

⁵⁹Co NMR Spectroscopy of Organocobalt(I) and -cobalt(III) Compounds and Its Relation to Chemical Properties of the Complexes

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⁵⁹Co NMR parameters of various organocobalt(I) and -cobalt(III) complexes with π -ligands have been determined in solution in order to find out whether they provide a measure for complex properties. The ⁵⁹Co shifts of $(\eta^3\text{-allyl})(\eta^5\text{-cyclopentadienyl})\text{Co}^{\text{III}}\text{R}$ complexes (R = Br, benzyl, methyl) range from 1100 to -1300 ppm. $(\eta^3\text{-Allyl})_3\text{Co}$ (1) and $(\eta^3\text{-2-methylallyl})_3\text{Co}$ (2) yield ⁵⁹Co signals close to the region typical for organocobalt(I) compounds. Even at -50 and -30 °C the line width of their resonances is relatively narrow (3750 and 13000 Hz, respectively). In $(\text{olefin})_2\text{Co}^{\text{I}}\text{R}$ complexes $\delta(^{59}\text{Co})$ is sensitive to the type of R ligand and increases in the series alkyl-substituted- η^5 -cyclopentadienyl, η^5 -indenyl, and η^3 -allyl. In the $(\eta^5\text{-cyclopentadienyl})\text{Co}^{\text{I}}\text{L}$ series, $\delta(^{59}\text{Co})$ increases within the sequence L = cyclobutadiene, $(\text{CO})_2$, η^4 -cyclohexadiene, η^4 -butadiene, η^4 -cyclopentadiene, and $(\text{ethylene})_2$. These orderings resemble the strength of complexation of the π -ligand. Extended Hückel molecular orbital calculations were performed to compare $(\text{cyclopentadienyl})\text{cobalt dicarbonyl}$ and $(\text{cyclopentadienyl})\text{cobalt bis(ethylene)}$ with respect to their HOMO/LUMO gap and their frontier MO composition, in order to probe the influence of different paramagnetic screening terms upon ⁵⁹Co shifts in these complexes. The increased shielding of the Co nucleus in the dicarbonyl complex can be rationalized by its 0.3-eV larger HOMO/LUMO energy separation and its smaller Co contribution in the LUMO wave function. Chemical applications and the relevance of ⁵⁹Co NMR data are pointed out. Additionally, structures and dynamic behavior of these complexes have been investigated by ¹H and ¹³C NMR spectroscopy.

Introduction

Cobalt-59 occupies an unique place in the history of nuclear magnetic resonance,² and due to the relatively high magnetic moment and the 100% natural abundance of this quadrupolar nucleus a considerable mass of ⁵⁹Co NMR data has been published.³ The overwhelming majority of these studies has dealt with inorganic salts of Co in the formal oxidation state of +III. These investigations have shown that limitations for the use of ⁵⁹Co NMR in chemistry resulting from the large line width of this quadrupolar nucleus are compensated, at least in part, by the large ⁵⁹Co shift range. Moreover, for octahedral complexes of Co(III) a linear relationship has been found between the screening constant σ ($\sigma \sim -\delta(^{59}\text{Co})$) and the reciprocal of the mean electronic excitation energy ΔE ,^{4,5} thus providing some experimental justification for Ramsey's theoretical model⁶ for the calculation of NMR chemical shifts. Despite this clear structural relationship and the facile recording of ⁵⁹Co spectra, only relatively few ⁵⁹Co investigations of organocobalt(III) complexes have been carried out. On the other hand, compounds like $(\eta^3\text{-allyl})_3\text{cobalt}$ (1)⁷ are of considerable chemical interest. For example, 1 is a catalyst for the dimerization of butadiene to 5-methyl-1,3,6-heptatriene.⁸

In the first part of this paper we present experimental proof that, despite the ⁵⁹Co quadrupolar moment, the low-temperature ⁵⁹Co NMR spectra of 1 and $(\eta^3\text{-2-methylallyl})_3\text{Co}$ (2)⁹ give relatively narrow resonances, which, in addition to ¹³C and ¹H NMR data, may be of central interest with respect to the nature of bonding in these complexes. The second part of this work deals with organocobalt(I) complexes of the general type $\text{Co}(\pi\text{-ligand})_n\text{R}$. These complexes may serve as catalysts, e.g., in hydroformylations (R = H, π -ligand = CO, $n = 4$)¹⁰ or in the trimerization of acetylenes and in the cocyclization of alkynes and nitriles (R = $\eta^5\text{-Cp}$, $(\pi\text{-ligand})_n = (\text{olefin})_2$ or $(\text{CO})_2$).¹¹ By varying R and the π -ligand, we hoped to find some simple trends governing the ⁵⁹Co shifts in these complexes and to be able to relate $\delta(^{59}\text{Co})$ to some of their chemical properties. A linear correlation between $\delta(^{59}\text{Co})$ of some substituted $\eta^5\text{-CpCoCOD}$ complexes^{12a} and their catalytic activity in the synthesis of pyridine derivatives has been reported previously.^{12b,c}

Experimental Section

Materials. The synthesis of pure $(\eta^3\text{-allyl})\text{Co}$ compounds 1 and 2 has been reported earlier,^{7a} and full details for the prep-

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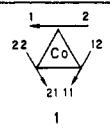
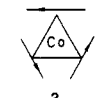
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Table I. 400-MHz ¹H and 100.6-MHz ¹³C NMR Data of 1 and 2^c

compd		1	2s	2a	11	12s	12a	21	22s	22a
 1	$\delta(^1\text{H})^a$	5.07	3.03	2.20	4.26	2.54	0.92	3.25	2.27	0.50
	$^3J_{\text{m,s}}^{\text{H}}$, Hz	6.8			6.9			6.8		
	$^3J_{\text{m,a}}^{\text{H}}$, Hz	12.0			11.9			12.0		
	$\delta(^{13}\text{C})^b$	100.48		51.31	99.00		46.92	100.30		43.78
	$^1J_{\text{C,H}}$, Hz	160.0		157.0	158.2		156.5	157.9		155.0
 2	$\delta(^1\text{H})^b$	(1.52)	2.48	1.45						
	$\delta(^{13}\text{C})^b$	110.54 (20.84)		50.35						
	$^1J_{\text{C,H}}$, Hz	(125.3)		156						

^a Solvent = toluene-*d*₆; *T* = 185 K. ^b Solvent = THF-*d*₆; *T* = 213 K. ^c m = meso proton; s = syn proton; a = anti proton. Data for the methyl group in parentheses.

aration of these complexes are given in ref 7b and 9. The synthesis of 3–5, 23, and 29–32 also has been described previously,¹³ and some of their NMR data have been already presented by these authors. Compounds 6, 12, 16, 17, and 18 have become available by reductive five-ring ligand abstraction. (This preparation technique is described in detail in ref 14 and 15.) These compounds are the starting materials for the preparation of 7–11, 13, 14, 22, 23, 26–29, 33, 36, 37, 40, 41, 43, and 44 which are obtained by the appropriate replacement reactions.¹⁶ The preparation of 10 and 11¹⁷ as well as 9, 22, 33, 36, and 41¹⁴ via this route has been carried out earlier. NMR data of the parent compound 6 are presented in ref 14c and 18. The preparation and characterization of 24 and 25 are described in ref 17, of 15 in ref 19, and of 21 in ref 20; 19 and 20 have been prepared by Bönnemann and co-workers (cf. ref 11d). The complexes 34, 35, 38, and 39 with substituents at the η⁴-bonded cyclohexadiene were obtained by treating the corresponding bis(ethylene)cobalt complexes with substituted acetylenes.¹⁵ Details of the preparation of these compounds as well as of the replacement products with indenyl and substituted cyclopentadienyl ligands and their full characterization by mass, ¹H NMR, and ¹³C NMR spectroscopy are given in the Ph.D. Thesis of K. Cibura.¹⁵ 45 was obtained from Li-(tmeda)₂Co(C₂H₄)₄,¹⁴ cycloheptatriene, and Me₃SiCl.¹⁵ The preparation of 42 has been reported recently.²¹

NMR Spectra. NMR spectra have been recorded on a WH 400 Bruker spectrometer equipped with a fast pulse programmer. All spectra were recorded under temperature control at the temperatures given in the tables. The proton spectra were obtained by using a selective probe head and sample tubes of 5-mm diameter. For the carbon-13 and cobalt-59 spectra the standard multinuclear 10-mm probe head was used for 5- and 10-mm

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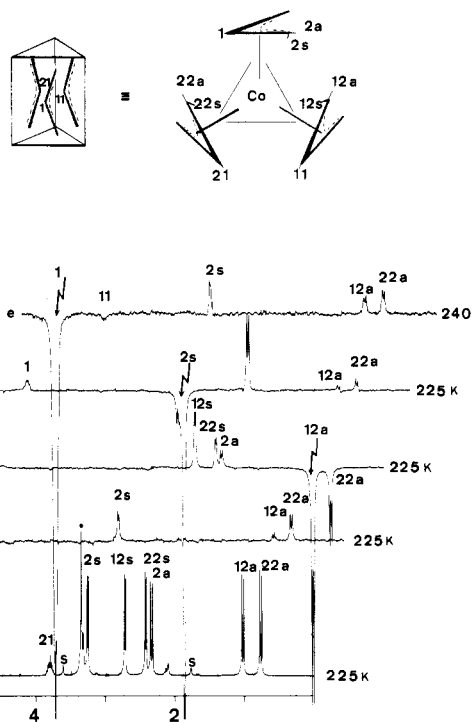


Figure 1. 400-MHz ¹H NMR spectra of 1 dissolved in a 1:1 mixture of THF-*d*₆ and toluene-*d*₆: (a) normal spectrum at *T* = 225 K and (b)–(e) magnetization transfer difference spectra. The arrows indicate the saturated multiplets and positive signals in (b)–(e) illustrate NOE enhancements, whereas the signals in emission indicate chemical exchange of the individual protons with those of the multiplet saturated.

sample tubes. For 1 and 41 two-dimensional NMR spectra²² were recorded. The 90° carbon pulse was 19 μs, and the proton pulse via the decoupler coil was 42 μs. The cobalt-59 90° pulse was 25 μs. All $\delta(^{59}\text{Co})$ shifts are given as δ values and referenced to K₃[Co(CN)₆] in D₂O at *T* = 310 K as external standard. Frequency changes due to different solvents were corrected by their ²H resonance frequencies when necessary. The ⁵⁹Co FID's were subjected to Lorentz gauss multiplication, and in some cases the first points of the FID's were set to zero in order to achieve an appropriate base line after the Fourier transformation.²³ Typical acquisition times were 0.001 s, and after zero filling in the transformed spectra the digital resolution varied between 1 and 20 Hz. The limits of error for $\delta(^{59}\text{Co})$ do not exceed ±10 ppm. The accuracy of the line widths is ±500 Hz.

MO Calculations. The parameters used in the extended Hückel calculations²⁴ are taken from earlier work.²⁵ The geometry

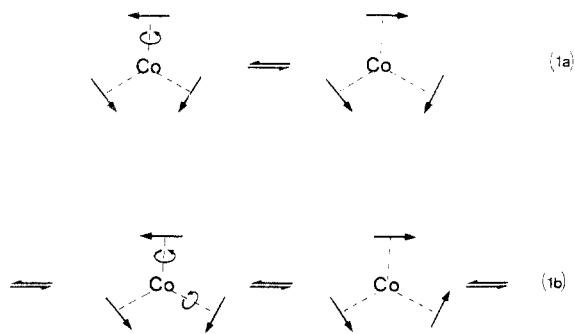
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of $\text{CpCo}(\text{CO})_2$ (46) was adapted from the experimental structure determination of $(\eta^5\text{-C}_5\text{Me}_5)\text{Co}(\text{CO})_2$ ²⁶ and that of $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{C}_2\text{H}_4)_2$ (6) was taken from X-ray structures of $\text{CpCo}(\text{C}_2\text{H}_4)_2$ itself and of $\text{CpCo}(\text{COD})$.²⁷ The (slightly idealized) values used are $\text{Co-C}_{\text{Cp}} = 208$ pm; C-C of Cp = 141 pm, (local D_{5h} symmetry for Cp); C-H of Cp = 108 pm; $\text{Co-C}_{\text{CO}} = 175$ pm; $\text{C-O} = 114$ pm; $\text{Co-C-O} = 180^\circ$; $\text{Co-C}_{\text{C}_2\text{H}_4} = 202$ pm; C-C of ethylene = 140 pm; C-H of ethylene = 108 pm, hydrogens "bent back"; C_s symmetry all over for 6 and 46.

Results

1. Organocobalt(III) Complexes. The structure and fluxional behavior of tris(η^3 -allyl)cobalt (1) and tris(η^3 -2-methylallyl)cobalt (2) could be fully deduced from their temperature-dependent ^1H and ^{13}C NMR spectra at 9.4 K. Some structural elements of 1 have been determined earlier from its conventional low-temperature ^1H NMR spectrum.^{7b} According to these results, Co has trigonal-prismatic coordination in 1. For simplification the structure of 1 may be illustrated by a triangle with Co in its center; the η^3 -coordination axis of the three allyl groups point to the metal and the terminal allyl carbon atoms are located above and below the coordination plane. Two of the allyl groups lie at the base of the triangle and the remaining one on its top. The three allyl groups are inequivalent but each of them is symmetrically η^3 -bonded to the metal. The detailed structure of 1 could be determined with the aid of ^1H NOE difference spectroscopy²⁸ at 400 MHz, by which the spatial neighborhood relations of the protons could be derived. The NOE effects (positive signals in the difference spectra b-e) of proton 1 with the anti proton 22a (trace b) as well as of the anti proton 12a with the anti proton 2a (trace c) confirm that the meso proton of the allyl groups at the base are directed toward one another. These observations also provide direct evidence for the upright arrangement of the allyl groups (cf. Figure 1) which was also favored from theoretical considerations.²⁹ At 225 K 1 is fluxional, as can be easily proven by the magnetization transfer of proton 12a with proton 22a (the negative signals confirm the slow exchange of their environments). Since there is no experimental indication for an exchange of the 2 syn with the 2 anti protons, the dynamic process can be rationalized to proceed by rotation of the top allyl group around the coordination axis (eq 1a).



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Table II. 94.5-MHz ^{59}Co NMR Shifts and Line Widths of Allylcobalt(III) Compounds

compd	no.	$\delta(^{59}\text{Co})$	$W_{1/2}$, Hz
$(\eta^3\text{-allyl})_3\text{Co}$	1 ^a	-796	3750
$(\eta^3\text{-2-methylallyl})_3\text{Co}$	2 ^b	-1306	13000
$(\eta^3\text{-allyl})(\eta^5\text{-Cp})\text{CoBr}$	3 ^c	+1050	10000
$(\eta^3\text{-allyl})(\eta^5\text{-Cp})\text{CoCH}_2\text{Ph}$	4 ^c	-455	11000
$(\eta^3\text{-allyl})(\eta^5\text{-Cp})\text{CoCH}_3$	5 ^c	-788	6600

^a $T = 223$ K. ^b $T = 243$ K; solvent, THF- d_6 . ^c $T = 310$ K; solvent, benzene- d_6 .

At higher temperatures ($T = 240$ K, trace e) a second fluxional process occurs as evidenced by the exchange of meso protons 1 with 11, indicating that all three allyl groups now become equivalent (eq 1b). There is no hint of an exchange of syn and anti protons in this process either. This behavior resembles the situation found in tris(η^3 -allyl)rhodium.³⁰ The ^{13}C NMR spectrum of 1 at -60°C is fully consistent with this interpretation: three triplets and three doublets are observed. These resonances were identified from the known proton assignment by help of a two-dimensional $^{13}\text{C}\{^1\text{H}\}$ correlation diagram.³¹ Additionally, in the low-temperature $^{13}\text{C}\{^1\text{H}\}$ spectrum of 1 two further signals at δ 52.34 (tr, $^1J(\text{C,H}) = 157$ Hz) and 102.37 (d, $^1J(\text{C,H}) = 161$ Hz) were detected.³²

For tris(η^3 -2-methylallyl)cobalt (2) only three resonances are observed in the low-temperature ^1H and ^{13}C spectra, indicating that the three ligands are equivalent and symmetrically bonded to Co. (In the low-temperature ^1H and ^{13}C NMR spectra ($T = 183$ K) there is no indication for an exchange process.) Probably 2 adopts the structure shown in eq 2 to avoid mutual steric hindrance of the



methyl substituents. For 1 and 2 ^{59}Co signals could be obtained at low temperatures (cf. Table II). The metal nucleus in 2 is ~ 500 ppm more shielded than that of 1. $\delta(^{59}\text{Co})$ of the Co complexes 1 and 2 lies close to the range which is usually covered by organocobalt(I) complexes (see below). The shifts of the $(\eta^3\text{-allyl})(\eta^5\text{-cyclopentadienyl})\text{CoR}$ complexes 3 ($R = \text{Br}$), 4 ($R = \text{CH}_2\text{Ph}$), and 5 ($R = \text{Me}$) vary over a large range. Apparently the decreasing acceptor capability of the σ -bonded substituent R leads to an increased shielding of the metal nucleus.

2. (Olefin)₂Co^IL Complexes. In this section the influence of substituents in the $(\text{olefin})_2\text{Co}^{\text{I}}\text{L}$ complexes upon their ^{59}Co shifts will be considered. First, $(\eta^5\text{-cyclopentadienyl})\text{Co}$ and $(\eta^5\text{-indenyl})\text{Co}$ moieties with different olefins will be presented. Second, variations at the $\eta^5\text{-cyclopentadienyl}$ ring will be followed by $\delta(^{59}\text{Co})$ while leaving the $(\text{ethylene})_2\text{Co}$ part unchanged.

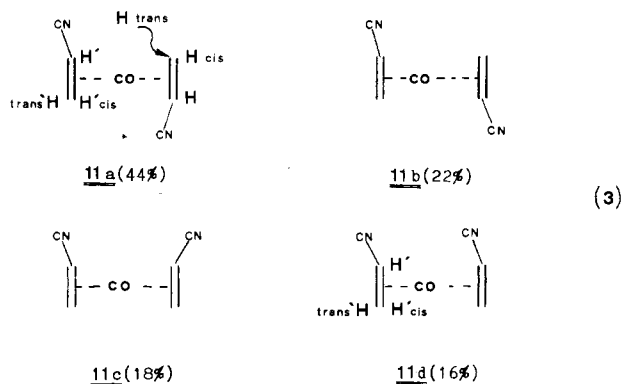
The ^{59}Co NMR parameters of the former group are listed in Table III. For 11, four of six possible isomers are present in solution as unequivocally deduced from its ^1H NMR spectrum using NOE difference spectroscopy.³³

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(b) For a recent review on two-dimensional ^1H - ^{13}C correlation spectroscopy, cf. ref 22b.

(32) These signals can be assigned to $(\eta^3\text{-allyl})_3\text{Co}$ with an C_{3v} structure analogous to that proposed for 2. Assignment of the corresponding proton signals of that minor component of 1 and the study of a possible exchange between these two isomers of 1 was not carried out, due to the low concentration ($\leq 1\%$) of the minor isomer.



co = CoCp

In the ⁵⁹Co spectrum of 11 only one broad line was observed. The ⁵⁹Co NMR parameters of 6–11 indicate that δ(⁵⁹Co) seems to be insensitive to the type of substituent on the olefin. For 6 and 12 solvent effects on δ(⁵⁹Co) could not be detected. The δ(⁵⁹Co) shifts are, however, altered by a constant amount of ~360 ppm when the η⁵-Cp ligand is replaced by a η⁵-indenyl ligand (compare 6, 7, and 9 with 12–14, respectively). Apparently, substituents within this part of the half sandwich complexes produce larger effects upon δ(⁵⁹Co). The relatively low shielding of complex 15 may be due to the 16-electron configuration of the metal. Electron-donating groups at Cp like methyl produce a significant stronger shielding of the cobalt nucleus.

3. (η⁴-1,3-Diene)Co^IL Complexes. The influence of the olefins on δ(⁵⁹Co) will be considered in more detail taking into account η⁴-bonded 1,3-dienes (cf. Table V). Just as found for (olefin)₂(η⁵-Cp)Co complexes, there are no significant changes in δ(⁵⁹Co) when the diene is alkyl substituted. According to its preparation by coupling of a vinyl and an allyl group,^{13b} 23 is obtained as a mixture of isomers. The ¹H and ¹³C NMR spectra show that the methyl group is in the syn position (75%) and in the anti position (25%) at C₁ of the diene. These isomers cannot be detected separately by ⁵⁹Co NMR. It must be also noted that our values for 22 differ markedly from what has been published previously.^{12a} Again, replacement of Cp by indenyl leads to a deshielding of the ⁵⁹Co nucleus in the same order as observed for bis(olefin) complexes.

In order to study the dependence of δ(⁵⁹Co) upon the steric prerequisites of the overlap of the metal orbitals with those of the olefins, complexes of several cyclic dienes were investigated. ⁵⁹Co NMR parameters of the corresponding complexes with η⁴-bonded 1,3-diene systems in five- to seven-membered rings are listed in Table VI. A simple correlation between δ(⁵⁹Co) and ring size cannot be detected. Both electron-withdrawing and -donating substituents at the diene produce an increase of δ(⁵⁹Co) (cf. 33, 34, and 37–39). The introduction of double bonds in conjugation to the diene (cf. 35, 36, 41–44) yields the same effect.

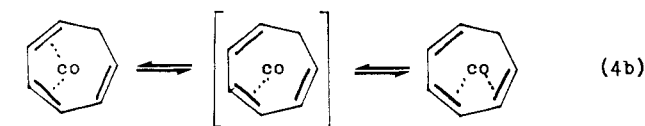
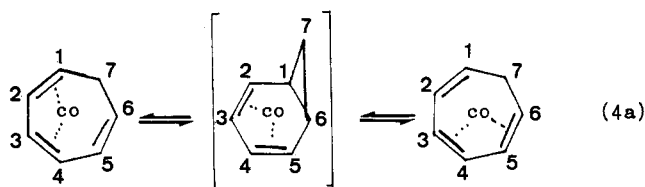
Just like 1 (cf. Figure 1) and 6,¹⁸ complex 41 is fluxional, as revealed by 2D chemical exchange spectroscopy at 310 K (cf. Figure 2).³⁴ According to this spectrum there is

Table III. 94.5-MHz ⁵⁹Co NMR Shifts and Line Widths of (Olefin)₂Co^IL Compounds (L = η⁵-Cyclopentadienyl or η⁵-Indenyl)^d

compd	no.	δ(⁵⁹ Co)	W _{1/2} , Hz
(η ⁵ -Cp)Co-	6 ^{a, b}	-1235 ^a -1231 ^b	6800 7000
(η ⁵ -Cp)Co-	7 ^c	-1109	8550
(η ⁵ -Cp)Co-	8 ^b	-1102	9750
(η ⁵ -Cp)Co-	9 ^{a, b}	-1178 ^a -1190 ^b	9150
(η ⁵ -Cp)Co-	10 ^c	-1229	9300
(η ⁵ -Cp)Co-	11 ^b	-1089	12 400
(η ⁵ -indenyl)Co-	12 ^a	-879	19 200
(η ⁵ -indenyl)Co-	13 ^{a, b}	-756 ^a -747 ^b	9750 10 500
(η ⁵ -indenyl)Co-	14 ^{a, b}	-849 ^a -851 ^b	9450 7700
(η ⁵ -indenyl)Co-	15 ^b	-275	3700

^a Solvent = THF-d₃. ^b Solvent = toluene-d₆. ^c Solvent = benzene-d₆. ^d T = 310 K unless for 12 (T = 253 K).

chemical exchange of carbons 1 with 6, 2 with 5, and 3 with 4. The methylene carbon 7 is not involved in the process. This behavior can be rationalized as proceeding via a series of two consecutive 1,2 shifts involving a norcaradiene intermediate³⁵ (cf. eq 4a) or via 1,3 shifts and also by a dissociation process with a 16-electron intermediate (eq 4b). Such mechanisms have also been encountered and



co = (η⁵-Cp)Co

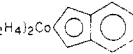
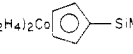
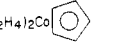
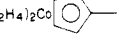
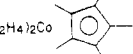
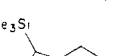


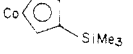

discussed in the dynamic NMR spectra of (CO)₃FeC₇H₈.³⁵ For our purposes it is essential that in 41 the rate constant for the exchange process is slow at T = 310 K (k ≤ 10⁻¹s⁻¹)

(33) In analogy to (η⁵-Cp)Rh(CH₂=CHF)₂, Cramer, R.; Reddy, G. S. *Inorg. Chem.* 1973, 12, 346, six isomers for 11 are possible; however, by ¹H NMR spectroscopy only four could be detected. In contrast to the ⁵⁹Co NMR data the 400-MHz ¹H NMR data of 11a–d differ significantly from one another: 11a, δ(H_{trans}) 3.77, δ(H_{trans}) 1.91, and δ(C₂H) 2.78, δ(H_{cis}) 1.74, δ(H_{trans}) 3.75, and δ(C₂H) 0.87; 11b, δ(H_{cis}) 2.22, δ(H_{trans}) 3.84, and δ(C₂H) 0.49; 11c, δ(H_{cis}) 1.25, δ(H_{trans}) 3.18, and δ(C₂H) 1.40; 11d, δ(H_{cis}) 3.36, δ(H_{trans}) 0.92, and δ(C₂H) 3.25, δ(H_{cis}) 1.83, δ(H_{trans}) 3.42, and δ(C₂H) 0.96 (T = 269 K; solvent, THF-d₃).

(34) (a) Meier, B. H.; Ernst, R. R. *J. Am. Chem. Soc.* 1979, 101, 6441. (b) Huang, Y.; Macura, S.; Ernst, R. R. *J. Am. Chem. Soc.* 1981, 103, 6327. (c) Benn, R. *Angew. Chem.* 1982, 94, 633; *Angew. Chem., Int. Ed. Engl.* 1982, 21, 626. (d) Cf. ref 22b.




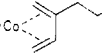
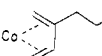
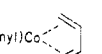
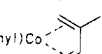
(35) (a) Li Shing Mau, L. K. K.; Takats, J. *J. Organomet. Chem.* 1976, 117, C104. (b) Karel, K. J.; Brookhart, M. *J. Am. Chem. Soc.* 1978, 100, 1619. (c) Mann, B. E. *J. Organomet. Chem.* 1977, 141, C33. (d) Karel, K. J.; Albright, T. A.; Brookhart, M. *Organometallics* 1982, 1, 419.

Table IV. 94.5-MHz ^{59}Co NMR Shifts and Line Widths of (Ethylene) $_2\text{Co}^{\text{I}}\text{L}$ and (Cycloocta-1,5-diene) $\text{Co}^{\text{I}}\text{L}$ Compounds (L = η^5 -Cyclopentadienyl Derivatives)^c

compd	no.	$\delta(^{59}\text{Co})$	$W_{1/2}$, Hz
	12 ^a	-879	19 200
	16 ^b	-1187	10 200
	6 ^a	-1235	6800
	17 ^b	-1294	7350
	18 ^b	-1470	9900
	19 ^b	-658	14 000
	14 ^b	-851	7650
	20 ^b	-1170	11 100
	9 ^b	-1190	6300
	21 ^b	-1284	8400

^a Solvent = THF-*d*₈. ^b Solvent = toluene-*d*₈. ^c *T* = 310 K unless for 12 (*T* = 253 K).

Table V. 94.5-MHz ^{59}Co NMR Shifts and Line Widths of (η^4 -1,3-Diene) $\text{Co}^{\text{I}}\text{L}$ Compounds (L = η^5 -Cp and η^5 -Indenyl)^d

compd	no.	$\delta(^{59}\text{Co})$	$W_{1/2}$, Hz
	22 ^{a, c}	-1620 ^a -1625 ^c	8650 8100
	23 ^c	-1571	10 200
	24 ^c	-1567	10 400
	25 ^c	-1601	14 400
	26 ^a	-1234	11 200
	27 ^b	-1180	11 400
	28 ^b	-1230	12 600

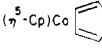
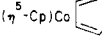
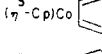
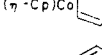
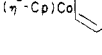
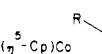
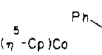

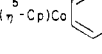
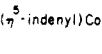

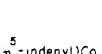

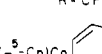
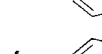
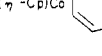
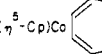
^a Solvent = THF-*d*₈. ^b Solvent = toluene-*d*₈. ^c Solvent = benzene-*d*₆. ^d *T* = 310 K.

and consequently this process cannot affect the ^{59}Co shifts.

Discussion

Although the line widths of organocobalt complexes are large (between 10 000 and 20 000 Hz at *T* = 310 K and 94.5 MHz), ^{59}Co NMR has relevant chemical applications since the shifts are spread over a large frequency range. As found for many metal resonances,³ an empirical correlation between the formal oxidation state of the metal and $\delta(^{59}\text{Co})$ also for the organocobalt complexes 1–45 can be established. The $\delta(^{59}\text{Co})$ values of the 18-electron organo-

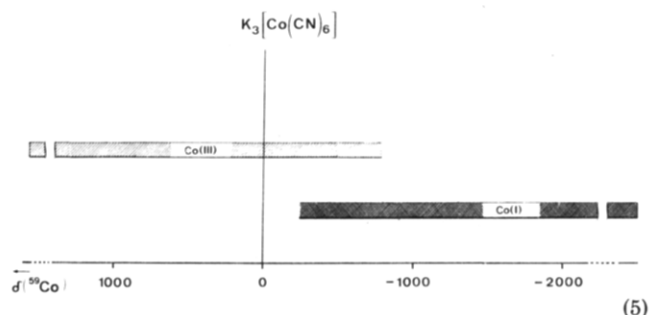
Table VI. 94.5-MHz ^{59}Co NMR Shifts and Line Widths of Cyclic (η^4 -1,3-Diene) $\text{Co}^{\text{I}}\text{L}$ Complexes^d (L = Ligand)

compd	no.	$\delta(^{59}\text{Co})$	$W_{1/2}$, Hz
	29 ^c	-1439	9600
	30 ^c	-1640	16 800
	31 ^c	-1627	16 800
	32 ^c	-1560	18 750
	33 ^b	-1820	13 000
	34 ^b	-1726	14 400
R = CF ₃			
	35 ^b	-930	18 800
	36 ^b	-1243	7600
	37 ^a	-1443	11 600
	38 ^b	-1275	18 000
R = CH ₃			
	39 ^b	-1236	13 000
R = CF ₃			
	40 ^b	-1400	10 100
	41 ^a	-1319	10 500
	42 ^b	-1319	20 000
	43 ^b	-1282	13 200
	44 ^a	-899	12 400
	45 ^b	-1036	12 500

^a Solvent = THF-*d*₈. ^b Solvent = toluene-*d*₈. ^c Solvent = benzene-*d*₆. ^d *T* = 310 K unless for 35 (*T* = 353 K).

cobalt(III) complexes 1–5 cover a range of more than 2000 ppm, and their shifts are centered around the standard (eq 5).

Organocobalt(I) complexes cover a similar range around -1800 ppm. Although these individual regions are partly overlapping, the relative high shielding of cobalt in the allyl compounds 1 and 2 is striking. The high shielding of the



(5)

metal in these cases may be rationalized with the help of a simple qualitative MO diagram, adopted from the corresponding interaction diagram for $(\eta^2\text{-C}_2\text{H}_4)_3\text{Ni}$ in the literature²⁹ (cf. Figure 3). According to these considerations, the highest filled orbital (a_2'' in D_{3h} ($\text{C}_2\text{H}_4)_3\text{Ni}$, for $(\eta^3\text{-allyl})_3\text{Co}$ only C_s or C_{3h} is possible, but, of course, pseudo- D_{3h} symmetry still is preserved) of 1 has mainly ligand character (Ψ_2 of allyl). The five orbitals lying below the HOMO are primarily 3d in composition. Therefore, 1 and 2 in a sense approach a d^{10} electron count, which produces a partial charge at Co, which, certainly, is smaller than in normal Co(III) complexes. Similar and still more pronounced effects have been found for $\delta(^{103}\text{Rh})$ in $(\eta^3\text{-allyl})_3\text{Rh}$,³⁶ $\delta(^{195}\text{Pt})$ in $(\eta^3\text{-allyl})_2\text{Pt}$,³⁷ and $\delta(^{25}\text{Mg})$ in $(\eta^5\text{-Cp})_2\text{Mg}$.³⁸ In the absence of detailed knowledge of the changes in the mean excitation energy ΔE , the significantly larger shielding of 2 cannot be explained within this qualitative scheme. The higher shielding of cobalt in 2 does, however, correlate with its higher thermal stability (compared with 1).

In the following section the influence of ligands upon $\delta(^{59}\text{Co})$ in Co(I) compounds will be discussed. Besides olefins, also phosphine and CO ligands will be considered. If one *exo*-methylene cyclopropane molecule in 10 is replaced by a triphenylphosphine ligand,³⁹ the metal becomes ~ 400 ppm more shielded. When both the ethylene molecules in 6 are replaced by cyclobutadiene or two CO ligands, $\delta(^{59}\text{Co})$ is -2880 and -2675 ppm, respectively.⁴⁰ In the latter complex the shielding seems to be governed by the CO ligands rather than by the $\eta^5\text{-Cp}$ moiety since its replacement by indenyl produces only a deshielding of 170 ppm (in contrast to the effect of $\eta^5\text{-indenyl}$ in 12–14 or 23–25). These findings indicate that in the series of the 18-electron Co(I) complexes the interpretation of the $\delta(^{59}\text{Co})$ shifts solely on the basis of charge density changes at Co is ambiguous since CO and cyclobutadiene both are fairly good π -acceptors. We therefore performed comparative model MO calculations⁴¹ for $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{C}_2\text{H}_4)_2$ (6) and $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{CO})_2$ (46) on the extended Hückel level. The results for both compounds are illustrated in

(36) Benn, R.; Brenneke, H.; Reinhardt, R. D. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.*, in press.

(37) Benn, R.; Reinhardt, R. D.; Ruffińska, A. *J. Organomet. Chem.* 1985, 282, 291.

(38) Benn, R.; Lehmkühl, H.; Mehler, K.; Ruffińska, A. *Angew. Chem.* 1984, 96, 521; *Angew. Chem., Int. Ed. Engl.* 1984, 23, 534.

(39) For the preparation of $(\eta^5\text{-cyclopentadienyl})(\eta^2\text{-exo-methylene-cyclopropane})(\text{triphenylphosphine})\text{Co}$: cf. ref 17. $\delta(^{59}\text{Co})$ of this compound, dissolved in benzene- d_6 , is -1633 ($W_{1/2} = 14000$ Hz).

(40) $\delta(^{59}\text{Co})$ of $(\eta^5\text{-Cp})\text{Co}(\text{CO})_2$ is -2675 ,³ $\delta(^{59}\text{Co})$ of $(\eta^5\text{-indenyl})\text{Co}(\text{CO})_2$ ¹⁵, dissolved in toluene- d_8 , is -2496 ($W_{1/2} = 10800$ Hz). The $\delta(^{59}\text{Co})$ value of $(\text{CO})_3\text{Co}(1\text{-}\eta^3\text{-}\eta^2\text{-}(\text{trimethylsilyl})\text{cyclooctenyl})$ is -2405 ($W_{1/2} = 12200$ Hz) at 343 K. The $\delta(^{59}\text{Co})$ shift of $(\eta^4\text{-cyclobutadiene})(\eta^5\text{-Cp})\text{Co}$ has been reported for the first time by Egolf and v. Philipsborn: cf. ref 12a.

(41) Separate descriptions of the basic electronic structures of 46 and 6 have been given earlier: Hofmann, P. *Angew. Chem.* 1977, 89, 551; *Angew. Chem., Int. Ed. Engl.* 1977, 16, 536. Lichtenberger, D. L. Calabro, D. C.; Kellogg, G. E. *Organometallics* 1984, 3, 1623. Albright, T. A.; Geiger, W. E.; Moraczewski, J.; Tulyathan, B. *J. Am. Chem. Soc.* 1981, 103, 4787.

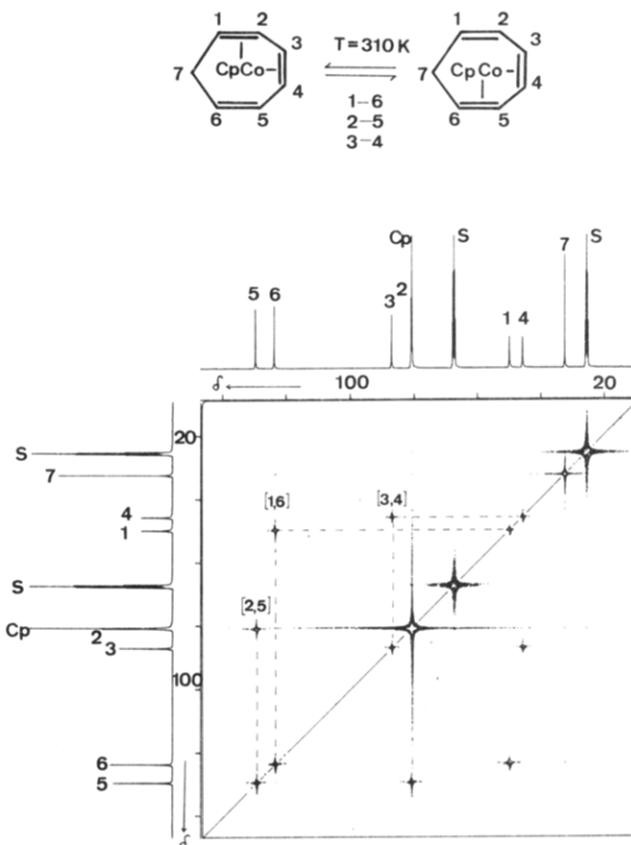


Figure 2. 100.6-MHz ¹³C spectra of 41. The traces on the horizontal and vertical present the conventional one-dimensional ¹³C{¹H} spectrum. The contour plot results from a two-dimensional exchange spectrum. In this presentation the chemical shifts of the carbons of 41 lie on the diagonal. The off-diagonal cross peaks are connected with their corresponding diagonal peaks by broken lines; they give proof of chemical exchange of the respective carbon atoms (S = solvent, THF-*d*₈).

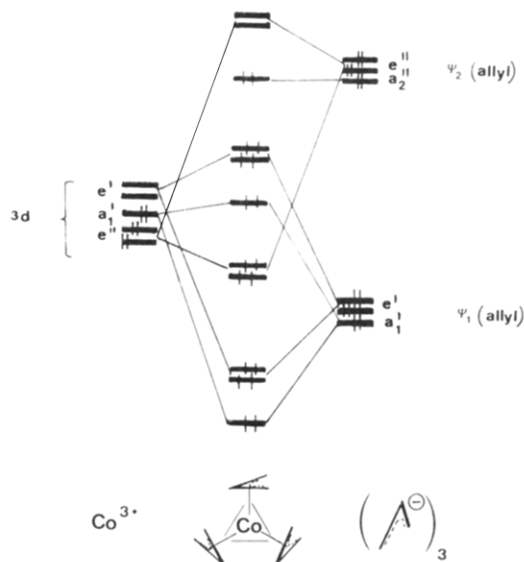


Figure 3. Schematic interaction diagram for $(\eta^3\text{-allyl})_3\text{Co}$, assuming pseudo- D_{3h} geometry, adopted from the case of $(\eta^2\text{-C}_2\text{H}_4)_3\text{Ni}$ in ref 29. The D_{3h} symmetry labels are used although the actual symmetry of 1 is lower.

Figure 4. The familiar fragment MO levels $1e-2a_1$ of CpCo are given in the middle of the diagram—they have been described in detail elsewhere⁴¹ and need not be discussed. For the complexes 6 (left) and 46 (right) the dominant interactions of CpCo and two ethylene or two carbonyl ligands, respectively, occur between the half-filled $2e$ set

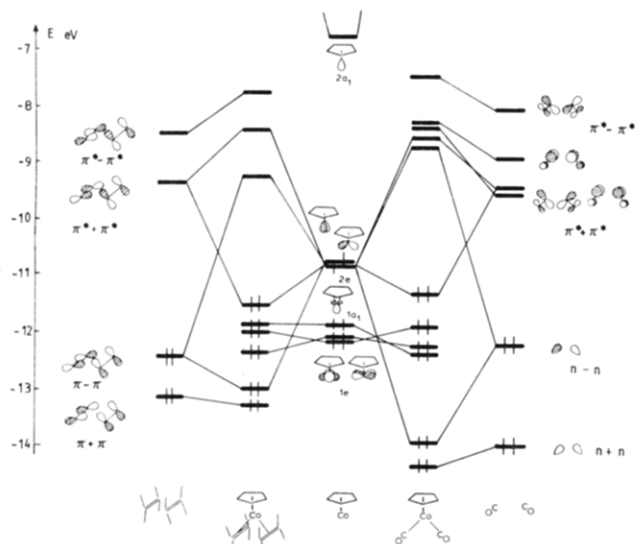


Figure 4. Comparative interaction diagram for $\text{CpCo}(\text{C}_2\text{H}_4)_2$, **6** (left), and $\text{CpCo}(\text{CO})_2$, **46** (right), from EH-MO calculations. Only relevant parts of the fragment MO wave functions of CpCo , C_2H_4 , and CO are shown.

of $\text{CpCo}(xz, yx)$ and the appropriate linear combination of filled and empty ligand MOs ($n_{\text{CO}}-n_{\text{CO}}$, $\pi-\pi$, $\pi_{\text{CO}}^* + \pi_{\text{CO}}^*$, $\pi^* + \pi^*$). The HOMO in both cases is yz at CpCo , stabilized by back-bonding. The LUMO is xz , destabilized by antibonding interactions with n_{CO} of carbonyl and π -levels of the ethylene units. Due to the much better directional (σ -type, single center) character of the CO donor orbitals, the LUMO of $\text{CpCo}(\text{CO})_2$ appears at higher energy than that of $\text{CpCo}(\text{C}_2\text{H}_4)_2$, where the corresponding overlap occurs between xz and $(\pi-\pi)$, less directional, and again of σ -type toward the two center C_2H_4 system. The highest occupied orbitals of both systems are less different in energy, and, consequently, the HOMO/LUMO gap is 0.31 eV smaller in **6** than in **46**.

Moreover, the LUMO of **6** has a much higher Co (and CpCo) contribution to the wave function,⁴² whereas the metal charges are very similar. The important results from the calculation are given in Table VII. In terms of a possible paramagnetic shielding contribution to the $\delta(^{59}\text{Co})$ shifts of **6** and **46**, the results support the assumption that in a series of $\text{CpCo}(\pi\text{-ligand})_2$ complexes the shifts are strongly influenced, or even dominated, by the paramagnetic shielding term and, in particular, by its $1/\Delta E$ dependence. If we refer to the correlation between $\delta(^{59}\text{Co})$ and $1/\Delta E$ as it has been established earlier for octahedral $\text{Co}(\text{III})$ complexes,^{4,5} a 1 ppm downfield shift of $\delta(^{59}\text{Co})$ on the average corresponds to a decrease of ΔE by ca. 2 cm^{-1} ($0.24 \cdot 10^{-3} \text{ eV}$). Since in **46** cobalt is 1448 ppm more shielded than in **6**, this would correspond to an increase of 0.35 eV for ΔE in **46**, which agrees surprisingly well with the calculated value of 0.31 eV.

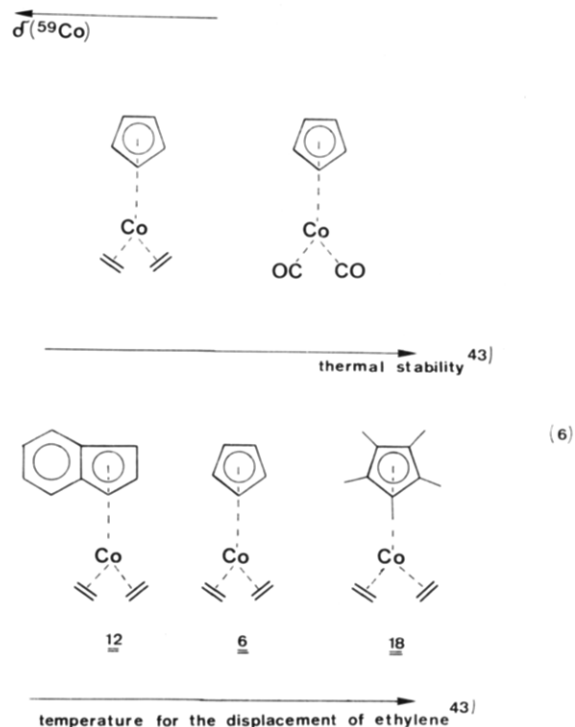
Within a sequence of homologous half-sandwich compounds where only substituents at the π -ligands are introduced the variations of $\delta(^{59}\text{Co})$ are smaller. Methyl as well as CF_3 substituents produce a deshielding of the cobalt nucleus (cf. **37-39**). On the other hand, electron-donating substituents at the $(\eta^5\text{-Cp})$ moiety produce an increased shielding of the metal nucleus, in contrast to electron-withdrawing substituents.¹² Since these substituents effects on cobalt shielding are small (≤ 400 ppm, the only exception is **35**), we regard this as due to second-order

(42) Note that a higher Co contribution to the LUMO wave function is also of importance with respect to the paramagnetic shielding of the Co nucleus.

Table VII. MO Results for $\text{CpCo}(\text{C}_2\text{H}_4)_2$ (6**) and $\text{CpCo}(\text{CO})_2$ (**46**)**

	$\text{CpCo}(\text{C}_2\text{H}_4)_2$ (6)	$\text{CpCo}(\text{CO})_2$ (46)
metal charge	+0.386	+0.361
energy of HOMO, eV	-11.54	-11.38
energy of LUMO, eV	-9.28	-8.81
HOMO-LUMO gap, eV	2.26	2.57
composition of wave functions		
HOMO		
% Co	34	38
% CpCo	70	72
% yz	24	28
LUMO		
% Co	50	26
% CpCo	83	48
% xz	50	22

effects. Consequently, at this stage, an interpretation of the ^{59}Co shifts on the basis of steric and charge density effects is not attempted. From the arguments given above we conclude that the ^{59}Co shifts in the $(\eta^5\text{-Cp})\text{Co}^I$ complexes are mainly governed by their HOMO/LUMO energy difference via the paramagnetic shielding term. If $\delta(^{59}\text{Co})$ correlates to the energy gap between the frontier orbitals of $(\eta^5\text{-Cp})\text{Co}^I$ complexes which in turn depends on the strength of ligand-metal interactions, it is no longer surprising that the chemical shifts of these compounds may serve as an indicator for complex properties (cf. **6**). In



fact within a series of related complexes⁴⁴ their thermal

(43) In the case of neat compounds comparable degrees of decomposition are observed when **12** is exposed to 10°C , **6** to 50°C , and **18** to 150°C , respectively, while **46** at 710 mmHg can be distilled at $139\text{-}140^\circ\text{C}$ (cf. Fischer, E. O.; Jira, R. Z. *Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* 1955, **10B**, 355). Also the temperatures required for the replacement of the ethylenes by other π -ligands increase in the order **12**, **6**, and **18**. For a discussion of the "indenyl effect" cf., e.g.: Rerek, M. E.; Ji, L.-N.; Basolo, F. *J. Chem. Soc., Chem. Commun.* 1983, 1208. Ji, L.-N.; Rerek, M. E.; Basolo, F. *Organometallics* 1984, **3**, 740.

(44) Note that **9** has a similar $\delta(^{59}\text{Co})$ shift as **6**, but **9** has a much higher thermal stability than **6**. This can be attributed to the chelating character of the cycloocta-1,5-diene ligand. Apparently, simple correlations between $\delta(^{59}\text{Co})$ and chemical properties only hold for a series of related compounds (cf. eq 6).

stability as well as the temperature for the replacement of ethylene follows the same order as the shielding of the cobalt nucleus.

Conclusion

It has been shown that despite of their large line width, the large shift range of ^{59}Co resonances in organocobalt complexes enables relevant chemical information to be obtained from ^{59}Co NMR spectra. In organocobalt(I) complexes with π -ligands $\delta(^{59}\text{Co})$ seems to be governed by the paramagnetic shielding term and its $1/\Delta E$ dependence. The ^{59}Co shielding then can be rationalized by changes of the energy gap between the frontier levels of the complexes when olefins of variable donor and acceptor properties are bound to CpCo. Within this concept $\delta(^{59}\text{Co})$ may be used

as an indication of relative chemical stability, at least within a series of closely related compounds.

Registry No. 1, 12082-45-0; 2, 12295-18-0; 3, 86900-89-2; 4, 94792-00-4; 5, 94791-96-5; 6, 69393-67-5; 7, 98704-25-7; 8, 98704-26-8; 9, 12184-35-9; 10, 98704-27-9; 11, 98704-28-0; 12, 98704-29-1; 13, 98704-30-4; 14, 84180-58-5; 15, 34829-55-5; 16, 98704-31-5; 17, 98704-32-6; 18, 80848-36-8; 19, 88228-63-1; 20, 84180-59-6; 21, 98704-33-7; 22, 1271-08-5; 23 (isomer 1), 98704-34-8; 23 (isomer 2), 98757-91-6; 24, 98704-35-9; 25, 93058-42-5; 26, 98704-36-0; 27, 98704-37-1; 28, 98704-38-2; 29, 33032-03-0; 30, 98704-39-3; 31, 79160-70-6; 32, 94791-70-5; 33, 38959-22-7; 34, 98704-40-6; 35, 55518-03-1; 36, 86900-88-1; 37, 98704-41-7; 38, 98704-42-8; 39, 98704-43-9; 40, 70210-70-7; 41, 78318-94-2; 42, 77070-14-5; 43, 98704-44-0; 44, 98704-45-1; 45, 98704-46-2; 46, 12078-25-0; ^{59}Co , 7440-48-4.

Communications

Stereochemical and Electrochemical Analyses of the Cyclopentadienyl and Methylcyclopentadienyl Dinitrosyl-Capped Tricobalt Analogues, $\text{Co}_3(\eta^5\text{-C}_5\text{H}_{5-x}\text{Me}_x)_3(\mu_3\text{-NO})_2$ (Where $x = 0, 1$), of the Classical Fischer-Palm $\text{Ni}_3(\eta^5\text{-C}_5\text{H}_5)_3(\mu_3\text{-CO})_2$

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Summary: The slow addition of $\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2$ to a photolyzed THF solution of the Fe-Fe double-bonded $\text{Fe}_2(\eta^5\text{-C}_5\text{H}_5)_2(\mu_2\text{-NO})_2$ unexpectedly afforded $\text{Co}_3(\eta^5\text{-C}_5\text{H}_5)_3(\mu_3\text{-NO})_2$ (**1**) in 3–5% yield. This 48-electron cluster (previously isolated and spectroscopically characterized) and its methylcyclopentadienyl derivative (**2**) were found from single-crystal X-ray diffraction analyses to possess analogous $\text{Co}_3(\text{NO})_2$ cores of D_{3h} — $3/m2m$ geometry (exact for **1** and ideal for **2**). Both **1** and **2** were shown from CV measurements to possess similar reversible electron-transfer properties with each neutral parent undergoing a one-electron oxidation to its 47-electron monocation and a one-electron reduction to its 49-electron monoanion.

As a part of our research involving the rational synthesis of triangular metal clusters with triply bridging nitrosyl ligands^{2,3} via metal fragment addition to the Fe-Fe dou-

ble-bonded $\text{Fe}_2(\eta^5\text{-C}_5\text{H}_5)_2(\mu_2\text{-NO})_2$,⁴ a photochemical reaction of the iron nitrosyl dimer with $\text{Co}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2$ was carried out. The anticipated cycloaddition product, the (as yet) unknown $\text{Fe}_2\text{Co}(\eta^5\text{-C}_5\text{H}_5)_3(\text{CO})(\text{NO})_2$ which is an isolobal analogue of $\text{Co}_3(\eta^5\text{-C}_5\text{H}_5)_3(\text{CO})_3$,⁵ was not obtained; instead, this reaction gave a small quantity of $\text{Co}_3(\eta^5\text{-C}_5\text{H}_5)_3(\mu_3\text{-NO})_2$ (**1**). This cobalt-dinitrosyl 48-electron analogue of the classical Fischer-Palm 49-electron $\text{Ni}_3(\eta^5\text{-C}_5\text{H}_5)_3(\mu_3\text{-CO})_2$ ⁶ was originally prepared by Müller and Schmidt⁷ via the thermolysis of $\text{Co}_2(\eta^5\text{-C}_5\text{H}_5)_2(\mu_2\text{-NO})_2$ in THF and was characterized by them from ¹H NMR, IR, and mass spectral data. In light of our structural-bonding-electrochemical investigations of the interrelated $[\text{Ni}_3(\eta^5\text{-C}_5\text{H}_{5-x}\text{Me}_x)_3(\mu_3\text{-CO})_2]^n$ series ($x = 0, 1, 5; n = 1+, 0, 1-$),⁶ the corresponding $[(\eta^5\text{-C}_5\text{Me}_5)\text{CoNi}_2(\eta^5\text{-C}_5\text{H}_5)_2(\mu_3\text{-CO})_2]^n$ series ($n = 0, 1-$)^{6c,d} the $[\text{Co}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-CO})_2]^n$ series ($n = 0, 1-$),⁸ the $[\text{Co}_3(\eta^5\text{-C}_5\text{H}_{5-x}\text{Me}_x)_3(\mu_3\text{-CO})(\mu_3\text{-NH})]^n$ series ($x = 0, 1; n = 2+, 0, 2-$),⁹ and the $[\text{Co}_3(\eta^5\text{-C}_5\text{H}_4\text{Me})_3(\mu_3\text{-NO})(\mu_3\text{-NH})]^n$ series ($n = 1+, 0$)⁹, we presumed that **1** should also possess reversible redox behavior. Herein are presented the X-ray crystallographic

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(3) "Synthesis, Structural Characterization, and Chemical-Electrochemical Activity of $(\eta^5\text{-C}_5\text{H}_4\text{Me})\text{MnFe}_2(\eta^5\text{-C}_5\text{H}_5)_2(\mu_3\text{-NO})(\mu_2\text{-NO})(\mu_2\text{-CO})_2$: The Rational Synthesis of a Mixed-Metal Cluster System Containing A Triply Bridging Nitrosyl Ligand", submitted by: Kubat-Martin, K. A.; Dahl, L. F. for presentation at the 190th National Meeting of the American Chemical Society, Chicago, IL, Sept 1985; American Chemical Society: Washington, D.C., 1985.