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Cotton Effect-Configuration Relationships in Mixed-Ligand Cobalt(III) Complexes. I. The Series $[\text{Co}(\beta\text{-diketonate})_n(\text{en})_{3-n}]^{3-n}$ and $[\text{Co}(\beta\text{-diketonate})_n((S)\text{-}\alpha\text{-amino acidate})_{3-n}]$

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Circular dichroism spectra of two series of mixed-ligand complexes, $[\text{Co}(\beta\text{-diketonate})_n(\text{en})_{3-n}]^{3-n}$ and $[\text{Co}(\beta\text{-diketonate})_n((S)\text{-}\alpha\text{-amino acidate})_{3-n}]$ where $n = 0-3$, are analyzed in an effort to ascertain the validity of an often-used Cotton effect-configuration rule for assigning absolute configurations to mixed-ligand complexes of low symmetry. CD spectra of the intermediate members ($n = 1, 2$) of both series can be related to those of the terminal members ($n = 0, 3$), for which Cotton effect-configuration relationships are known, if reasonable assumptions are made regarding (1) the energy separation of ligand field terms and (2) the contribution of vicinal effects of chiral ligands. Absolute configurations of the mixed-ligand complexes containing (S)- α -amino acidate ligands assigned from CD results agree in all cases with configurations assigned independently from analysis of anisotropic shielding in proton nmr spectra.

One of the most convenient methods of deducing relative or absolute configurations of dissymmetric coordination compounds is through analysis of Cotton effects in the region of ligand field transitions.²⁻⁷ Although theoretical treatments of Cotton effect-configuration relationships are not generally satisfactory at present, some empirical relationships have been established for tris-bidentate complexes of cobalt(III) by a combination of X-ray structural determinations,⁸⁻¹¹ investigations of single-crystal polarized spectra,^{12,13} and solution CD studies.^{2-7,10,14-16} The low-energy, magnetic dipole allowed octahedral ligand field transition is split into two transitions, A_2 and E, in D_3 symmetry (or A and E in C_3 symmetry) and into three transitions, A + 2 B, in C_2 symmetry. An empirical rule which applies at least to tris(β -diketonato)cobalt(III), tris(1,2-diamine)cobalt(III), and

tris((S)- α -amino acidato)cobalt(III) complexes may be stated as follows. A stereoisomer has the Λ^{17} configuration with respect to its C_3 or pseudo- C_3 ¹⁸ axis if the Cotton effect for the E transition is positive and that for the A_2 or A transition (if it is apparent) is negative. Use of this rule in configurational assignments requires that these transitions be identifiable in the ORD or CD spectra. They are generally not resolved in absorption spectra. The E transition has by far the larger CD in cases where it has been identified by single-crystal polarization studies, and it has been assigned to the predominant CD band in numerous tris-bidentate and mixed-ligand complexes of cobalt(III).²⁻⁷

The energy order of the A and E transitions has been shown to be $E < A$ for the 1,2-diamine complexes from single-crystal polarization¹² and magnetic CD studies.¹⁹ This order is believed to hold true also for the amino acidate complexes based on the relative magnitudes of the CD bands.¹⁵ However the order is $E > A$ for tris(β -diketonate) complexes.¹³ In view of this energy reversal it was of interest to ascertain whether the above empirical rule could be used for making configurational assignments in mixed-ligand complexes of the types $[\text{Co}(\beta\text{-diketonate})_2(L)]^{0,+}$ and $[\text{Co}(\beta\text{-diketonate})(L)_2]^{0,2+}$, where L is an (S)- α -amino acid anion or a 1,2-diamine. This paper summarizes the Cotton effect-configuration relationships established previously for the series $[\text{Co}(\beta\text{-diketonate})_n(\text{en})_{3-n}]^{3-n}$ and presents previously unpublished data concerning the series $[\text{Co}(\beta\text{-diketonate})_n((S)\text{-}\alpha\text{-amino acidate})_{3-n}]$, where $n = 0-3$.

Experimental Section

Syntheses. $\text{Co}(\text{acac})_2(\alpha\text{-amino acidate})$ complexes where the amino acid is (S)-alanine, (S)-valine, *N*-methyl-(S)-alanine, and *N*-methyl-(S)-valine were prepared from $\text{Na}[\text{Co}(\text{acac})_2(\text{NO}_2)_2]$ using the method described by Laurie.²⁰ The Δ and Λ diastereomeric forms of each complex were separated by column chromatography on alumina as described previously.²¹ $\text{Co}(\text{acac})(\text{S-val})_2$ was prepared in a similar fashion from $\text{Na}[\text{Co}(\text{acac})_2(\text{NO}_2)_2]$ or by ligand exchange of (S)-valine

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with $\text{Co}(\text{acac})_3$.²² Five of the six possible diastereomers were isolated by column chromatography on alumina. The synthesis of this complex, diastereomer separation, and configurational assignments using nmr will be described more fully in a separate publication.²³

Physical Measurements. ORD and CD spectra of the $\text{Co}(\text{acac})_2(\alpha\text{-amino acidate})$ complexes were obtained in chloroform solution at ambient temperature using a Cary Model 60 spectropolarimeter with the Cary Model 6001 CD accessory. Absorption spectra in chloroform solution were recorded on a Cary Model 14 spectrophotometer. Spectra of the $\text{Co}(\text{acac})(S\text{-val})_2$ diastereomers were obtained in a similar fashion using water as the solvent.

Results and Discussion

$[\text{Co}(\beta\text{-diketonate})_n(\text{en})_{3-n}]^{3-n}$ Complexes. The Cotton effect-configuration relationships for tris(β -diketonato)cobalt(III) complexes in the region of the low-energy ligand field transition were established only recently.^{10,11,16} Isomers having the Λ configuration show a small negative CD band around 14,500–15,000 cm^{-1} assigned¹³ to the A transition followed by a positive band *ca.* 17,000 cm^{-1} which has a $\Delta\epsilon$ approximately 4 times larger and is assigned¹³ to the E transition. A negative band at higher energy is assigned to the second octahedral transition. The signs of these bands are reversed for the Δ isomers.¹⁶ CD spectra of $\Lambda(+)$ - $[\text{Co}(\text{en})_3]^{3+}$ and $\Lambda(+)$ - $[\text{Co}(+)\text{pn}]_3^{3+}$, on the other hand, are characterized by a large positive band (E) at low energy ($\sim 20,300 \text{ cm}^{-1}$) followed by a much smaller negative band (A) around 23,400 cm^{-1} .^{2-7,19}

Boucher recently achieved resolution of $[\text{Co}(\text{acac})_2\text{en}]^+$ through formation of diastereomeric (+)-arsenyltartrate salts.²⁴ The CD spectrum of the (+)₅₄₆ isomer in the region of the low-energy ligand field transition shows a small negative band *ca.* 17,300 cm^{-1} followed by a positive band at 19,500 cm^{-1} which has a larger $\Delta\epsilon$ by a factor of 4. Another negative band attributed to the second octahedral transition occurs at higher energy. Except for an overall shift toward higher energy as a result of the larger crystal field strength of en over acac⁻, the CD spectrum of (+)₅₄₆- $[\text{Co}(\text{acac})_2\text{en}]^+$ is extremely similar to those found for tris(β -diketonato)cobalt(III) complexes having the Λ configuration. The mixed-ligand complex has only C_2 symmetry, and three CD bands are expected to arise from the low-energy octahedral transition. A transition of B symmetry is derived from the A_2 transition in D_3 symmetry, and the $E(D_3)$ transition splits into components having A and B symmetries. Since three transitions are not apparent in the CD spectrum, the assumption was made that the stronger band contains the A and B transitions of E parentage and that the positive sign of this CD band indicates the complex has the Λ configuration with respect to its pseudo- C_3 axis. McCaffery, *et al.*,²⁵ have discussed in detail the rationale for use of this method of assigning configurations to complexes of C_2 symmetry, and "parentage arguments" of this sort have been used to assign configurations to a number of low-symmetry complexes having bidentate ligands. This procedure has been questioned by Schaffer, however.²⁶

Resolution of $[\text{Co}(\beta\text{-diketonate})(\text{en})_2]^{2+}$ complexes using several β -diketonate ligands has been reported.^{25,27} CD spectra of the (+)_D isomers are all very similar and are characterized by a single, broad, positive band in the region of the low-energy octahedral transition, *ca.* 20,000 cm^{-1} .

These complexes have been assigned the Λ configuration on basis of the sign of this band.^{25,27}

If the arguments of McCaffery, *et al.*,²⁵ are valid for these complexes of C_2 symmetry, the variation in CD spectra with decreasing n in the series $[\text{Co}(\beta\text{-diketonate})_n(\text{en})_{3-n}]^{3-n}$ may be explained in the following way. Where $n = 3$ or 2 the E transition (D_3) or the combined A + B transitions of E parentage (C_2) lie sufficiently far to the high-energy side of the $A_2(D_3)$ or $B(C_2)$ transition that both are seen. The CD of the E or A + B transition predominates, and a positive sign for this band is diagnostic of the Λ (C_3 or pseudo- C_3) configuration. For $n = 1$ all three transitions are close in energy and a single, broad CD band results. The overall sign of the band is determined by the sign of the transitions having E parentage, *i.e.* positive for the Λ configuration. Finally, for $n = 0$ the A_2 and E transitions are again well separated in energy and both are seen; however the energy order of these transitions is now opposite that of the $n = 3$ case.

$[\text{Co}(\beta\text{-diketonate})_n((S)\text{-}\alpha\text{-amino acidate})_{3-n}]$ Complexes. The absolute configuration of *trans*-(+)_D- $[\text{Co}(S\text{-ala})_3]$ has been shown to be Λ by a single-crystal X-ray study.⁹ The CD spectrum¹⁵ of this complex in the ligand field region is representative of those of most *cis*- or *trans*-tris(S)- α -amino acidato)cobalt(III) diastereomers having the Λ configuration. A strong, positive CD at low energy ($\sim 19,000 \text{ cm}^{-1}$) believed to be of E parentage is followed by a much smaller, negative band maximizing around 22,000 cm^{-1} . Both Δ -*cis* and Δ -*trans* diastereomers of tris(S)- α -amino acidato)cobalt(III) complexes, on the other hand, generally have a single, broad, negative CD band centered around 19,000 cm^{-1} . The difference in the number of CD bands observed for Δ and Λ diastereomers in this region has been attributed to the occurrence of vicinal effects.^{15b} The E transition is believed to lie at lower energy than A, and the vicinal contribution of (S)-amino acidate ligands on a Λ complex reduces positive CD at the wavelength of the E transition and enhances negative CD at the wavelength of A. In the Δ diastereomers, negative CD is enhanced in the E region to such an extent that A is canceled. In either case the band associated with the E transition is dominant and may be used to assign the absolute configuration. Thus although the energy order of the E and A transitions appears to be reversed on going from the tris(S)- α -amino acidato)cobalt(III) complexes, $n = 0$, to the tris(β -diketonato)cobalt(III) complexes, $n = 3$, the Cotton effect-configuration rule stated above is applicable to both.

When one acetylacetonate ligand in $\text{Co}(\text{acac})_3$ is replaced by an amino acid anion, two diastereomeric species, Δ and Λ , are formed. These have been separated chromatographically for the complexes where the amino acid is *S*-ala, *N*-Me-*S*-ala, *S*-val, and *N*-Me-*S*-val.²¹ The Λ configuration has been assigned²¹ to the (+)_D isomer in each case from proton nmr spectra using anisotropy-shielding arguments developed previously for related series of complexes.²⁸

CD spectra of the eight $n = 2$ complexes are presented in Figures 1 and 2. In each case two CD bands of opposite sign are clearly seen in the region of the low-energy absorption envelope. These spectra are very similar to those observed for the $n = 3$ complexes with regard to both the relative intensities of the two bands and the position of the dominant band. The positions of both bands in Figures 1 and 2 are shifted toward higher energy than for the $n = 3$ complexes as a result of the stronger average ligand field. A reasonable assumption is that the order of electronic energy

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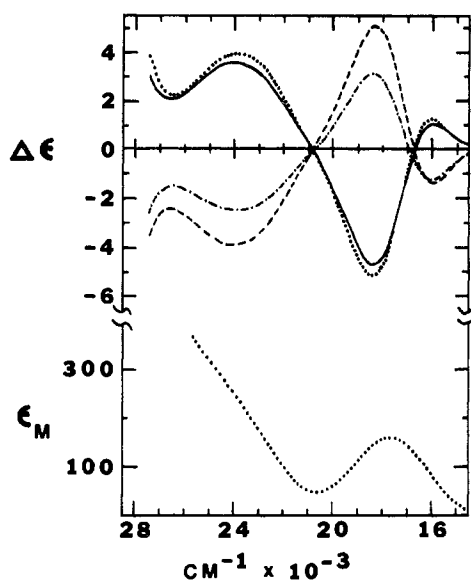


Figure 1. CD spectra in chloroform solution: —, (–) D -[Co(acac) $_2$ (*S*-ala)]; - - -, (+) D -[Co(acac) $_2$ (*S*-ala)]; ···, (–) D -[Co(acac) $_2$ (*N*-Me-*S*-ala)]; ·-·-·, (+) D -[Co(acac) $_2$ (*N*-Me-*S*-ala)]. Absorption spectrum in chloroform solution: ···, (–) D -[Co(acac) $_2$ (*N*-Me-*S*-ala)].

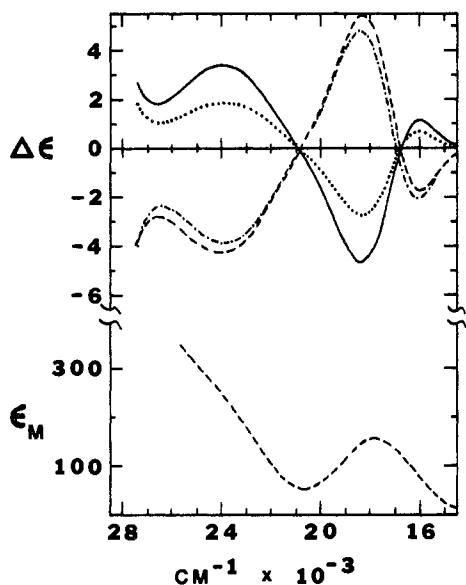


Figure 2. CD spectra in chloroform solution: —, (–) D -[Co(acac) $_2$ (*S*-val)]; - - -, (+) D -[Co(acac) $_2$ (*S*-val)]; ···, (–) D -[Co(acac) $_2$ (*N*-Me-*S*-val)]; ·-·-·, (+) D -[Co(acac) $_2$ (*N*-Me-*S*-val)]. Absorption spectrum in chloroform solution: - - -, (+) D -[Co(acac) $_2$ (*S*-val)].

levels for Co(III) in these complexes of C_1 symmetry is not significantly different from that in the $n = 3$ complexes, and the dominant CD band has E parentage. Thus the Λ configuration is assigned to diastereomers having a positive dominant band, and the Δ configuration is assigned to those for which this band is negative. These configurational assignments are in complete agreement in all cases with those made earlier by the nmr method.²¹ Vicinal effects are not as pronounced in Co(*S*-ala)(acac) $_2$ and Co(*S*-val)(acac) $_2$ as is the case for $n = 0$ as may be seen by the fact that the CD spectra for Δ and Λ forms of a given complex are nearly mirror images. Vicinal effects apparently have a stronger influence on CD spectra of the complexes containing *N*-methyl-substituted amino acidate ligands.

Three geometric isomers are possible for complexes in this series where $n = 1$, and each of these can have Δ or Λ configurations. Geometric isomers are named with regard to the

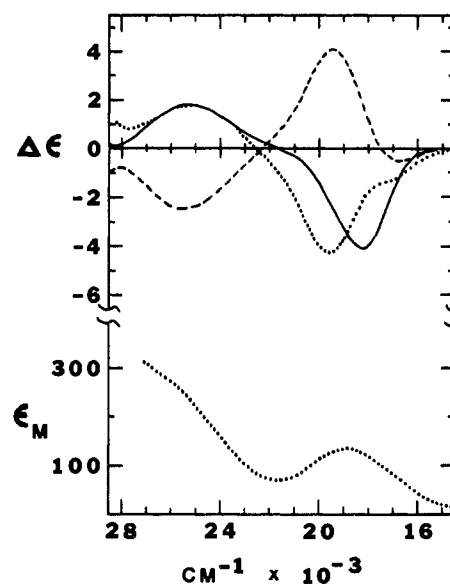


Figure 3. CD spectra in aqueous solution: —, (–) D -*cis*- N - C_2 -[Co(acac)(*S*-val) $_2$]; - - -, (+) D -*trans*- N - C_2 -[Co(acac)(*S*-val) $_2$]; ···, (–) D -*trans*- N - C_2 -[Co(acac)(*S*-val) $_2$]. Absorption spectrum in aqueous solution: ···, (–) D -*trans*- N - C_2 -[Co(acac)(*S*-val) $_2$].

arrangement of nitrogen donor atoms, *cis* or *trans*, and with regard to the point group symmetry of the molecule, C_1 or C_2 . Thus the isomers are labeled Δ - or Λ -*trans*- N - C_2 , Δ - or Λ -*cis*- N - C_2 , and Δ - or Λ -*cis*- N - C_1 . Five of the six possible diastereomers for Co(acac)(*S*-val) $_2$ have recently been isolated by column chromatography. Those having C_1 symmetry are readily distinguished from those having C_2 symmetry by proton nmr, and *cis* and *trans* diastereomers can be differentiated on basis of their visible absorption spectra.²³ The helicity has been assigned to four of the diastereomers from proton nmr anisotropy-shielding considerations.²³

CD spectra of the five diastereomers in the ligand field region are shown in Figures 3 and 4. CD spectra of the (+) D -*trans*- N - C_2 and the (+) D -*cis*- N - C_1 diastereomers resemble those of the $n = 2$ complexes in this series having the Λ configuration. A small negative CD band at low energy is followed by a much stronger positive band at higher energy. Another negative band at higher energy is attributed to the second octahedral transition. All three transitions occur at higher energy than for the $n = 2$ complexes as a result of the greater average ligand field. In view of the arguments presented earlier in this paper, these isomers are assigned the Λ configuration. The remaining diastereomers have dominant negative CD's in the region of the low-energy transition followed by positive CD's in the region of the second octahedral transition. Accordingly, these are assigned the Δ configuration.

The relative amplitude of the low-energy, negative CD band for the Λ isomers is smaller than that of any other member of the Co(acac) $_n$ (*S*-val) $_{3-n}$ series. Since the transition of E parentage lies lower than that of A for the $n = 0$ complexes and higher than A for the $n = 3$ and 2 complexes, it is likely that these transitions are close in energy for the $n = 1$ species. Thus it is more probable that the small negative CD band arises from a vicinal effect of the (*S*)-valine ligands than from the transition of A parentage. Vicinal effects, when evaluated by Douglas' method,^{15b} enhance negative CD in this wavelength region for Co(*S*-val) $_3$.^{15d} In the Δ isomers the vicinal effect reinforces the negative CD of the E transition, resulting in strong negative CD in the low-energy region.

Configurational assignments based on the sign of the domi-

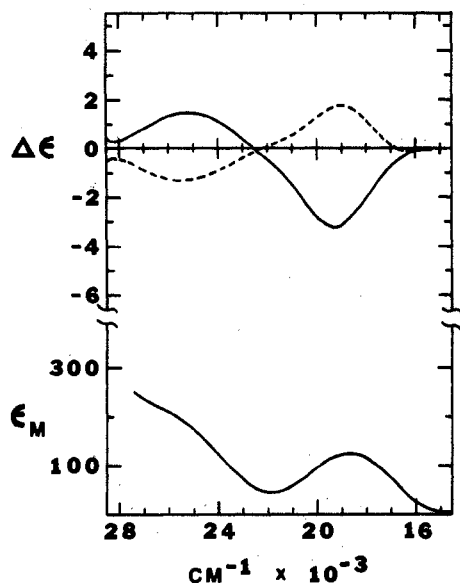


Figure 4. CD spectra in aqueous solution: —, (–)_D-*cis-N-C*₁-[Co(acac)(*S-val*)₂]; - - -, (+)_D-*cis-N-C*₁-[Co(acac)(*S-val*)₂]. Absorption spectrum in aqueous solution: —, (–)_D-*cis-N-C*₁-[Co(acac)(*S-val*)₂].

nant low-energy CD band are in agreement with those made by the nmr method for four diastereomers of Co(acac)(*S-val*)₂. The configuration of the (–)_D-*cis-N-C*₂ diastereomer was not assigned by the nmr method since the *cis-N-C*₂ isomer of opposite helicity was not isolated, thereby precluding a comparison of proton chemical shifts.²³ The (–)_D-*cis-N-C*₂ diastereomer is assigned the Δ configuration by the CD

method. Thus the missing diastereomer must be Λ-*cis-N-C*₂-[Co(acac)(*S-val*)₂].

In summary, the results presented herein indicate that CD spectra of intermediate members ($n = 1, 2$) of the two series, [Co(β-diketonate)_{*n*}(en)_{3-*n*}]^{3-*n*} and [Co(β-diketonate)_{*n*}((*S*)-α-amino acidate)_{3-*n*}], can be related to those of the terminal members ($n = 0, 3$) for which Cotton effect-configuration relationships are well established. In the region of the low-energy octahedral transition CD spectra generally show either a single band or two bands of opposite sign, one of which predominates. The number of bands occurring in this region can be explained on basis of the energy separation between transitions of E and A₂(D₃) parentage and, where chiral ligands are present, on basis of a vicinal contribution to the CD. Configurational assignments made by analysis of Cotton effects for the [Co(acac)_{*n*}((*S*)-α-amino acidate)_{3-*n*}] series where $n = 1, 2$ are in complete agreement with those made by an independent nmr method. Thus there is good justification for extending (using the parentage arguments of McCaffery, *et al.*²⁵) the Cotton effect-configuration rule stated earlier in this paper to include mixed-ligand complexes of the type discussed here and perhaps also others for which this rule has often been applied with no strong justification.

Registry No. (–)_D-[Co(acac)₂(*S-ala*)], 39670-35-4; (+)_D-[Co(acac)₂(*S-ala*)], 39670-34-3; (–)_D-[Co(acac)₂(*N-methyl-S-ala*)], 43211-93-4; (+)_D-[Co(acac)₂(*N-methyl-S-ala*)], 43211-94-5; (–)_D-[Co(acac)₂(*S-val*)], 36300-71-7; (+)_D-[Co(acac)₂(*S-val*)], 36300-70-6; (–)_D-[Co(acac)₂(*N-methyl-S-val*)], 43211-78-5; (+)_D-[Co(acac)₂(*N-methyl-S-val*)], 43211-97-8; (–)_D-*cis-N-C*₂-[Co(acac)(*S-val*)₂], 43211-98-9; (+)_D-*trans-N-C*₂-[Co(acac)(*S-val*)₂], 43211-99-0; (–)_D-*trans-N-C*₂-[Co(acac)(*S-val*)₂], 43212-00-6; (–)_D-*cis-N-C*₁-[Co(acac)(*S-val*)₂], 43212-01-7; (+)_D-*cis-N-C*₁-[Co(acac)(*S-val*)₂], 43212-02-8.

Contribution from CNR, Centro Stabilità e Reattività dei Composti di Coordinazione, Istituto di Chimica Analitica dell'Università di Padova, Padua, Italy

Novel Formally Three-Coordinate Rhodium(I)-Carborane Complexes Containing Metal-Carbon σ Bonds

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The reaction of C-monosubstituted lithium derivatives of 1,2- and 1,7-dicarba-*closo*-dodecaborane(12) with [(C₆H₅)₃P]₂RhCl and [(C₆H₅)₃P]₂Rh(CO)Cl in ethereal solvents gives rise to a novel series of neutral rhodium(I)-carborane complexes containing a metal-carbon σ bond. In particular, by treating [(C₆H₅)₃P]₂RhCl with lithium derivatives of 2-R-1,2- and 7-R-1,7-B₁₀C₂H₁₁ (R = CH₃, C₆H₅), unusual three-coordinate complexes of the type [(C₆H₅)₃P]₂Rh(σ-carb) have been obtained. The preparation and characterization of these compounds and their reactions with carbon monoxide and benzonitrile are reported and the proposed structures are discussed.

Introduction

The research described herein comes from our long-range interest in the synthesis and the characterization of transition metal-*o*-carborane and -*m*-carborane (1,2- and 1,7-dicarba-*closo*-dodecaborane(12), respectively) complexes containing metal-carbon σ bonds.¹⁻⁴ In this paper we

report an account of the preparation and characterization of some novel three-coordinate neutral rhodium(I)-carborane complexes incorporating the 2-R-1,2-B₁₀C₂H₁₀[−] and 7-R-1,7-B₁₀C₂H₁₀[−] (R = CH₃, C₆H₅) ligands through metal-carbon σ bonds. The four-coordinate compounds obtained by allowing these complexes to react with CO and C₆H₅CN are also described.

Results and Discussion

We have been able to prepare a series of rhodium(I)-carborane complexes whose formulas and analytical data are listed in Table I.

The complexes of general formula [(C₆H₅)₃P]₂Rh(σ-carb), where carb is 1,2- or 1,7-dicarba-*closo*-dodecaborane(12)

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