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# Infrared and Nuclear Magnetic Resonance Studies of Some π-Allyl Type Complexes

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Reaction of hydrocobalt tetracarbonyl with 1,3-butadiene, 2-methyl-1,3-butadiene, 1,3-pentadiene, 1,4-pentadiene, and 2,3-dimethyl-1,3-butadiene gives products which have been identified as substituted π-allyl cobalt tricarbonyls. The infrared and nuclear magnetic resonance spectra of the complexes are discussed. Isomers are reported for the complexes of 1,3-butadiene, 1,3-pentadiene, and 1,4-pentadiene.

Introduction

Complexes of various metal carbonyls with allylic radicals have been the subject of several recent papers.[1-4] The first such compound was prepared by Prichard,[5] who erroneously reported the formula as $C_4H_7Co(CO)_4$; the correct formula was shown to be $C_4H_7Co(CO)_3$.[6a,b] Later, a structure involving σ and π-bonds was proposed, the possibility of a symmetrical structure between the cobalt and the C_4H_7 group was suggested, and two different isomers were recognized.[7,8] A similar compound was prepared from allyl bromide and potassium cobalt tetracarbonylate and a symmetrically bonded structure suggested.[9] Similar to allyl palladium chloride complexes[2b] a planar allyl group was inferred for the $C_4H_7Co(CO)_3$ complex.[1] A sandwich-type structure involving π-bonding was given for the compound and the two isomers were pictured as I and II, I being the stable form.
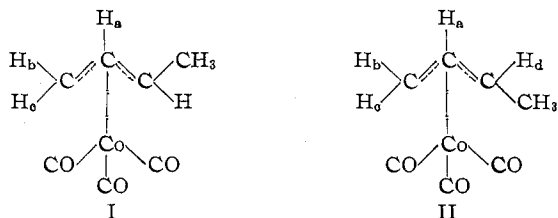
Names suggested for the two isomers are *anti*-1-methyl-π-allyl cobalt tricarbonyl for II and *syn*-1-methyl-π-allyl cobalt tricarbonyl for I.[3]

A series of complexes which are derivatives of π-allyl cobalt tricarbonyl have been studied. They were prepared by reaction of hydrocobalt tetracarbonyl with the following conjugated and unconjugated diolefins: 1,3-butadiene, 2-methyl-1,3-butadiene, 1,3-pentadiene, 2,3-dimethyl-1,3-butadiene, and 1,4-pentadiene. The

formula of all of the complexes can be represented as $RCo(CO)_3$, with R representing 1-methylallyl, 1,1-dimethylallyl, 1,3-dimethylallyl, 1,1,2-trimethylallyl, and 1-ethylallyl for the diolefins in the order listed.

Experimental

Preparation of Potassium Cobalt Tetracarbonylate.—This preparation is a modification of Gilmont and Blanchard's method.[10] A solution was prepared consisting of 86.6 g. of KOH, 6.6 g. of KCN, and 300 ml. of distilled H_2O. A 23-g. sample of $CoCO_3$ was added with stirring to form a slurry. The mixture then was placed in a 1-l. steel autoclave, pressured to 1000 p.s.i. with CO, and heated to 80°, with rocking, for 3 hr. The resulting yellow solution contained approximately 0.2 mole of $K[Co(CO)_4]$.

Preparation of Complexes.—Without mixing, 120 ml. of concentrated H_3PO_4 and 0.2 mole of one of the diolefins was added to the above solution in the autoclave. The acid and diolefin were added in separate bottles which were carefully lowered into the vessel, the bottles being of sufficient length that the necks remained above the level of solution. The autoclave then was closed and inverted to mix the reactants. Rocking was continued for 24 hr. with all reactions except that of 2,3-dimethyl-1,3-butadiene, which was rocked for several days.

The vessel was vented to the atmosphere, opened under a stream of nitrogen, and 100 ml. of hexane was added to extract the complex. The two layers then were transferred to a separatory funnel through a siphon arrangement and the hexane layer separated. The hexane layer was washed with distilled water, dried over Na_2SO_4, transferred to a vacuum distillation apparatus, and the hexane was removed by aspirator vacuum. The product was distilled under high vacuum. Yields were approximately 30% for all of the conjugated diolefins; a much lower yield was obtained for the 1,4-pentadiene reaction.

1,3-Butadiene Product.—This distilled at 33° (1 mm.). *Anal.* Calcd. for $(CO)_3CoC_4H_7$: C, 42.4; H, 3.6. Found: C, 42.7; H, 3.7.

2-Methyl-1,3-butadiene Product.—The product distilled at 42° (1 mm.). *Anal.* Calcd. for $(CO)_3CoC_5H_9$: C, 45.3; H, 4.3. Found: C, 46.5; H, 4.9.

1,3-Pentadiene Product.—The product distilled at 42° (1 mm.). *Anal.* Calcd. for $(CO)_3CoC_5H_9$: C, 45.3; H, 4.3. Found: C, 45.7; H, 4.5.

1,4-Pentadiene Product.—The yield of complex was low due to considerable amounts of organic compounds from competing reactions; fractional distillation was necessary to separate the complex. The complex was collected at 45° (1 mm.). *Anal.* Calcd. for $(CO)_3CoC_5H_9$: C, 45.3; H, 4.3. Found: C, 44.7; H, 4.7.

Isomerization Studies.—A previous publication from these Laboratories[7] discussed the two isomers of the 1,3-butadiene complex. The above preparation gives a mixture of the two

(1) D. W. Moore, H. B. Jonassen, T. B. Joyner, and J. A. Bertrand, *Chem. Ind.* (London), 1304 (1960).

(2) (a) H. C. Dehm and J. C. W. Chien, *J. Am. Chem. Soc.*, **82**, 4429 (1960); (b) J. M. Rowe, *Proc. Chem. Soc.*, 66 (1962).

(3) W. R. McClellan, H. H. Hoehn, H. N. Cripps, E. L. Muetterties, and B. W. Howk, *J. Am. Chem. Soc.*, **83**, 1601 (1961).

(4) H. D. Kaesz, R. B. King, and F. G. A. Stone, *Z. Naturforsch.*, **15b**, 682 (1960).

(5) W. W. Prichard, U. S. Patent 2,600,571 (1952).

(6) (a) H. B. Jonassen, R. I. Stearns, and J. Kenttamaa, *J. Am. Chem. Soc.*, **80**, 2586 (1958); (b) W. W. Prichard, U. S. Re 24,653 (1959).

(7) C. L. Aldridge, H. B. Jonassen, and E. Pulkkinen, *Chem. Ind.* (London), 374 (1960).

(8) H. B. Jonassen, Vth International Conference on Coördination Compounds, London, 1959.

(9) R. F. Heck and D. S. Breslow, *J. Am. Chem. Soc.*, **82**, 750 (1960).

(10) P. Gilmont and A. S. Blanchard, *Inorg. Syn.*, **2**, 238 (1946).

TABLE I

N.M.R. Spectrum Parameters of Cobalt Tricarbonyl π-Allyl Complexes[a]

Compound	Chemical shifts, c.p.s. (rel. to benzene)						Spin-coupling constants, c.p.s.					
	H_a	H_b	H_c	H_d	CH_3	CH_3'	J_{ab}	J_{ac}	J_{ad}	J_{bc}	J_{bd}	$J(H_d\text{-}CH_3)$
1-Methyl-π-allyl (I)	114	223	279	209	302	...	6.3	10.5	10.5	<0.2	<0.2	6.5
1-Methyl-π-allyl (II)	99	201	228	143	...	327	7.1	12.3	6.8	0.6	1.6	7.0
1,2-Dimethyl-π-allyl	114	214	248	...	293	321	6.4	11.2	...	1.2	...	...
1,1,2-Trimethyl-π-allyl	...	210	239	280[b]	289	319	...	...	...	0.8	...	...
1,3-Dimethyl-π-allyl (I)	124	...	223	223	305	...	...	9.8	9.8	...	...	6.5
1,3-Dimethyl-π-allyl (II)	111	...	225	166	299	327	...	11.3	7.2	...	...	6.5,6.5
1-Ethyl-π-allyl (I)	114	222	281	217	...	330	6.2	10.4	10.0	<0.2	<0.2	...
			δ(CH₂) = 294					J(CH₂-CH₃) = 7.1; J(H_d-CH₂) = 6.3				
1-Ethyl-π-allyl (II)	104	203	233	147	337		6.4	10.9	7.0	0.8	1.6	...
		δ(CH₂) ≈ δ(CH₃) ≈ 310						J(CH₂-CH₃) not observable; J(H_d-CH₂) = 6.3				

[a] All spectra obtained at 60 Mc.   [b] 2-Methyl group.

isomers in a ratio of about 60:40; by heating to 120° the mixture was found to isomerize to a ratio of about 95:5. Samples of each of the described complexes were treated in a similar manner. For the 1,3-butadiene, 1,3-pentadiene, and the 1,4-pentadiene complexes an appreciable change in infrared or n.m.r. spectra for samples was noted on heating.

Nuclear Magnetic Resonance Spectra.—Proton magnetic resonance spectra of the hydrocobalt tetracarbonyl adducts formed with the five previously mentioned diolefins have been obtained at 60 Mc. In three of these the spectra confirm the formation of isomeric pairs of derivatives.

Samples were vacuum-distilled at room temperature into 4.0-mm. Pyrex tubes immediately prior to each spectrometer run, since it was found that the decomposition products which form at normal temperatures cause severe spectral broadening. The sample tubes were sealed off and inserted into standard 5.0-mm. thin-walled tubes with benzene in the annular volume as an external chemical-shift reference.

Infrared Spectra.—Infrared spectra of all complexes were ob-

tained in carbon tetrachloride. A Beckman IR-5 instrument was used.

Results and Discussion

(a) Nuclear Magnetic Resonance Spectra.—The unusual features of the n.m.r. spectra of these materials may be interpreted in terms of structures which have a considerable aromatic character. The similarity of the π-allylic structure to a partial benzene ring is emphasized by spin-coupling interactions corresponding to those observed between ring protons in benzene. In isomer II the constants J_{ab} and J_{bd} correspond to normal values for *ortho*- and *meta*- substituted ring protons. The chemical shift values show large variations with position of proton substitution. The latter effect may be explained by shielding anisotropy arising from the charge asymmetry of the π-allyl group.

1,3-Butadiene.—The measured spectral parameters are given in Table I. Figure 1 shows the observed spectra for the stable 1-methyl-π-allyl complex. Figure 2 shows the spectra of the two 1-methyl-π-allyl isomers. The equality of the coupling constants J_{a2} and J_{ad} in isomer I and J_{ab} and J_{ad} in isomer II offers the best proof of the symmetry of bonding in the π-allylic structure. The absence of observable coupling between H_b and H_c is not surprising, since the angular dependence of the coupling constant as shown by Gutowsky, Karplus, and Grant[11] predicts zero coupling for *gem*-protons when the bond angle is 125°.

The abnormally high shielding observed for H_c in isomer I, and the corresponding upfield shift of H_d for isomer I compared to isomer II, suggests an anisotropic shielding effect which might arise from the asymmetric π-electron cloud.

2-Methyl-1,3-butadiene (Isoprene).—The addition of hydrocobalt tetracarbonyl to this compound apparently results in protonation in the 1-position and thus can give only one isomer
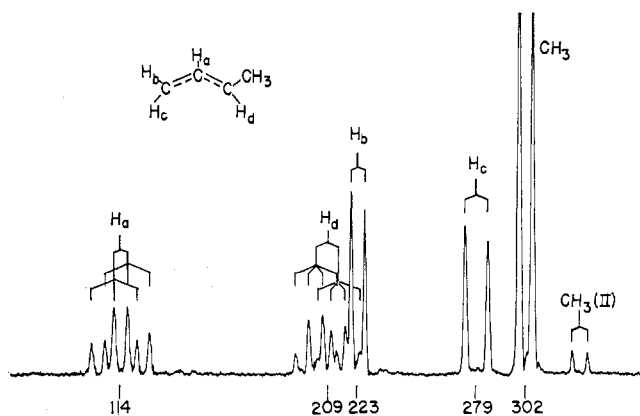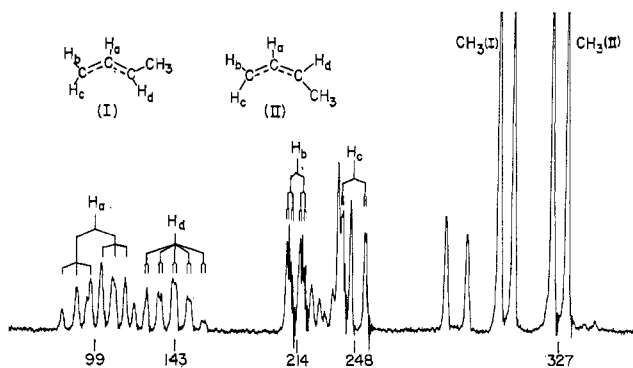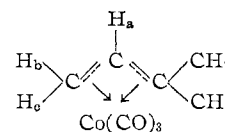

Figure 1.

Figure 2.

(11) H. S. Gutowsky, M. Karplus, and D. M. Grant, *J. Chem. Phys.*, **31**, 1278 (1959).

The 60 Mc. spectrum is shown in Fig. 3 and the measured parameters are in Table I. The weak spin-coupling of H_b and H_c observed in this complex is more typical of terminal olefinic methylene groups. The large chemical shift separating them again is suggestive of a strong diamagnetic anisotropy, which is further evidenced by the separation of the methyl group signals.

2,3-Dimethyl-1,3-butadiene.—Only one isomer is possible. The spectrum, Fig. 4, shows the expected three methyl signals, which have been assigned on the basis of shift values observed in previous compounds. As in the isoprene derivative, a weak J_{bc} coupling is observed.

1,3-Pentadiene.—In theory, three isomers are possible from protonation of a terminal CH_2.

I

II

III
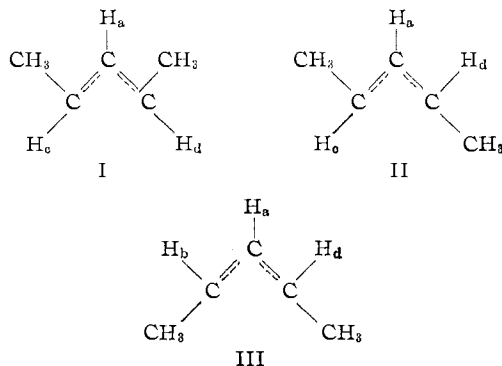
Actually only I and II are found in the usual products, with the symmetrical structure I predominating. The proton spectrum, Fig. 5, shows both isomers. The simple multiplet pattern of I can be readily assigned, and affords additional proof for the symmetric structure of the π-allylic grouping. The spectrum of the asymmetric isomer II is partially obscured by the lines of the major component, but can be assigned by reference to parameters determined for butadiene isomers. These values are given in Table I.

1,4-Pentadiene.—The addition of hydrocobalt tetracarbonyl to this non-conjugated diolefin brings about a surprising proton rearrangement to form the ethyl-π-allyl structures

I

II
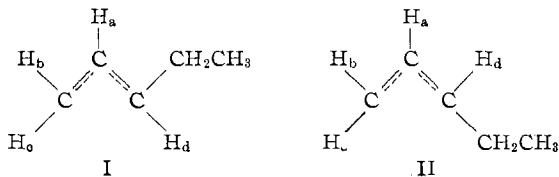
The original reaction product is a mixture of isomers with I predominating; thermal isomerization of II is nearly complete in 1.5 hr. at 90°. Figure 6 shows the proton spectra of the mixture and Fig. 7 that of the purified stable isomer. A slight amount of methyl-containing impurity, perhaps the 1,3-pentadiene adduct, appears in the methylene proton of the spectrum. The parts of the spectra corresponding to the π-allylic grouping are nearly identical with the corresponding spectra of the two butadiene adducts. Table I lists the measured spectral values.
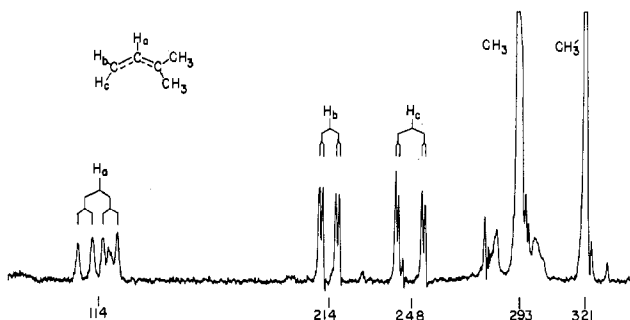
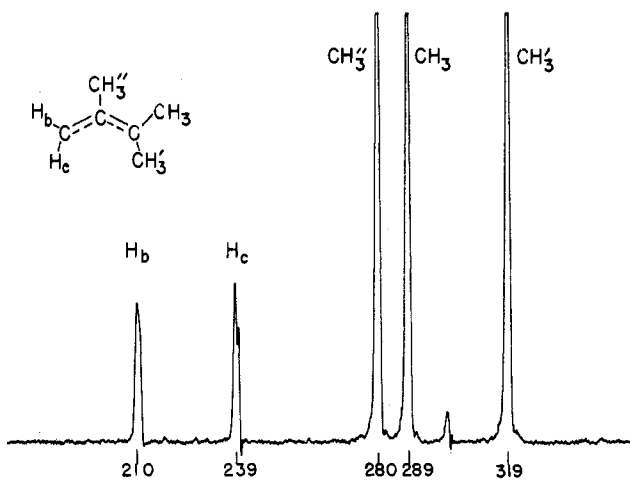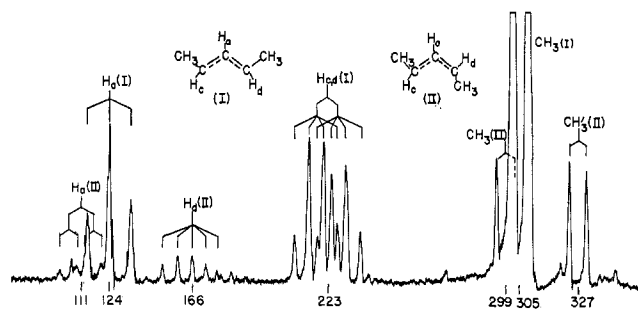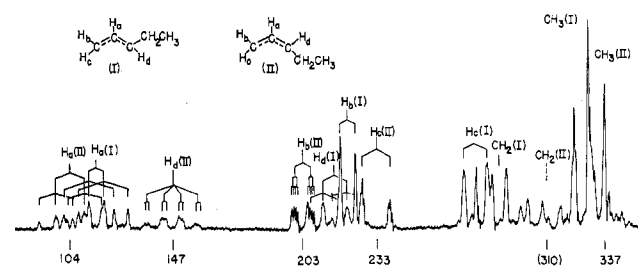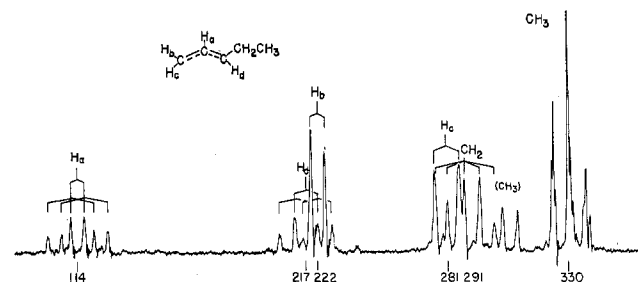A recent publication,[3] which verified the existence of

Figure 3.

Figure 4.

Figure 5.

Figure 6.

Figure 7.

Table II
Characteristic Infrared Bands of Complexes

1,3-Butadiene (stable isomer)	1,3-Butadiene (unstable isomer)[a]	1,3-Pentadiene	2,3-Dimethyl-1,3-butadiene	2-Methyl-1,3-butadiene	1,4-Pentadiene
3030 (sh)			3077 (vw)	3030 (w)	
			3003 (w)		
2994 (m)		2941 (m)	2959 (w)	2955 (sh)	2950 (s)
2924 (m)		2890 (m)	2899 (m)	2890 (s)	2890 (m)
2873 (sh)		2041 (s)	2045 (s)		2040 (vs)
2049 (s)					
2000–1960 (vs)		2000–1960 (vs)	2000–1960 (vs)	2000–1960 (vs)	2000–1960 (vs)
1460 (m)	1488 (w–m)	1451 (m)	1462 (sh)	1450 (sh)	1740 (m)
1441 (m)	1389 (w–m)	1433 (m)	1449 (m)	1425 (s)	1690 (s)
1433 (sh)	1174 (w)	1397 (w)	1437 (sh)	1370 (s)	1450 (s)
1379 (m)	1067 (w)	1370 (m)	1374 (s)	1230 (sh)	1425 (s)
1235 (m)		1239 (w)	1190 (w)	1205 (m)	1390 (m)
1182 (w)		1176 (w)	1160 (m)	1190 (m)	1300 (m)
1031 (s)		1053 (sh)	1066 (s)	1065 (s)	1180 (m)
		1032 (s)	1031 (s)	1030 (sh)	1050 (w)
980 (w)		943 (m)	935 (s)	990 (w)	990 (w)
943 (w)		917 (w)		940 (m)	920 (m)
926 (w)					
870 (m)	860 (m)	877 (w)	893 (w)	880 (s)	860 (m)
840 (w)		862 (w)		840 (sh)	
		833 (w)			

[a] Absorption peaks in spectrum of mixture of isomers which disappear on heating.

two isomers of the complex formed from 1,3-butadiene, questioned the results previously reported[7] concerning the conversion of a mixture of the two isomers, in the ratio 60:40, to a product which is almost entirely the stable isomer. The authors report that their complex was unchanged by heating. Comparison of their n.m.r. spectra with those previously published[2] shows that their product, before and after heating, is very similar to the product we obtained by heating, ca. 95% of the stable isomer. Possibly the different method of preparation employed does not give the same mixture of isomers. Work in these Laboratories has indicated that the reaction of different halo-butene isomers with potassium cobalt tetracarbonylate does give different isomer ratios in the product.[12]

(b) **Infrared Spectra.**—Infrared absorptions are summarized in Table II. The spectra of these complexes showed the absence of an absorption around 1600 cm.$^{-1}$, the normal carbon–carbon double bond region. McClellan[3] associated the corresponding band of π-allylcobalt tricarbonyl with carbon–carbon stretching of the π-allyl group; a similar absorption in the spectrum of 1,3-butadiene–iron tricarbonyl was attributed to double-bond character in the diolefin group.[13] An absorption band in the range 1500–1560 cm.$^{-1}$ in the spectra of substituted allylic anions of alkali metals was assigned by Lanpher[14] to carbon–carbon unsymmetrical stretching. Evidence that this absorption actually is due to carbon–carbon double bonding is suggested by a peak at 1487 cm.$^{-1}$ for the unstable isomer of 1,3-butadiene, which, as is verified by lower field shifts in nuclear magnetic resonance spectra, has more double bond character than the stable isomer.

Strong absorptions are observed for all of the complexes of conjugated diolefins in the region between 1030 and 1070 cm.$^{-1}$. Absorptions in this region in the spectra of ferrocene and similar compounds have been attributed to carbon–hydrogen bonding[15]; absorptions in the same region in various acetylacetonates have been assigned to methyl-rocking modes.[16] The presence of absorptions at both 1030 and 1068 cm.$^{-1}$ in the spectrum of the 2,3-dimethyl-1,3-butadiene and isoprene complex and only one such absorption for each of the other complexes suggests that the absorption is due to methyl rocking. The absence of strong absorptions in this region for the 1,4-pentadiene complex is consistent with this assignment. The 1030 cm.$^{-1}$ absorption, furthermore, is found for the stable isomer of the 1,3-butadiene complex and for the 1,3-pentadiene complex, both of which have free, or unhindered, methyl groups, whereas the 1070 cm.$^{-1}$ absorption is found for the unstable 1,3-butadiene, the 1,3-pentadiene, and the isoprene complex, all of which have methyl groups in hindered positions. The 2,3-dimethyl-1,3-butadiene and isoprene complex gives both absorptions, as both hindered and unhindered methyl groups are present.

All other absorptions in the spectra can be assigned to vibrations of the carbonyl groups or to carbon–hydrogen vibrations.

(12) H. B. Jonassen and C. Cioni, work to appear in a future publication.
(13) O. S. Mills and R. Robinson, *Proc. Chem. Soc.*, 421 (1960).
(14) E. J. Lanpher, *J. Am. Chem. Soc.*, **79**, 5578 (1957).
(15) E. R. Lippincott and R. D. Nelson, *J. Chem. Phys.*, **21**, 1307 (1953).
(16) K. Nakamoto, P. J. McCarthy, and A. E. Martell, *J. Am. Chem. Soc.*, **83**, 1272 (1961).