

PREPARATIVE AND NMR STUDIES OF 1,3-DIENECOBALT(I) COMPLEXES

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Summary

The synthesis and the characterization of cobalt(I) complexes of the type $[\text{Co}(\text{diene})(\text{phosphine})_3]\text{Y}$ (diene = 1,3-butadiene and isoprene; phosphine = PMe_3 , PMe_2Ph , and HPPH_2 ; $\text{Y} = \text{ClO}_4$, BF_4 , or BPh_4) are reported. The fluxional nature of the five-coordinate cations $[\text{Co}(\text{diene})(\text{phosphine})_3]^+$ is shown by variable-temperature NMR spectroscopy (^1H and ^{31}P). Low-temperature spectra are consistent with a square-pyramidal structure in which the diene occupies two basal coordination sites.

Introduction

Alcoholic solutions of secondary or tertiary phosphines and cobalt(II) salts of low-coordinating anions have been found to be useful starting systems for the synthesis of several cobalt(I) and cobalt(III) complexes [1]. In the present paper we describe the reactions of these systems with conjugated dienes, and the preparation and characterization of complexes of the type $[\text{Co}(\text{diene})(\text{phosphine})_3]\text{Y}$ (diene = 1,3-butadiene and 2-methyl-1,3-butadiene (isoprene); phosphine = PMe_3 , PMe_2Ph , and HPPH_2 ; $\text{Y} = \text{ClO}_4$, BF_4 or BPh_4). These complexes, together with those of the type $[\text{Co}(\text{diene})(\text{CO})_{3-n}(\text{PPh}_3)_n]^+$ ($n = 0, 1, 2$) previously reported [2], are closely related to the isoelectronic $[\text{Fe}(\text{diene})(\text{CO})_{3-n}(\text{phosphine})_n]$ complexes ($n = 0-3$, phosphine = PF_3 or PPh_3) [3], which aroused a great deal of interest, owing to their dynamic behaviour in solution. Also the $[\text{Co}(\text{diene})(\text{phosphine})_3]^+$ cations are found to be fluxional, and their stereochemistry has been investigated here by NMR spectroscopy. Stereochemical non-rigidity appears to be a feature of several five-coordinate complexes of d^8 metal ions. Among them, MHL_4 and ML_5 adducts of the Group VIII metals have been extensively studied [4]. As far as cobalt(I) is concerned, the fluxional complexes $[\text{Co}(\text{tripphosphine})(\text{CO})_2]^+$ and $[\text{Co}(\text{tripphosphine})(\text{L})(\text{CO})]^+$ ($\text{L} = \text{phosphine}$ or phosphite) [5], and $[\text{Co}(1,3\text{-butadiene})(\text{P}(\text{OMe})_3)_3]^+$ [6] have been reported since our previous report on this work [1a].

Experimental

Microanalyses were performed by Mr. L. Turiaco, Istituto di Chimica Analitica, University of Padova. Literature methods were used to prepare the phosphines. All the reactions and measurements were carried out under an atmosphere of nitrogen; yields of the preparations were in the range 70–80%. Electrical conductivities were measured with a LKB 3216B conductivity bridge. IR spectra were recorded on a Perkin–Elmer 457 spectrophotometer. GLC analysis were carried out on a Hewlett Packard 5750 instrument. NMR spectra were recorded on a Bruker WP-60 spectrometer operating at 14.09 kG in the FT mode (^1H and ^{31}P) and on a Bruker 90 MHz HFX spectrometer (^1H). The acetone- d_6 resonance from the solvent was used as internal reference from proton spectra and chemical shift data were referred to tetramethylsilane. Simulated spectra were obtained by means of the computer of the Bruker WP-60 spectrometer.

$[\text{Co}(\text{diene})(\text{PMe}_3)_3]\text{BPh}_4$. Trimethylphosphine (1.1 g, 15 mmol), generated from the adduct $(\text{PMe}_3)\text{AgI}$ by heating the solid compound in a microdistillation unit under nitrogen at 100–150°C, was condensed in a deaerated solution of $\text{Co}(\text{ClO}_4)_2 \cdot 6 \text{H}_2\text{O}$ (1 g, 3 mmol) in isopropyl alcohol (20 ml) cooled at –70°C. The red mixture which formed immediately, was stirred at room temperature under an atmosphere of butadiene (or in the presence of an excess of isoprene (ca. 1 ml)) until a clear orange solution was obtained (24–48 h). Addition of an excess of NaBPh_4 in ethanol gave yellow-orange crystals, which were recrystallized from tetrahydrofuran/isopropyl alcohol and dried under vacuum.

$[\text{Co}(\text{diene})(\text{PMe}_2\text{Ph})_3]\text{Y}$ (*diene* = butadiene, $\text{Y} = \text{BF}_4$ and ClO_4 ; *diene* = isoprene, $\text{Y} = \text{ClO}_4$). To a solution of $\text{CoY}_2 \cdot 6 \text{H}_2\text{O}$ (1 g, 3 mmol) in isopropyl alcohol (20 ml) the phosphine (ca. 2.1 ml, 15 mmol) was added, and the solution stirred at ambient conditions under an atmosphere of butadiene or in the presence of an excess of isoprene (ca. 1 ml) for 1 h. A clear orange oil was formed; this was separated, washed with 2-propanol and dissolved in methanol. Addition of isopropyl alcohol gave yellow crystals, which were recrystallized from methanol/isopropyl alcohol and dried under vacuum.

$[\text{Co}(\text{diene})(\text{HPPh}_2)_3]\text{Y}$ ($\text{Y} = \text{ClO}_4$ and BF_4). (a) The phosphine (2.8 ml, 15 mmol) was added to $\text{CoY}_2 \cdot 6 \text{H}_2\text{O}$ (1 g, 3 mmol) in isopropyl alcohol (20 ml) and the solution stirred at room temperature under an atmosphere of butadiene (or in the presence of an excess of isoprene (ca. 1 ml)), for 3 h. The precipitated yellow compounds were recrystallized from dichloromethane/tetrahydrofuran and dried under vacuum. (b) *cis* $[\text{CoH}_2(\text{HPPh}_2)_4]\text{Y}$ [1a] was stirred in tetrahydrofuran under an atmosphere of butadiene (or in the presence of an excess of isoprene) for 30 min. The precipitated compounds were purified as above.

Results and discussion

Preparation of the complexes

The complexes $[\text{Co}(\text{diene})(\text{phosphine})_3]\text{Y}$ are diamagnetic, slightly air-sensitive, yellow or yellow-orange, crystalline solids. The compounds were characterized by elemental analyses and NMR spectra and shown to be 1/1 electrolytes in nitromethane (Table 1). The presence of one π -bonded conjugated diene was confirmed by GLC analysis of the products of thermal decomposition and of

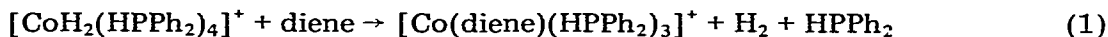
TABLE 1
ANALYTICAL DATA AND PHYSICAL PROPERTIES

Compound	M.p. ^a (°C)	Λ_M ^b	Analysis (found (calcd.) (%))	
			C	H
[Co(C ₄ H ₆)(PMe ₃) ₃]BPh ₄	189	98	67.21 (67.30)	8.05 (8.09)
[Co(C ₅ H ₈)(PMe ₃) ₃]BPh ₄	199	97	67.51 (67.68)	8.66 (8.22)
[Co(C ₄ H ₆)(PMe ₂ Ph) ₃]BF ₄ ^c	139	95	54.41 (54.70)	6.34 (6.40)
[Co(C ₅ H ₈)(PMe ₂ Ph) ₃]ClO ₄ ^d	121	92	53.50 (54.34)	6.46 (6.45)
[Co(C ₄ H ₆)(HPPPh ₂) ₃]BF ₄ ^c	175	94	61.84 (63.34)	5.15 (5.18)
[Co(C ₅ H ₈)(HPPPh ₂) ₃]BF ₄ ^c	168	92	62.72 (63.75)	5.21 (5.35)

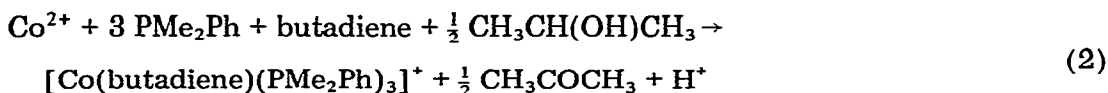
^a In sealed tube under vacuum. ^b S cm² mol⁻¹, in nitromethane at 20°C for 10⁻³ M solutions. ^c Analytical data and physical properties for the corresponding perchlorate derivatives have been reported previously (see [1a]). ^d From [1a].

the products of the displacement reaction with carbon monoxide, which gives the di-carbonyl derivatives, [Co(CO)₂(phosphine)₃]Y [1c].

The [Co(diene)(phosphine)₃]Y complexes were prepared by the reaction of the diene with a mixture of CoY₂ · 6 H₂O and the phosphine in isopropyl alcohol at room temperature. An alternative synthetic route for the diphenylphosphine derivatives involves treatment of the compounds *cis*-[CoH₂(HPPPh₂)₄]Y [1a] with an excess of the diene, according to equation 1.

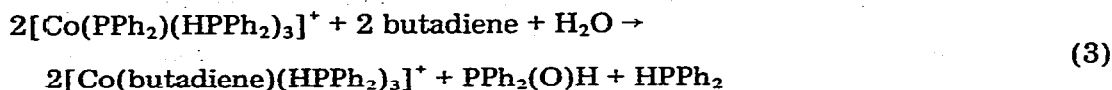


The stoichiometry of the reaction of formation of the complexes [Co(diene)-(phosphine)₃]Y from the CoY₂ · 6 H₂O salts has been examined in detail in the case of the dimethylphenyl- and diphenyl-phosphine butadiene derivatives. In all the cases a dismutative route, 2Co^{II} → Co^I + Co^{III}, followed by addition of the diene to the cobalt(I) intermediate can be ruled out, since the cobalt(II) originally present is found to give over 70% yield of the cobalt(I) product. Gas chromatography of the reaction mixture formed from PMe₂Ph in isopropyl alcohol shows that the reduction of cobalt(II) is accompanied by the formation of acetone (ca. 0.5 mol per mol of Co). On the basis of this observation the stoichiometry shown in eq. 2 can be proposed.



The CoY₂/PMe₂Ph system has been found to react with carbon monoxide in isopropyl alcohol in a similar manner to give the cobalt(I) adduct [Co(CO)₂(PMe₂Ph)₃]⁺ [1c]. In contrast, the formation of the adduct with diphenylphosphine does not involve oxidation of isopropyl alcohol, since no acetone could be detected in the reaction mixture. In this case the first product of the interac-

tion is presumably the cobalt(II) phosphido derivative $[\text{Co}(\text{PPh}_2)(\text{HPP}_2)_3]^+$ [7], which then slowly reacts with the diene to give $[\text{Co}(\text{diene})(\text{HPP}_2)_3]^+$. The IR spectra of the reaction mixture from $[\text{Co}(\text{PPh}_2)(\text{HPP}_2)_3]\text{BF}_4$ and butadiene in isopropyl alcohol (in the presence of water) after separation of the phosphine-diene-cobalt(I) product, contains free phosphine and phosphine oxide. Therefore, in this case the reducing agent appears to be the phosphine itself, and the redox reaction can be tentatively represented as in eq. 3.



The method of synthesis of the $[\text{Co}(\text{diene})(\text{phosphine})_3]\text{Y}$ complexes from the salts $\text{CoY}_2 \cdot 6 \text{H}_2\text{O}$ is not generally applicable and fails with a number of secondary and tertiary phosphines, e.g. PCy_3 , PPh_3 , PPh_2R ($\text{R} = \text{Me}, \text{Et}$), PR_3 ($\text{R} = \text{Et}, \text{n-Pr}, \text{n-Bu}$), and HPCyR ($\text{R} = \text{Cy}, \text{Ph}$). It is noteworthy that the largest phosphines of the series (PPh_2R , PPh_3 , PCy_3 , HPCy_2 , HPCyPh) do not interact appreciably at room temperature with the cobalt(II) salts in isopropyl alcohol in the absence of the diene. It is possible that the formation of a phosphine-diene-cobalt(II) adduct is required as a first step in the reduction to cobalt(I), and a poor coordinative ability of the phosphine toward cobalt(II) may be responsible for the lack of reactivity of the above CoY_2 -diene-phosphine systems. In the case of the "small" secondary phosphines HPR_2 ($\text{R}_2 = \text{EtPh}, \text{MePh}, \text{Et}_2$), different behavior is observed. If the reaction is carried out at a molar ratio HPR_2/Co 3/1, yellow solutions are slowly formed in the presence of the dienes, which probably contain the $[\text{Co}(\text{diene})(\text{HPR}_2)_3]^+$ derivatives. However, from these solutions only yellow oils can be recovered, containing paramagnetic impurities which prevent NMR characterization. By contrast, in the presence of a five-fold excess of HPR_2 no reaction with the conjugated dienes were observed. Under these conditions the stable low-spin five-coordinate $[\text{Co}(\text{HPR}_2)_5]^{2+}$ adducts are immediately formed [7]. It must be noted that only the conjugated dienes are able to promote the reduction of cobalt(II) to the cobalt(I) organometallic derivatives. Analogous reactions were not observed with mono-olefins (1-hexene, cyclohexene), with activated olefins, e.g. *trans*-dicyanoethylene, and with non-conjugated dienes, such as 1,5-cyclooctadiene.

NMR studies

Proton spectra were recorded at various temperature in acetone- d_6 . The spectra were found to be temperature dependent, showing the fluxional nature of the complex cations $[\text{Co}(\text{diene})(\text{phosphine})_3]^+$. In all the cases slow exchange limit spectra could be obtained, whereas fast exchange limit conditions could not be reached. ^1H NMR parameters are quoted in Tables 2 and 3. Numbering of the diene atoms is presented in Fig. 1. In addition to the reported resonances, phosphine and/or BPh_4 phenyl proton resonances at ca. τ 2.5 ppm are observed.

$[\text{Co}(\text{diene})(\text{PMe}_3)_3]\text{Y}$. The methyl resonance of the butadiene complex appears at room temperature as a broad band (width ca. 10 Hz), superposed on the H(1B)—H(4B) olefin resonances. When the temperature is lowered, splitting of the methyl resonance into two groups of signals is observed. The slow exchange limit spectrum displays a doublet (P—CH₃ (A)) and a pseudotriplet

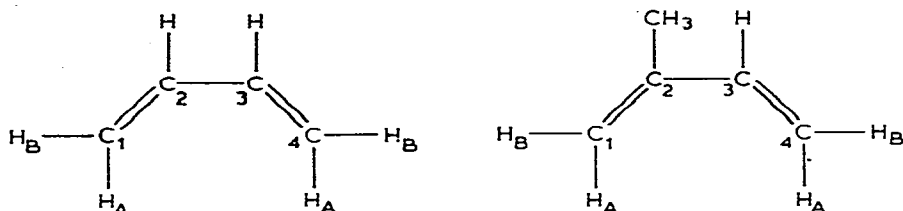


Fig. 1.

(P—CH₃ (B)) with intensities in the ratio 1/2. This pattern is accounted for by the presence of a phosphine ligand in a unique position (X_nA spin system) and of two chemically equivalent groups with strongly coupled phosphorus nuclei (X_nAA'X'_n spin system [8]). The splitting of the outer lines of the pseudotriplet can be reasonably assumed to be equal to $|^2J(\text{PH})|$. Assignment of two separate spin systems for (A) and (B) phosphines would strictly require no coupling between P_A and P_B nuclei; however, a weak P_A—P_B coupling (of the order of, say, 10 Hz) could still be consistent with the spectrum appearance. Spectra of CH₂Cl₂ or CDCl₃ solutions in the range -70—60°C have also been measured at 60 and 90 MHz. Time averaging of the P—CH₃ (A) and P—CH₃ (B) resonances with increasing temperature is in agreement with a dynamic structure, where coordination site exchange of the phosphine ligands occurs. For the isoprene complex also the phosphine methyl resonance appears at room temperature as a broad band (with ca. 10 Hz), and splitting into two groups of signals is observed when the temperature is lowered. The slow exchange limit spectrum shows a doublet (P—CH₃ (A)) and a pseudoquintet (P—CH₃ (B), splitting of the outer lines 10 Hz) with intensity in the ratio 1/2. The resonances are respectively ascribed to a unique phosphine ligand and to a system of two PMe₃ groups with strongly coupled phosphorus nuclei. The departure of the P—CH₃ (B) resonance from the pseudotriplet pattern expected for an X_nAA'X'_n system, where $|J_{AA'}| \gg |J_{AX} - J_{AX'}|$ [8], can be accounted for by the presence of two phosphine ligands in two slightly different chemical environments.

[Co(diene)(PMe₂Ph)₃]Y. The P—CH₃ ¹H NMR behaviour of the butadiene complex is similar to that of the trimethylphosphine complexes. In the slow exchange limit spectrum a doublet (P—CH₃ (A)) and a pseudoquartet (P—CH₃ (B), splitting of the outer lines 12 Hz) with relative intensities 1 and 2 are observed. The departure of the P—CH₃ (B) resonance from a pseudotriplet pattern can be accounted for by a small chemical shift between P—CH₃ (B) protons, due to the presence of two phosphines in slightly different environments and/or to intrinsic non-equivalence of the methyl groups on each ligand. Also the isoprene adduct displays in the range τ 7.5—9 ppm a temperature-dependent spectrum. The set of overlapping resonances from diene and phosphine protons is complex even at 90 MHz and has not been analyzed.

[Co(diene)(HPPH₂)₃]Y. The PH proton resonance of the butadiene and isoprene complexes at room temperature can be regarded as the X pattern of an XX'X''AA'A'' spin system [9], although fine structure cannot be observed and fast exchange limit conditions are not attained. The splitting of the sharp doublet apparent in these systems [10] is referred to as $\Sigma J(\text{P—H})$ in the Tables;

TABLE 2
¹H NMR DATA FOR BUTADIENE COMPLEXES

Complex	Temperature (°C)	Chemical shifts, τ (ppm)					
		H(2)-H(3)	H(1B)-H(4B)	H(1A)-H(4A)	P-CH ₃ (A)	P-CH ₃ (B)	P-H
[Co(butadiene)(PMe ₃) ₃]BPh ₄	25	4.50	<i>a</i>	9.92	8.48	8.48	
	-40	4.76	<i>a</i>	9.92	8.28	8.56	
[Co(butadiene)(PMe ₂ Ph) ₃]BF ₄	25	4.34	<i>a</i>	10.29	ρ_2 (PH) 7.8 Hz	ρ_2 (PH) 7.8 Hz	
	-30	4.30	8.11	10.36	7.78	8.48	
[Co(butadiene)(HPPH ₂) ₃]BF ₄	25	3.79	8.19	9.95	ρ_2 (PH) 7.8 Hz	...	3.34
	-40	3.68	8.88	10.06			ΣJ (PH) 372 Hz <i>b</i>

a Resonance overlapping with other signals, *b* Complex pattern (see text).

TABLE 3
¹H NMR DATA FOR ISOPRENE COMPLEXES

Complex	Temperature (°C)	Chemical shifts, τ (ppm)					
		H(3)	H(1B)-H(4B)	H(1A)-H(4A)	CH ₃ (2)	P-CH ₃ (A)	P-CH ₃ (B) P-H
[Co(isoprene)(PMe ₃) ₃]BPh ₄	25	4.76	<i>a</i>	10.10 ^b	7.78 ^c	8.49	
	-40	4.76	<i>a</i>	10.16 ^b	7.77 ^c	8.57	
[Co(isoprene)(PMe ₂ Ph) ₃]X ^d	25	4.35	<i>c</i>	10.35 ^b	<i>c</i>	<i>c</i>	3.68
	-55	4.15	<i>c</i>	10.39 ^b	<i>c</i>	<i>c</i>	ΣJ (PH) 363 Hz
[Co(isoprene)(HPPH ₂) ₃]BF ₄	25	4.27	8.31 ^b	10.29 ^b	7.60	...	<i>c</i>
	-10	4.19	8.52 ^b	10.43 ^b	7.48		<i>c</i>

a Resonance overlapping with other signals, *b* Asymmetric signal; value of maximum, *c* Signal partly overlapping with the solvent resonance, *d* X = BPh₄, ClO₄, *c* Complex pattern (see text).

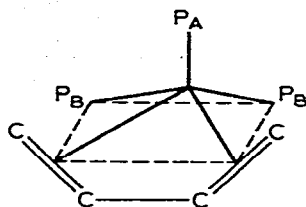


Fig. 2.

the chemical shift of the PH protons is calculated as the doublet midpoint. Temperature dependence of the PH signals is observed, but slow exchange limit spectra could not be analyzed because of partial overlap with other resonances and poor resolution.

The low temperature spectrum of the phosphine protons for the complex $[\text{Co}(\text{butadiene})(\text{PMe}_3)_3]\text{BPh}_4$ is a first indication of the presence of a basic structure of the type represented in Fig. 2. In order to achieve conclusive structural informations on these complexes, the NMR behaviour of the olefinic protons has been studied in detail.

For the butadiene complexes chemical equivalence between the $\text{C}(1)\text{H}_2\text{C}(2)\text{H}$ and the $\text{C}(4)\text{H}_2\text{C}(3)\text{H}$ groupings would be presented by a square-pyramidal structure with the diene occupying two basal coordination sites (Fig. 2). By contrast, non-equivalence would be presented both by a square-pyramidal structure with the diene spanning an apical and a basal coordination site, and by a bipyramidal structure involving apical-equatorial coordination of the diene. Equatorial binding of both diene ends in a bipyramidal structure seems not consistent with the chelate bite angle of the olefin and is not considered.

The olefin proton spectra of the butadiene adducts studied are similar; for the trimethylphosphine adduct at all temperatures and for the dimethylphenylphosphine adduct at room temperature the $\text{H}(1\text{B})$ and $\text{H}(4\text{B})$ resonances are hidden by other signals. The observed spectra are complex and have been compared with $\text{AA}'\text{MM}'\text{XX}'$ spectra calculated on the basis of chemical shift data of Table 2. In the computer simulation of spectra $J(\text{HH})$ values equal to those reported for the five-coordinated iron(0) complex $[\text{Fe}(\text{butadiene})(\text{CO})_3]$ [3b] have been assumed. Significantly, very similar coupling constants have been found also for a different *s-cis*-butadienemetal adduct [11]. Comparison of calculated and measured spectra of the three complexes at room temperature shows that the $\text{H}(2)\text{—H}(3)$ signals are very close to the simulated resonances, indicating either intrinsic or dynamic equivalence of $\text{H}(2)$ and $\text{H}(3)$ protons. The appearance of the $\text{H}(1)$ and $\text{H}(4)$ resonances is different from the calculated $\text{AA}'\text{MM}'\text{XX}'$ spectra, due to the presence of $^{31}\text{P}\text{—}^1\text{H}$ couplings. Very close measured and simulated signals of $\text{H}(2)\text{—H}(3)$ protons are also obtained for decoupling conditions from $\text{H}(1)$ or $\text{H}(4)$ protons. In the slow exchange limit spectra the shape of the $\text{H}(2)\text{—H}(3)$ signals is not changed, apart from slight line-broadening, with respect to the room temperature spectra. This result indicates a very small, if any, relative chemical shift between $\text{H}(2)$ and $\text{H}(3)$ protons and is consistent with a basic structure of the type described in Fig. 2. Analogous comparison cannot be made for the temperature dependent $\text{H}(1)$ and $\text{H}(4)$ proton resonances, because of the

presence of ^{31}P — ^1H couplings. However, the width of the H(1A)—H(4) signal of the complex $[\text{Co}(\text{butadiene})(\text{PMe}_3)_3]\text{BPh}_4$ at -40°C has been found to be independent of the spectrometer frequency, indicating no significant chemical shift between these protons.

The H(3) proton resonance of the isoprene complexes resembles the H(2)—H(3) signal of the butadiene adducts and is temperature independent. These observations rule out the presence of different isomers. The terminal olefinic protons of coordinated isoprene give rise in all the cases to two groups of asymmetric and temperature dependent signals, which are complex, even under decoupling conditions from the H(3) nucleus, due to ^{31}P — ^1H couplings.

Some proton-decoupled ^{31}P spectra of the complexes have been measured. Line-broadening due to effects of ^{59}Co nuclear quadrupole prevents observation of fine structure; however, apparent features of the spectra are in agreement with the ^1H NMR assignments. Thus, in the low temperature limit spectrum of the complex $[\text{Co}(\text{butadiene})(\text{PMe}_2\text{Ph})_3]\text{BF}_4$ two signals with relative intensities 1 and 2 are ascribed to P_A and P_B nuclei. A chemical shift of 110 Hz between P_A and P_B and signal widths of ca. 20 and ca. 15 Hz, respectively, are measured. In the low temperature limit spectrum of the complex $[\text{Co}(\text{isoprene})(\text{PMe}_2\text{Ph})_3]\text{BPh}_4$, P_A and P_B signals with a relative chemical shift of 146 Hz and widths of ca. 30 and ca. 20 Hz, respectively, are measured. Splittings due to possible P_A — P_B spin—spin coupling or to chemical shift between P_B nuclei are under resolution limits. For both complexes broadening and overlap of P_A and P_B signals are observed in the intermediate exchange conditions.

Assignment of the structure in Fig. 2 for the $[\text{Co}(\text{diene})(\text{phosphine})_3]^+$ complexes is also in agreement with ^{31}P NMR data recently reported on different five-coordinated cobalt(I) adducts of P-donors [5]. Among a series of $^2J(\text{P}—\text{P})$ values for complexes having either trigonal-bipyramidal or square-pyramidal structures smallest values of $|^2J(\text{P}—\text{P})|$ (down to ca. 10 Hz) are found for P(apical)—P(basal) couplings in complexes with square-pyramidal geometry.

There is no evidence for basic structural changes of the complexes $[\text{Co}(\text{diene})(\text{phosphine})_3]^+$ with temperature. The observed variable temperature NMR behaviour is consistent with an intramolecular rearrangement which leads to interchange of apical and basal phosphine groups. Possible mechanisms of analogous intramolecular processes have been discussed for five-coordinated iron(0)—diene complexes [3f]. A dissociative mechanism of $[\text{Co}(\text{diene})(\text{phosphine})_3]^+$ involving intermolecular phosphine exchange can be eliminated, since in this case loss of ^{31}P — ^1H coupling of the olefinic H(1) and H(4) protons would be expected in the rapid limit of exchange. By contrast, the H(1) and H(4) resonances of the butadiene adducts (also measured under decoupling conditions from H(2) and H(3) protons) are found to approach with increasing temperature limit splitting patterns more complex than those calculated for coordinated butadiene in the absence of ^{31}P — ^1H couplings.

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