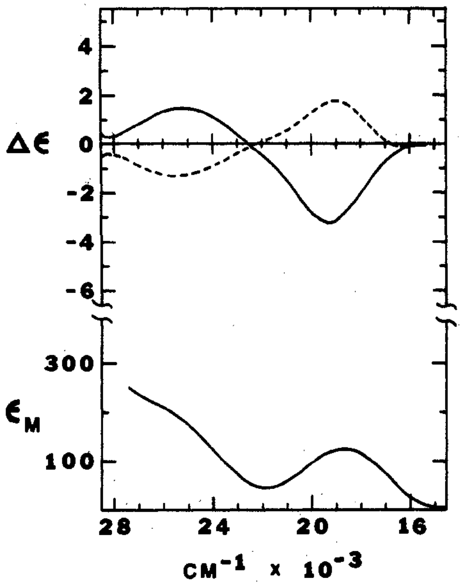

Figure 4. CD spectra in aqueous solution: —, $(-)_D$-*cis-N-C*$_1$-[Co(acac)(*S*-val)$_2$]; - - -, $(+)_D$-*cis-N-C*$_1$-[Co(acac)(*S*-val)$_2$]. Absorption spectrum in aqueous solution: —, $(-)_D$-*cis-N-C*$_1$-[Co(acac)(*S*-val)$_2$].

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, $[Co(\beta\text{-diketonate})_n(en)_{3-n}]^{3-n}$ 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 $A_2 (D_3)$ 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 Stabilita e Reattivita dei Composti di Coordinazione, Instituto di Chimica Analitica dell'Universita di Padova, Padua, Italy

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

S. BRESADOLA* and B. LONGATO

Received June 11, 1973

The reaction of C-monosubstituted lithium derivatives of 1,2- and 1,7-dicarba-*closo*-dodecaborane(12) with $[(C_6H_5)_3P]_3RhCl$ and $[(C_6H_5)_3P]_2Rh(CO)Cl$ 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 $[(C_6H_5)_3P]_3RhCl$ with lithium derivatives of 2-R-1,2- and 7-R-1,7-$B_{10}C_2H_{11}$ (R = CH_3, C_6H_5), unusual three-coordinate complexes of the type $[(C_6H_5)_3P]_2Rh(\sigma\text{-carb})$ 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-$B_{10}C_2H_{10}^-$ and 7-R-1,7-$B_{10}C_2H_{10}^-$ (R = CH_3, C_6H_5) ligands through metal–carbon σ bonds. The four-coordinate compounds obtained by allowing these complexes to react with CO and C_6H_5CN 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 $[(C_6H_5)_3P]_2Rh(\sigma\text{-carb})$, where carb is 1,2- or 1,7-dicarba-*closo*-dodecaborane(12)

---

(1) S. Bresadola, P. Rigo, and A. Turco, *Chem. Commun.*, 1205 (1968).

(2) S. Bresadola, G. Cecchin, and A. Turco, *Gazz. Chim. Ital.*, 100, 628 (1970).

(3) S. Bresadola, G. Cecchin, and A. Turco, *Proc. Int. Conf. Coord. Chem., 13th*, 1, 160 (1970).

(4) B. Longato, F. Morandini, and S. Bresadola, *Atti Conv. Naz. Chim. Inorg.*, A24 (1972).

Table I. σ-Bonded Rhodium–Carborane Complexes

No.	Compd[a]	Color	Mp,[b] °C	Yield, %	Analysis, %
I	1-[$(PPh_3)_2Rh$]-2-CH_3-1,2-(σ-$B_{10}C_2H_{10}$)	Burgundy red	188–190	80	Calcd: C, 59.68; H, 5.52; P, 7.89 Found: C, 59.10; H, 5.46; P, 7.80
II	1-[$(PPh_3)_2Rh$]-2-C_6H_5-1,2-(σ-$B_{10}C_2H_{10}$)	Red-violet	178–181	87	Calcd: C, 62.40; H, 5.35; P, 7.31. Found: C, 62.21; H, 5.18; P, 7.45
III	1-[$(PPh_3)_2Rh$]-7-CH_3-1,7-(σ-$B_{10}C_2H_{10}$)	Orange	182–184	70	Calcd: C, 59.68; H, 5.52; P, 7.89 Found: C, 59.64; H, 5.50; P, 8.15
IV	1-[$(PPh_3)_2Rh$]-7-C_6H_5-1,7-(σ-$B_{10}C_2H_{10}$)	Orange	167–168	75	Calcd: C, 62.40; H, 5.35; P, 7.31 Found: C, 61.41; H, 5.72; P, 7.25
V	1-[$(PPh_3)_2Rh(C_6H_5CN)$]-2-C_6H_5-1,2-(σ-$B_{10}C_2H_{10}$)	Orange	150–152	~100	Calcd: C, 64.48; H, 5.30; N, 1.47 Found: C, 64.25; H, 5.23; N, 1.44
VI	1-[$(PPh_3)_2Rh(CO)$]-2-C_6H_5-1,2-(σ-$B_{10}C_2H_{10}$)	Yellow	126–127	80	Calcd: C, 61.78; H, 5.18 Found: C, 61.97; H, 5.24
VII	1-[$(PPh_3)Rh(CO)_2$]-2-C_6H_5-1,2-(σ-$B_{10}C_2H_{10}$)·1/2CH_2Cl_2	Yellow	176	~100	Calcd: C, 50.12; H, 4.57; Cl, 5.19; P, 4.53 Found: C, 50.30; H, 4.64; Cl, 5.05; P, 4.57

[a] $PPh_3 = P(C_6H_5)_3$. [b] All compounds melt with decomposition in a capillary tube sealed under vacuum.

(compounds I–IV), have been synthesized by treating a suspension of $[(C_6H_5)_3P]_3RhCl$ in diethyl ether with an excess of 1-Li-2-R-1,2-$B_{10}C_2H_{10}$ or 1-Li-7-R-1,7-$B_{10}C_2H_{10}$ (R = CH_3, C_6H_5). Great difficulties were experienced in the purification of the reaction products owing to their high sensitivity in solution toward air and moisture. Elemental analyses performed upon very pure compounds are fully consistent with the formulations assigned (see Table I). These complexes are nonelectrolytes at 25° in CH_2Cl_2 solution and are diamagnetic (Gouy method), as expected for d^8 complexes. Attempts to derive the molecular weights of these complexes by cryoscopic methods were unsuccessful owing to their poor solubility at low temperatures. On the other hand the osmometric method gave molecular weight values lower than the expected ones. This can be attributed to the high reactivity in solution of these compounds, dissociation being ruled out on the basis of spectrophotometric measurements in the 450–600-nm range. In fact, complex II kept in benzene solution, from which oxygen had been rigorously excluded, follows Beer's law when the concentration is varied within the range 5×10^{-4}–10^{-2} M and shows an absorption maximum at 510 nm, ϵ 800. Moreover, the electronic spectra of this complex recorded in solution and in the solid state are exactly alike, thus showing that no structural changes occur on dissolving the complex. The ir spectra (Nujol mulls) of the complexes I–IV exhibit, in addition to the absorption bands due to the triphenylphosphine ligands, the strong absorptions in the region 2540–2620 cm^{-1} due to the B–H stretching of the dicarba-*closo*-dodecaborane(12) ligand. No carborane C–H stretching absorption was observed around 3060 cm^{-1}, indicating the compounds to be C(1)-substituted derivatives. Moreover, rhodium-bonded hydrogens are absent in these complexes (I–IV) as shown by the facts that (i) the ir spectra do not exhibit absorption bands in the region 1600–2540 cm^{-1} and (ii) the ^1H nmr spectra do not show resonances in the range τ 8–60.

The 90-MHz ^1H nmr spectrum of the methylcarborane derivative, complex I, in dichloromethane solution (TMS as internal standard) consisted of a sharp singlet of intensity 3 at τ 8.0, which was assigned to the 2-methyl protons of the carborane ligand[5] and a multiplet of total intensity 30 centered at τ 2.8 which was assigned to the protons of triphenylphosphine ligands. Hence, this nmr spectrum is in agreement with the proposed formulation.

Complexes I–IV are the first examples which can be regarded as three-coordinate species of rhodium(I). To our knowledge three-coordinate rhodium(I) complexes do not appear to have been prepared previously, although they are supposed to exist in solution. Thus, molecular weight data,[6,7] a ^{31}P nmr study,[8] and spectrophotometric measurements[9] show that the complex $[(C_6H_5)_3P]_3RhCl$ is partially dissociated in solution to give the formally three-coordinate species $[(C_6H_5)_3P]_2RhCl$. Attempts[10] to prepare a complex containing three-coordinate rhodium(I) by using a sterically hindered triarylphosphine, such as tri-*o*-tolylphosphine, yielded a "stilbene" complex of rhodium(I) of the type XRh[(*o*-tolyl)$_2PC_6H_4CH$:]$_2$ in which the new ligand (*o*-tolyl)$_2PC_6H_4CH$=CHC_6H_4P(*o*-tolyl)$_2$ is coordinated to the metal atom as a tridentate ligand. Moreover, it was suggested that the coordinatively unsaturated species [P(*o*-tolyl)$_3$]$_2$-RhCl likely is the precursor to the "stilbene" complex.

Although several factors may appear to favor the three-coordination, we think that the three-coordination exhibited by rhodium(I) complexes when carboranes are used as anionic ligands is likely to be mainly attributed to the high steric requirements of the carborane moiety. Steric factors have already been invoked to explain the unusual behavior found in the reactions between *cis*- and *trans*-$(PR_3)_2PtCl_2$, where R = C_2H_5, *n*-C_3H_7, and C_6H_5, and lithium derivatives of dicarba-*closo*-dodecaborane(12).[11]

The complexes I–IV easily undergo addition reactions with neutral ligands to give four-coordinate species provided that their steric requirements are smaller than those of triphenylphosphine, *e.g.*, benzonitrile and carbon monoxide. Thus, by treating II with C_6H_5CN in diethyl ether at room temperature we have isolated an orange crystalline compound which, on the basis of the analytical and spectroscopic data, was formulated as the four-coordinate adduct 1-[$(PPh_3)_2Rh(C_6H_5CN)$]-2-C_6H_5-1,2-(σ-$B_{10}C_2H_{10}$), V. Its ir spectrum (Nujol mull) shows a medium band at 2230 cm^{-1} which was assigned to CN stretching absorption of the coordinated nitrile.

The four-coordinate carbonylrhodium(I) complex, VI, containing carborane σ bonded to the metal atom, was prepared by reaction of $[(C_6H_5)_3P]_2Rh(CO)Cl$ with 1-Li-2-

---

(5) D. A. Owen, S. C. Smart, P. M. Garret, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **93**, 1362 (1971).

(6) M. A. Bennett and P. A. Longstaff, *Chem. Ind.* (*London*), 846 (1965).

(7) J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc. A*, 1711 (1966).

(8) D. R. Eaton and S. R. Suart, *J. Amer. Chem. Soc.*, **90**, 4170 (1968).

(9) H. Arai and J. Halpern, *Chem. Commun.*, 1571 (1971).

(10) M. A. Bennett and P. A. Longstaff, *J. Amer. Chem. Soc.*, **91**, 6266 (1969).

(11) S. Bresadola, A. Frigo, B. Longato, and G. Rigatti, *Inorg. Chem.*, **12**, 2788 (1973).

Scheme I[a]

$$\begin{tikzcd}
(PPh_3)_3RhCl \arrow[r, "Li(carb)"] \arrow[d, "+CO"', "-PPh_3{}^{b}"] & \underset{\mathrm{II}}{(PPh_3)_2Rh(\sigma\text{-carb})} \arrow[r, shift left, "+2CO{,}\ -PPh_3"] & \underset{\mathrm{VII}}{(PPh_3)Rh(CO)_2(\sigma\text{-carb})} \arrow[l, shift left] \\
trans\text{-}(PPh_3)_2Rh(CO)Cl \arrow[rr, "Li(carb)"] & & \underset{\mathrm{VI}}{trans\text{-}(PPh_3)_2Rh(CO)(\sigma\text{-carb})} \arrow[u, "+CO", "-PPh_3"']
\end{tikzcd}$$

[a] $PPh_3 = P(C_6H_5)_3$; Li(carb) = 1-Li-2-C_6H_5-1,2-$B_{10}C_2H_{10}$. [b] Reference 7.

C_6H_5-1,2-$B_{10}C_2H_{10}$ in diethyl ether. The product, air and moisture sensitive, is diamagnetic and is a nonelectrolyte. The analytical and spectroscopic data are in agreement with the reported formula. The infrared spectrum (Nujol mull) exhibited, other than the expected absorption bands due to the phosphine and carborane ligands, a strong band at 2000 cm^{-1}, which was attributed to CO stretching absorption, and a medium band centered at 553 cm^{-1} which could be assigned to the δ(RhCO) out-of-plane vibration.[12] These frequencies, which appear *ca.* 40 cm^{-1} above and *ca.* 20 cm^{-1} below, respectively, the values found for the frequencies of *trans*-$[(C_6H_5)_3P]_2Rh(CO)Cl$, are consistent with the replacement of Cl by $-CB_{10}H_{10}CC_6H_5$ trans to CO; therefore, the obtained complex can be reasonably formulated as trans.[13] In fact, the electron-withdrawing carborane ligand bonded to the metal atom reduces the partial $d\pi$–$p\pi$ double bond between the rhodium atom and the carbon atom of the carbonyl group. Thus, the bond order of this metal–carbon bond is also reduced and it is reflected in the relatively high frequency of the ν(CO) band, whereas the low δ(Rh-CO) frequency may be indicative of the drop of the elastic resistance of the Rh–CO π bond to bending.

Complex VI in benzene suspension takes up, at 25° and 1 atm, 1 mol of carbon monoxide per mole of complex yielding a carborane-containing dicarbonyl derivative (complex VII). The latter complex can be also prepared by treating the parent complex II suspended in benzene with carbon monoxide at 25° and 1 atm (eq 1).

$$\begin{tikzcd}
\underset{\mathrm{II}}{[(C_6H_5)_3P]_2Rh(\sigma\text{-carb})} \arrow[r, shift left, "+2CO{,}\ -PPh_3"] & \underset{\mathrm{VII}}{[(C_6H_5)_3P]Rh(CO)_2(\sigma\text{-carb})} \arrow[l, shift left]
\end{tikzcd} \qquad (1)$$

$$\text{carb} = -CB_{10}H_{10}CC_6H_5$$

These carbonylations are reversed on flushing with dry nitrogen. Thus, when a suspension of the complex II in benzene is treated with a CO atmosphere, the color rapidly changes from red to bright yellow. On sweeping with nitrogen the solution regains its initial red color and resaturation with CO restores the bright yellow color.

Complex VII, which crystallized with one-half molecule of CH_2Cl_2, is diamagnetic and is a nonelectrolyte in CH_2Cl_2 solution at 25°, and its ir spectrum (Nujol mull) shows two absorption bands centered at 1995 (strong) and 2068 cm^{-1} (very strong), respectively, which can be assigned to CO stretching absorptions.

Scheme I reports the reactions of the rhodium(I)–carborane complexes with carbon monoxide. The reactions of the rhodium(I)–carborane complexes carried out with CO at 25° and 1 atm do not provide evidence for the formation of acyl-type derivatives.

It may be noted that the rhodium(I) complexes incorporating, as an anionic ligand, a derivative of 1,2-$B_{10}C_2H_{11}^-$ in the solid state are stable indefinitely in air, whereas those incorporating a derivative of the isomer 1,7-$B_{10}C_2H_{11}^-$ slowly absorb oxygen. On the other hand, solutions or suspensions in organic solvents of all of these complexes react very rapidly with oxygen as well as hydrogen and halogens.

Manometric studies indicate that complex II in dichloromethane or benzene suspension at 25° and 1 atm absorbs very rapidly 1 mol of oxygen/mol of complex yielding presumably a dioxygen complex. The ir spectrum of a Nujol mull of the isolated product exhibited a sharp absorption at 900 cm^{-1} which may be attributed to O–O stretching vibration. Although complex II shows catalytic activity in homogeneous hydrogenation reactions of olefins and absorbs 1 mol of hydrogen/mol of complex at 25° and 1 atm in benzene suspension, no hydrogen adducts could be isolated or detected by ir and ^1H nmr spectroscopy. However, the ^1H nmr spectrum of the reaction mixture shows the presence of paramagnetic species.

Detailed studies on the reactivity of these rhodium(I)–carborane complexes are in progress together with X-ray crystal structure investigations in order to gain more information on the unusual three-coordinate nature of complexes I–IV.[14]

Experimental Section

Methods and Materials. The solvents were of reagent grade quality and were dried and degassed before use. 1-Li-2-R-1,2-B_{10}-C_2H_{10}, 1-Li-7-R-1,7-R-1,7-$B_{10}C_2H_{10}$ (R = CH_3, C_6H_5), $[(C_6H_5)_3P]_3RhCl$, and $[(C_6H_5)_3P]_2Rh(CO)Cl$ were prepared by literature methods.[6,15] All reactions were carried out under argon atmosphere. Infrared spectra were obtained as Nujol mulls with Perkin-Elmer Model 457 and Beckman IR-9 spectrometers. Electronic spectra were obtained using an Optica CF-4 spectrophotometer. ^1H nmr spectra were recorded with a Bruker HFX-90 spectrometer. Conductivity measurements (25°, 10^{-3} *M* in CH_2Cl_2 solutions) were obtained with a LKB bridge.

1-[$(PPh_3)_2Rh$]-2-CH_3-1,2-(σ-$B_{10}C_2H_{10}$), I. Under argon, 8.22 mmol of a solution of 1-Li-2-CH_3-1,2-$B_{10}C_2H_{10}$ in 25 ml of anhydrous diethyl ether was slowly added to a stirred suspension of 2.5 g (2.7 mmol) of $[(C_6H_5)_3P]_3RhCl$ in 30 ml of anhydrous ether at 0°. The reaction mixture was stirred for a 4 hr at 0°. The dark red precipitate formed was separated by filtration in an argon atmosphere and washed with methanol. The crystalline product obtained was further purified by recrystallization from CH_2Cl_2–methanol to give 1.7 g (80%) of burgundy red crystals, mp 188–190° dec.

1-[$(PPh_3)_2Rh$]-2-C_6H_5-1,2-(σ-$B_{10}C_2H_{10}$), II. This complex was prepared as above from a solution of 11.36 mmol of 1-Li-2-C_6H_5-

---

[12] Yu. S. Varshavskii, M. M. Singh, and N. A. Buzina, *Russ. J. Inorg. Chem.*, 16, 725 (1971).

[13] G. Yagupsky, C. K. Brown, and G. Wilkinson, *J. Chem. Soc. A*, 1392 (1970).

[14] By preliminary X-ray data the molecular weight in the solid state is in accordance with the suggested formulations and the rhodium atom appears to be coordinated with two triphenylphosphine molecules and linked with one carborane group through a metal–carbon σ bond: work to be published by Allegra, Calligaris, Furlanetto, Nardin, and Randaccio, University of Trieste, Trieste, Italy; *Cryst. Struct. Commun.*, in press.

[15] D. Grafstein, J. Bobinski, J. Dvorak, H. Smith, N. Schwartz, M. S. Cohen, and M. M. Fein, *Inorg. Chem.*, 2, 1120 (1963); D. Grafstein and J. Dvorak, *ibid.*, 2, 1128 (1963).

1,2-B$_{10}$C$_2$H$_{10}$ in 30 ml of anhydrous ether added to a suspension of 5.0 g (5.4 mmol) of [(C$_6$H$_5$)$_3$P]$_3$RhCl in 50 ml of ether. The yield of pure product, red-violet crystals, was 4.0 g (87%), mp 178–181° dec.

1-[(PPh$_3$)$_2$Rh]-7-CH$_3$-1,7-(σ-B$_{10}$C$_2$H$_{10}$), III. This complex was prepared from 8.22 mmol of 1-Li-7-CH$_3$-1,7-B$_{10}$C$_2$H$_{10}$ (25 ml ether) and 2.5 g (2.7 mmol) of [(C$_6$H$_5$)$_3$P]$_3$RhCl suspended in 30 ml of ether. The yield of pure product, orange crystals, was 1.5 g (70%), mp 182–184° dec.

1-[(PPh$_3$)$_2$Rh]-7-C$_6$H$_5$-1,7-(σ-B$_{10}$C$_2$H$_{10}$), IV. Complex IV was prepared in the same manner from 9.0 mmol of 1-Li-7-C$_6$H$_5$-1,7-B$_{10}$C$_2$H$_{10}$ and 2.5 g (2.7 mmol) of [(C$_6$H$_5$)$_3$P]$_3$RhCl. The yield of pure product, orange crystals, was 1.7 g (75%), mp 167–168° dec.

1-[(PPh$_3$)$_2$Rh(C$_6$H$_5$CN)]-2-C$_6$H$_5$-1,2-(σ-B$_{10}$C$_2$H$_{10}$), V. A solution of 3.0 mmol of C$_6$H$_5$CN in 10 ml of dry diethyl ether was added under an argon atmosphere at 25° to a stirred suspension of 0.42 g (0.5 mmol) of 1-[(PPh$_3$)$_2$Rh]-2-C$_6$H$_5$-1,2-(σ-B$_{10}$C$_2$H$_{10}$) in 10 ml of ether. In the course of the reaction the deep red color turned to orange. After stirring for 4 hr at room temperature, the reaction mixture was rotary evaporated to an orange solid. The solid thus obtained was dissolved in 10 ml of dry CH$_2$Cl$_2$ under argon atmosphere and then reprecipitated by addition at 0° of 5 ml of ethanol. The yield of pure product was essentially quantitative. The orange crystals melted at 150–152° with decomposition.

1-[(PPh$_3$)$_2$Rh(CO)]-2-C$_6$H$_5$-1,2-(σ-B$_{10}$C$_2$H$_{10}$), VI. Under argon, a solution of 9.0 mmol of 1-Li-2-C$_6$H$_5$-1,2-B$_{10}$C$_2$H$_{10}$ in 25 ml of dry ethyl ether was slowly added at 0° to a stirred suspension of 2.5 g (3.61 mmol) of [(C$_6$H$_5$)$_3$P]$_2$Rh(CO)Cl in 30 ml of ether. The mixture was stirred for 4 hr at 0° and the yellow precipitate separated by filtration in an argon atmosphere was washed with dry *n*-hexane. Further purification was performed by recrystallization from benzene–*n*-hexane. The yield of pure product, yellow crystals, was 2.5 g (80%), mp 126–127° dec;

1-[(PPh$_3$)Rh(CO)$_2$]-2-C$_6$H$_5$-1,2-(σ-B$_{10}$C$_2$H$_{10}$)·$^1/_2$CH$_2$Cl$_2$, VII. A suspension of 0.38 g (0.45 mmol) of 1-[(PPh$_3$)$_2$Rh]-2-C$_6$H$_5$-1,2-(σ-B$_{10}$C$_2$H$_{10}$) in 10 ml of dry benzene at 25° was treated with carbon monoxide at 1 atm. The deep red color rapidly turned yellow and a fine yellow precipitate was formed. The precipitate was collected by filtration under CO atmosphere and washed with a little methanol. The crude product was further purified by recrystallization under CO atmosphere from CH$_2$Cl$_2$–CH$_3$OH. The yield of dichloromethane-solvated product was essentially quantitative. The bright yellow crystals melted at 176° with decomposition. The half molecule of CH$_2$Cl$_2$ present was found by gas chromatographic analysis. The complex is unstable in solution and can be handled only under an atmosphere of carbon monoxide.

Absorption of CO by 1-[(PPh$_3$)$_2$Rh]-2-C$_6$H$_5$-1,2-(σ-B$_{10}$C$_2$H$_{10}$). In a standard gas absorption apparatus 10 ml of dry benzene was saturated with carbon monoxide at 1 atm pressure and 25°. Then the rhodium–carborane complex (0.1–0.15 g) was tipped into the solvent from a bucket and the additional carbon monoxide uptake at 25° was measured. The uptake stopped after 10 min and the absorption was found to correspond to 1.44 mol of CO/mol of complex II (72% of the calculated value). The isolated product was identified as complex VII, mp 175–176° dec. The absorption was measured also at 18° and 1 atm and the uptake was found to correspond to 1.88 mol of CO/mol of complex II (94% of the calculated value).

Absorption of CO by 1-[(PPh$_3$)$_2$Rh(CO)]-2-C$_6$H$_5$-1,2-(σ-B$_{10}$C$_2$H$_{10}$). The absorption of CO was performed in the same conditions above reported. The uptake stopped after 10 min and the absorption at 25° was found to correspond to 0.64 mol of CO/mol of complex VI. The product isolated was identified as the complex VII, mp 175–176° dec.

Acknowledgment. We thank Mr. F. Bergamin for technical assistance in the preparation of the carboranes.

Registry No. I, 43202-53-5; II, 43202-54-6; III, 43202-55-7; IV, 43164-55-2; V, 43202-56-8; VI, 43202-57-9; VII, 43202-58-0; [(C$_6$H$_5$)$_3$P]$_3$RhCl, 14694-95-2; *trans*-[(C$_6$H$_5$)$_3$P]$_2$Rh(CO)Cl, 15318-33-9; 1-Li-2-CH$_3$-1,2-B$_{10}$C$_2$H$_{10}$, 32630-05-0; 1-Li-2-C$_6$H$_5$-1,2-B$_{10}$C$_2$H$_{10}$, 41655-52-1; 1-Li-7-CH$_3$-1,7-B$_{10}$C$_2$H$_{10}$, 32630-07-2; 1-Li-7-C$_6$H$_5$-1,7-B$_{10}$C$_2$H$_{10}$, 42012-25-9.

Contribution from Centro di Chimica e Tecnologia dei Composti Metallorganici degli Elementi di Transizione, Consiglio Nazionale Ricerche, Facolta Chimica Industriale, The University, Calle Larga, Venice, Italy

Mechanism of the Reaction of Zeise's Salt with DL-α-Alanine

G. CARTURAN, P. UGUAGLIATI,* and U. BELLUCO

Received June 12, 1973

The reaction of Zeise's anion, [Pt(C$_2$H$_4$)Cl$_3$]$^-$, with DL-α-alanine (AlaH) to give *N-trans*-[Pt(Ala)(C$_2$H$_4$)Cl] in water at 25° proceeds stepwise. In the pH range 3.2–4.0, *i.e.*, at very low concentrations of the anionic form of the amino acid, one single stage is observed. This involves bimolecular reactions of both [Pt(C$_2$H$_4$)Cl$_3$]$^-$ and the aquo species *trans*-[Pt(C$_2$H$_4$)(H$_2$O)Cl$_2$] to give the intermediate *N-trans*-[Pt(Ala)(C$_2$H$_4$)Cl$_2$]$^-$ in which the alaninate anion is linked to platinum only through the nitrogen-bearing end. This step is followed by the more rapid closure of the chelate ring by the carboxylate end to give *N-trans*-[Pt(Ala)(C$_2$H$_4$)Cl]. The second-order rate constants for the reactions of Zeise's anion and its aquo complex with Ala are 6.1 ± 3.5 × 10^3 and 1.70 ± 0.15 × 10^5 M^{-1} sec^{-1}, respectively. In the pH range 6–9, *i.e.*, when Ala is the predominant amino acid species, the first step becomes too fast to measure, thus enabling the subsequent closure of the chelate ring to be studied kinetically. The first-order rate constant for this intramolecular process is 6.11 ± 0.14 × 10^{-3} sec^{-1}.

Introduction

The stability of the metal-olefin bond in platinum(II) complexes as related to the formal charge on the complex has been the subject of studies in the past few years. While negative and neutral π-olefin complexes of Pt^{II} with monodentate ligands had long been known, only recently have π-olefin Pt^{II} complexes with bidentate ligands been described, of the type [Pt(amino acid)(C$_2$H$_4$)Cl].[1-3] In these complexes the coordinated olefin may be in a trans position either to the nitrogen or to the oxygen atom of the amino acid. Upon treatment with aqueous hydrochloric acid, these complexes dissociate completely into Zeise's anion and the amino acid. Facile exchange of the coordinated olefin also takes place.[3c,4] No examples of nucleophilic attack on the coordi-

---

(1) A. Panunzi, R. Palumbo, C. Pedone, and G. Paiaro, *J. Organometal. Chem.*, 5, 586 (1966).

(2) J. A. Kieft and K. Nakamoto, *J. Inorg. Nucl. Chem.*, 30, 3103 (1967).

(3) (a) J. Fujita, K. Konya, and K. Nakamoto, *Inorg. Chem.*, 9, 2794 (1970); (b) *ibid.*, 10, 1699 (1971); (c) K. Konya, J. Fujita, H. Kido, and K. Saito, *Bull. Chem. Soc. Jap.*, 45, 2161 (1972).

(4) For a survey see U. Belluco, "Organometallic and Coordination Chemistry of Platinum," Academic Press, London, 1973, Chapter VI.