3$ . 5 is expected to have the best olefin-metal overlap due to the fact that COD is flexible enough for the  $\pi$  system to orient toward the  $d_{xz}$  orbital of cobalt. Likewise the duroquinone exhibits notable flexibility in order to maximize the metal-ligand overlap in 4,<sup>27</sup> but the olefin-to-metal electron transfer is reduced because the ketone groups compete with the metal for the diene electrons. As a result, in spite of the distortion of the duroquinone to optimize overlap, the diminished electron density in the  $m_l = \pm 1$  orbitals of cobalt (eq 1) produces the observed larger  $^{59}\text{Co}$  coupling constant in 4 compared to 5. There is about 10–15% less electron density in the  $m_l = \pm 1$  set in 4 than 5.

The substituted cyclopentadienone ligands produce the smallest population of the  $d_{xz}$  orbital according to the high value of the  $^{59}\text{Co}$  coupling constant in 3. Not only are the double bonds ineffectively oriented for the optimum overlap, but also the five-membered ring is relatively rigid. Accordingly, the electron transfer from the olefin to the cobalt  $d_{xz}$  orbital will not be as effective in 3 as in 4 or 5. These experimental NQR data support the conclusions of EHMO calculations where it is found that parallel dienes produce more strongly bonding MO's with the CpCo unit than do nonparallel dienes.<sup>28</sup>

The localization of  $\pi$ -electron density in 3–5 generates considerable asymmetry in the electron distribution on perpendicular planes of the molecule. The  $d_{xz}$  and  $d_{yz}$  orbitals lie on these planes, and their population will reflect this difference. The relationship of the asymmetry parameter to the occupation of these orbitals is given in eq 2. An inverse relationship between  $\eta$  and  $(e^2Qq/h)_{\text{mol}}$  would be observed if the quantity  $(N_{d_{xz}} - N_{d_{yz}})$  were constant in the series. This situation is sometimes observed<sup>5,6</sup> and means that proportional changes in the electron

density take place simultaneously in the two d orbitals. In Table II the trend in  $\eta$  does not match the trend in  $(e^2Qq/h)_{\text{mol}}$  and therefore the magnitude of  $(N_{d_{xz}} - N_{d_{yz}})$  is altered by the olefin. The largest value occurs in 5 where the lobes of the  $d_{yz}$  are directed at the atomic framework of the ketone groups. A semiempirical MO analysis suggests<sup>9</sup> this interaction is repulsive and is, in part, responsible for the distortion of the duroquinone ligand toward  $C_{2v}$  symmetry. The decrease in  $N_{d_{yz}}$  relative to  $N_{d_{xz}}$  is reflected in the large value of  $\eta$  observed with 4. The quantity  $(N_{d_{xy}} - N_{d_{yz}})$  is about 0.3 e in 4 and 0.2 e in 5 assuming  $(e^2Qq/h)_{\text{at.}}$  is about 280 MHz.<sup>16</sup> The lower values of  $\eta$  in 3 compared to that in 5 may result from a moderation of the difference between  $N_{d_{xz}}$  and  $N_{d_{yz}}$  due to the overall weaker cobalt-cyclic olefin bonding.

The NQR spectra of 3 with R =  $\text{C}_6\text{H}_5$  and  $\text{CF}_3$  (Table II) provide subjective information on the method of metal-olefin bonding in 3. The large values of  $\eta$  for cobalt are indicative of relatively localized double bonds in the cyclic olefin portion as opposed to highly delocalized molecular orbitals as found in Cp.<sup>25</sup> Differences in bonding in 3 when R is alternately an electron donor or acceptor substituent have been proposed.<sup>26,29-31</sup> The fact that  $e^2Qq/h$  and  $\eta$  are very similar in 3 when R =  $\text{CF}_3$  and R =  $\text{C}_6\text{H}_5$  reveals that the bonding modes in these two complexes are very similar insofar as the electron occupations of the d orbitals of cobalt are concerned.

**Acknowledgment.** We wish to thank Thomas M. Haller for help with the syntheses and to Professor D. Seyferth for a sample of  $[\text{C}_5\text{H}_4\text{C}(\text{OH})(\text{C}_6\text{H}_5)_2][\text{C}_4(\text{C}_6\text{H}_5)_4]\text{Co}$ .

**Registry No.** 1, R = COOH, 40759-57-7; 2, R = H, 1278-02-0; 2, R = C(OH)Ph, 68893-17-4; 3, R =  $\text{CF}_3$ , 12212-31-6; 3, R = Ph, 12119-11-8; 4, 41611-29-4; 5, 12184-35-9.

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