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### $\pi$ -Allyl Derivatives of Transition Metals

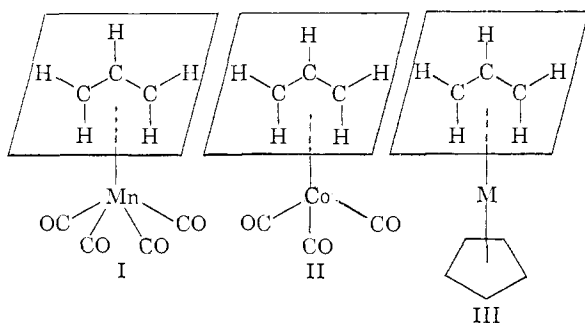
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Preparations and properties of  $\pi$ -allyl derivatives of manganese, cobalt, nickel and palladium are described.

In recent years, unusually stable organometallic derivatives of the transition metals have been prepared in which the metal atom utilizes  $\pi$ -electrons from a suitable organic ligand to become iso-electronic with the next rare gas. Familiar examples of such compounds are ferrocene,<sup>1</sup> dibenzenechromium<sup>2</sup> and the arene derivatives of the Group VI carbonyls.<sup>3,4</sup>

Studies in this Laboratory and elsewhere<sup>5</sup> have shown that stable "allyl sandwich compounds" of manganese, I, cobalt, II, nickel, III (M = Ni) and palladium, III (M = Pd) can be prepared.



The physical properties, elemental composition, n.m.r. spectra and infrared spectra of these and related compounds are in accord with a planar group that effectively contributes three electrons to the central metal atom.<sup>6</sup>

In this Laboratory we have used the term  $\pi$ -allyl to distinguish the sandwich structure from the allyl compounds that contain a single covalent bond. In the  $\pi$ -allyl group all atoms are essentially coplanar, and the bond angles around the carbon atoms are probably 120°. Lanpher<sup>7</sup> has pointed out that there should be considerable energy barrier to rotation about the carbon-carbon bonds in an allylic anion and therefore two isomers, IV and V, might be possible in a terminally substituted  $\pi$ -allyl group.

(1) (a) T. J. Kealy and P. C. Pauson, *Nature*, **168**, 1030 (1951); (b) S. A. Miller, J. A. Tebboth and J. F. Tremaine, *J. Chem. Soc.*, 632 (1952); (c) G. Wilkinson, M. Rosenblum, M. C. Whiting and R. B. Woodward, *J. Am. Chem. Soc.*, **74**, 2125 (1952).

(2) E. O. Fischer and W. Hafner, *Z. Naturforsch.*, **10b**, 665 (1955).

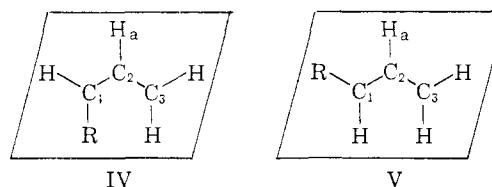
(3) B. Nichols and M. C. Whiting, *Proc. Chem. Soc.*, 152 (1958).

(4) E. O. Fischer and K. Olefele, *Z. Naturforsch.*, **13b**, 458 (1958).

(5) (a) Allylcobalt tricarbonyl was recently described by R. F. Heck and D. S. Breslow, *J. Am. Chem. Soc.*, **82**, 750 (1960); (b) J. Smidt and W. Hafner, *Angew. Chem.*, **71**, 284 (1959), proposed that the stable compound (C<sub>3</sub>H<sub>5</sub>PdCl)<sub>2</sub>, prepared by the reaction of allyl alcohol and palladium chloride, has the allyl sandwich structure; (c) R. F. Heck and D. S. Breslow, *J. Am. Chem. Soc.*, **82**, 4438 (1960); (d) H. C. Dehn and J. C. Chien, *ibid.*, **82**, 4429 (1960); (e) B. L. Shaw, *Proc. Chem. Soc.*, 247 (1960).

(6) Another group known to contribute three electrons to a transition metal is the NO group.

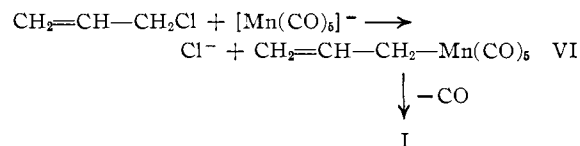
(7) E. J. Lanpher, *J. Am. Chem. Soc.*, **79**, 5578 (1957), found evidence for two such isomers in pentenyl sodium.



We propose that the  $\pi$ -allyl group be numbered as shown in IV and V. The stereochemistry of such isomers as IV and V can be related to the middle hydrogen atom, a, in IV and V. Thus, IV would be designated as an *anti*-1-alkyl- $\pi$ -allyl group and V as a *syn*-1-alkyl- $\pi$ -allyl group.

$\pi$ -Allylmanganese Compounds.—The  $\pi$ -allyl derivatives of manganese are discussed first because isolation of the intermediate allyl derivatives gives a clear picture of the difference between allyl and  $\pi$ -allyl bonding.

Allyl chloride and sodium (or lithium) manganese carbonyl react at room temperature to give a distillable yellow liquid. Elemental analyses and spectral studies indicate that this is allylmanganese pentacarbonyl, VI, admixed with a small amount of  $\pi$ -allylmanganese tetracarbonyl, I.



The infrared spectrum of VI has absorption for the vinyl group at 3085 and 3010 cm.<sup>-1</sup> (CH stretch), at 1620 cm.<sup>-1</sup> (C=C stretch), at 1410 cm.<sup>-1</sup> (=CH<sub>2</sub> in plane), at 1310 cm.<sup>-1</sup> (=CH in plane), at 985 cm.<sup>-1</sup> (CH out of plane), and at 925 cm.<sup>-1</sup> (=CH<sub>2</sub> out of plane). A doublet at 2925 cm.<sup>-1</sup> for -CH<sub>2</sub>- group and absorption for the metal carbonyl groups at 2110, 2079, 2024 and 2004 cm.<sup>-1</sup> are also present. The n.m.r. spectrum of VI (Fig. 1) is consistent with a simple allyl structure. The aliphatic CH<sub>2</sub> is coupled with the vinyl CH to give a doublet. The hydrogen atoms in the vinyl CH<sub>2</sub> group are non-equivalent, and each is split by the vinyl CH into doublets; these doublets overlap to give the observed three line pattern at -4.77 p.p.m. The vinyl CH hydrogen atom gives rise to a multiline resonance due to coupling with the aliphatic CH<sub>2</sub> and vinyl CH<sub>2</sub> hydrogen atoms; the precise number of lines cannot be determined unambiguously from the spectrum.

One mole of carbon monoxide is eliminated when VI is heated to around 100° and  $\pi$ -allylmanganese tetracarbonyl, I, is isolated as a pale yellow solid. The infrared and n.m.r. spectra of I are strikingly different from those of VI. In the infrared spectrum of I, the characteristic absorption for the

TABLE  
A. Allyl and  $\pi$ -allyl

Compound	Reactants <sup>a</sup>	Solvent, <sup>b</sup> ml.	Time, hr.	Temp., °C.
Method A				
$\text{CH}_2=\text{CH}-\text{CH}_2\text{Mn}(\text{CO})_5$	$\text{LiMn}(\text{CO})_5 + \text{CH}_2=\text{CH}-\text{CH}_2\text{Cl}$ (0.065) (0.074)	100 THF	18	25
$\pi\text{-CH}_2-\text{CH}-\text{CH}_2$ Mn(CO) <sub>4</sub>	$\text{CH}_2=\text{CH}-\text{CH}_2\text{Mn}(\text{CO})_5$	...	3	86
$\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_2-\text{Mn}(\text{CO})_5$	$\text{NaMn}(\text{CO})_5 + \text{CH}_3-\text{CH}=\text{CH}-\text{CH}_2\text{Cl}$ (0.1) (0.1)	THF		25
$\pi\text{-CH}_3-\text{CH}-\text{CH}-\text{CH}_2$ Mn(CO) <sub>4</sub>	$\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_2\text{Mn}(\text{CO})_5$	...		87
$\pi\text{-CH}_2-\overset{\text{CH}_3}{\underset{\text{Mn}(\text{CO})_4}{\text{C}}}-\text{CH}_2^c$	$\text{NaMn}(\text{CO})_5 + \text{CH}_2=\overset{\text{CH}_3}{\text{C}}-\text{CH}_2\text{Cl}$ (0.0084) (0.008)	20 THF	10	70
$\text{Cl}-\text{CH}=\text{CH}-\text{CH}_2\text{Mn}(\text{CO})_5$	$\text{NaMn}(\text{CO})_5 + \text{ClCH}=\text{CH}-\text{CH}_2\text{Cl}$ (0.24) (0.26)	53 THF	2	25
$\pi\text{-Cl}-\text{CH}-\text{CH}-\text{CH}_2$ Mn(CO) <sub>4</sub>	$\text{Cl}-\text{CH}=\text{CH}-\text{CH}_2\text{Mn}(\text{CO})_5$	...	3	85
Method B				
$\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_2\text{Mn}(\text{CO})_5$	$\text{HMn}(\text{CO})_5 + (\text{CH}_2=\text{CH})_2$ (0.03) (0.24)	...	6	-3
$(\text{CH}_3)_2\text{C}=\text{CH}-\text{CH}_2\text{Mn}(\text{CO})_5$	$\text{HMn}(\text{CO})_5 + \text{CH}_3-\overset{\text{CH}_3}{\text{C}}-\text{CH}=\text{CH}_2$ (0.046) (0.081)	...	96	25
$(\text{CH}_3)_2\text{C}-\text{CH}-\text{CH}_2$ Mn(CO) <sub>4</sub>	$(\text{CH}_3)_2\text{C}=\text{CH}-\text{CH}_2\text{Mn}(\text{CO})_5$	...	6	95
$\text{CH}_3-\overset{\text{Cl}}{\text{C}}=\text{CH}-\text{CH}_2\text{Mn}(\text{CO})_5$	$\text{HMn}(\text{CO})_5 + \text{CH}_2=\overset{\text{Cl}}{\text{C}}-\text{CH}=\text{CH}_2$ (0.041) (0.056)	...	7	0
B. $\pi$ -Allyl				
$\text{CH}_2-\text{CH}-\text{CH}_2$ Co(CO) <sub>3</sub>	$\text{KCo}(\text{CO})_4 + \text{CH}_2=\text{CH}-\text{CH}_2\text{Cl}$ (0.16) (0.16)	MeOH 50		25
$\text{CH}_3-\text{CH}-\text{CH}-\text{CH}_2$ Co(CO) <sub>3</sub>	$\text{Co}_2(\text{CO})_8 + (\text{CH}_2=\text{CH}-)_2$ (0.1) (0.37)	HOAc 50 g.	12	40
$\text{CH}_3-\text{CH}-\text{CH}-\text{CH}_2$ Co(CO) <sub>3</sub>	$\text{KCo}(\text{CO})_4 + \text{CH}_3-\overset{\text{Cl}}{\text{C}}-\text{CH}=\text{CH}_2$ (0.084) (0.078)	MeOH 25	4	25
$\text{CH}_2-\overset{\text{Cl}}{\text{C}}-\text{CH}_2^d$ Co(CO) <sub>3</sub>	$\text{LiCo}(\text{CO})_4 + \text{Cl}-\text{CH}_2-\overset{\text{Cl}}{\text{C}}=\text{CH}_2$ (0.049) (0.049)	THF 35	4	-20- -25
$\text{Cl}-\text{CH}-\text{CH}-\text{CH}_2^e$ Co(CO) <sub>3</sub>	$\text{LiCo}(\text{CO})_4 + \text{Cl}-\text{CH}=\text{CH}-\text{CH}_2\text{Cl}$ (0.054) (0.054)	THF 33	4	-20- -45

<sup>a</sup> Numbers in ( ) are moles. <sup>b</sup> MeOH = methanol, HOAc = acetic acid and THF = tetrahydrofuran. <sup>c</sup> Methallyl manganese pentacarbonyl not isolated. <sup>d</sup> N.m.r. spectrum had 2 peaks of equal intensity at -3.83 and -292 p.p.m., infrared spectrum had weak 1640 and 885  $\text{cm}^{-1}$ , indicating some  $\text{CH}_2=\overset{\text{Cl}}{\text{C}}-\text{CH}_2-\text{Co}(\text{CO})_4$  impurity. <sup>e</sup> N.m.r. spectrum

vinyl and methylene of the allyl group has disappeared. Bands at 3030 and 3080  $\text{cm}^{-1}$  for  $=\text{CH}$  stretching are the only absorption in the 2700-3100  $\text{cm}^{-1}$  region. A strong band at 1505  $\text{cm}^{-1}$  is present in place of the 1620  $\text{cm}^{-1}$  (C=C stretch) band in the allyl group. Lanpher<sup>7</sup> reported that the carbon-carbon stretching frequency of allylsodium occurs at 1535  $\text{cm}^{-1}$ . Thus the 1505  $\text{cm}^{-1}$  band in  $\pi$ -allylmanganese tetracarbonyl is tentatively assigned as a carbon-carbon stretching vibration. Absorption for the metal carbonyl groups in I is present at 1950, 2049, 2060 and 2110  $\text{cm}^{-1}$ .

Further confirmation of the  $\pi$ -allyl structure for I (Fig. 2) is obtained from the n.m.r. spectrum. The spectrum is in full accord with that expected for I. The observed pair of doublets arises from the

non-equivalent pairs of *syn* and *anti* hydrogens of the  $\pi$ -allyl group; the splitting in each case is due to coupling with the hydrogen on the middle carbon atom. The nine line absorption for the middle hydrogen is in accord with a single hydrogen being split by two pairs of equivalent hydrogens. All the n.m.r. spectra of the unsubstituted  $\pi$ -allyl derivatives studied have the same basic features. The chemical shifts vary somewhat as the central metal atom and other groups are changed. In some cases, because of second order effects there is some perturbation of the basic nine line pattern representing the  $\text{H}_a$  hydrogen atom.

The reaction of sodium (or lithium) manganese pentacarbonyl with allylic halides provides a general route to allyl and  $\pi$ -allyl derivatives of manganese. In some cases, the allyl compounds

## I

derivatives of manganese

Yield, %	B.p., °C. (mm.)	M.p., °C.	Color	C		H		Analytical Metal		X		Mol. wt.	
				Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.
71	45 (5)	...	Yellow	41.3	40.7	2.6	2.2	23.1	23.2	..	..		
88	66 (14)	55-56	Yellow	41.2	40.4	2.7	2.4	25.8	26.4	..	..		
70	48 (2)	...	Yellow	Not analyzed, infrared same as product prepared by Method B									
80	68 (7)	...	Yellow	43.8	43.7	3.1	3.2	23.8	24.9	..	..	206	222
56	50 (2.5)	...	Yellow	44.7	43.2	3.6	3.2	21.6	24.8	..	..		
72	50 (0.5)	...	Yellow	35.7	35.5	1.8	1.5	19.1	20.3	..	..		
40	85 (6)	...	Yellow	34.3	34.7	1.6	1.7	23.1	22.6				
42	56 (4)	...	Yellow	43.4	43.2	3.2	2.8	22.0	21.9	..	..		
30	50-51 (0.2)	12-14	Yellow	45.4	45.4	3.6	3.4	20.7	20.8	..	..	235	264
16	48-52 (1)	...	Yellow	46.4	45.7	3.9	3.8	22.7	23.2	..	..	268	236
17	64-68 (1)	...	Yellow	37.7	37.9	2.2	2.1	19.6	19.3	10.4	12.4 (Cl)	265	284

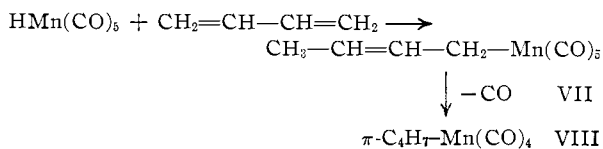
derivatives of cobalt

66	39 (15)		Orange red	39.2	39.1	2.7	2.7	32.5	32.0	..	..	182	184
68	36 (4-5)		Red	42.6	42.4	3.6	3.5	29.9	29.7	..	..	192	198
51	36 (4-5)		Red	42.6	42.4	3.7	3.5	30.2	29.7	..	..	188	198
8 <sup>f</sup>	30 (2)		Amber	33.7	32.9	2.3	1.8	27.9	26.9	15.5	16.2 (Cl)	..	..
22	38 (2)		Amber	32.6	32.9	2.2	1.8	27.7	26.9	16.0	16.2 (Cl)	..	..

had three doublets of equal intensity for hydrogen atoms on carbon atoms 1 and 3 at  $-4.75$ ,  $-4.61$  (p.p.m.), at  $-3.42$ ,  $-3.28$  (p.p.m.) and at  $-2.43$ ,  $-2.33$  (p.p.m.) with  $J = 8$ ,  $J = 8$  and  $J = 11$  c.p.s., respectively. A multiline pattern for hydrogen atom on carbon atom 2 was centered at  $-5.99$  (p.p.m.). <sup>f</sup> Low yield due to accidental mechanical losses during work-up.

were converted without isolation to the  $\pi$ -allyl compound. The results of these experiments are summarized in Table I (Method A).

**Addition of Manganese Carbonyl Hydride to 1,3-Dienes.**—The addition of manganese carbonyl hydride to 1,3-dienes provides another route to allyl and  $\pi$ -allyl derivatives of manganese. For example, manganese carbonyl hydride and excess butadiene gives 2-butenylmanganese pentacarbonyl, VII, as a pale yellow liquid.



The infrared spectrum of VII has absorption at 1381

$\text{cm}^{-1}$  for the methyl group, at  $1642 \text{ cm}^{-1}$  for the carbon-carbon double bond and at  $2110$ ,  $2070$  and  $1992 \text{ cm}^{-1}$  (broad) for the metal carbonyl groups. Absorption bands at  $964 \text{ cm}^{-1}$  (*trans*) and  $721 \text{ cm}^{-1}$  (*cis*) indicated that the product is a mixture of stereoisomers. When a solution of VII in tetrahydrofuran is heated at reflux, one mole of carbon monoxide is eliminated and 1-methyl- $\pi$ -allylmanganese tetracarbonyl, VIII, is isolated as a yellow liquid.

The infrared spectrum of VIII has the expected absorption at  $1521 \text{ cm}^{-1}$  for the  $\pi$ -allyl C=C vibration and at  $1379 \text{ cm}^{-1}$  for the methyl group. Three bands at  $2958$ ,  $2906$  and  $2958 \text{ cm}^{-1}$  are present for the metal carbonyl groups. Absorption at  $3067$  and  $3012 \text{ cm}^{-1}$  for the =CH stretch is also present. The n.m.r. spectrum of VIII is compatible

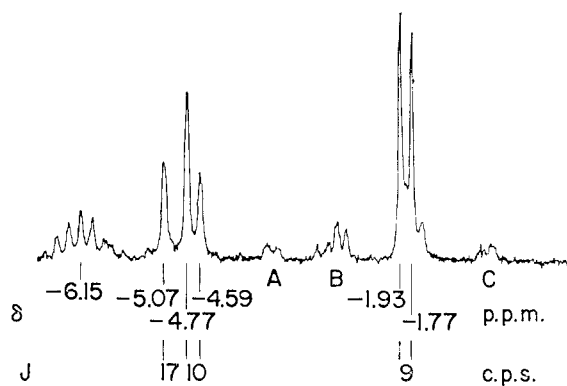


Fig. 1.— $H^1$  magnetic resonance spectrum at 56.4 Mc. of allylmanganese pentacarbonyl. (Areas A, B and C are impurities.)

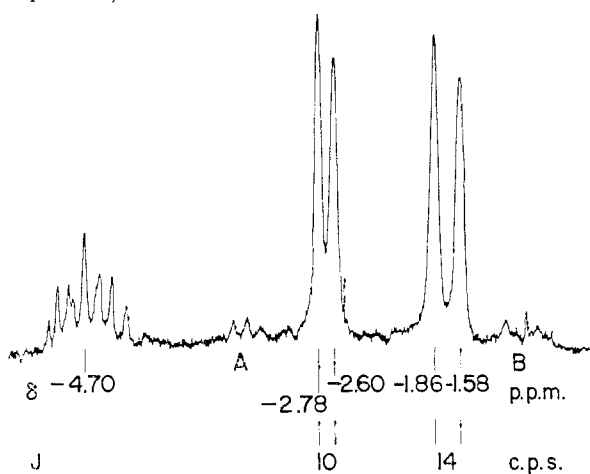


Fig. 2.— $H^1$  magnetic resonance spectrum at 56.4 Mc. of  $\pi$ -allylmanganese tetracarbonyl. (Areas A and B are impurities.)

with the  $\pi$ -allyl structure and is basically the same as that of 1-methyl- $\pi$ -allylcobalt tricarbonyl which is described in the next section.

The addition of manganese carbonyl hydride has been used to prepare other substituted allyl and  $\pi$ -allyl manganese compounds. These experiments are summarized in Table I (Method B).

The reaction of manganese carbonyl hydride with 2,3-dimethyl-1,3-butadiene does not proceed normally to give an organomanganese compound. Instead, the products are 2,3-dimethyl-1-butene, 2,3-dimethyl-2-butene and manganese carbonyl.

**$\pi$ -Allylcobalt Compounds.**—These compounds may be prepared by the reaction of an allylic halide with a salt of cobalt tetracarbonyl and by the addition of cobalt carbonyl hydride to a 1,3-diene.

The simplest member of the series,  $\pi$ -allylcobalt tricarbonyl, II, was prepared recently by Heck and Breslow<sup>5a</sup> by the reaction of allyl bromide with sodium cobalt tetracarbonyl. The initial reaction product, allylcobalt tetracarbonyl, IX, was shown by infrared studies to be present but was not iso-

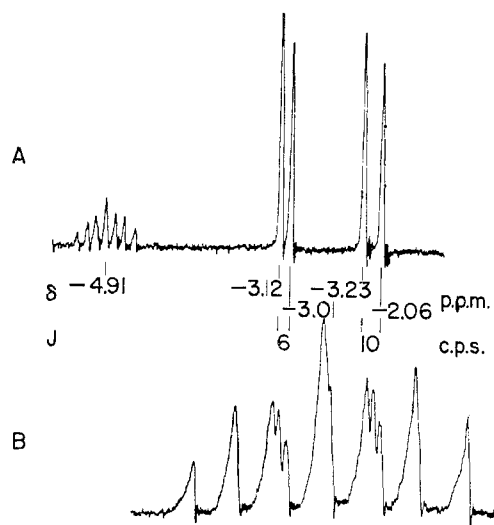
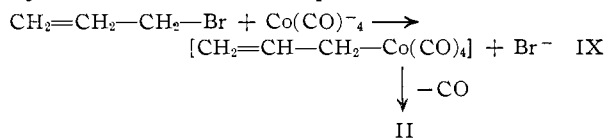


Fig. 3.—A,  $H^1$  magnetic resonance spectrum at 56.4 Mc. of  $\pi$ -allylcobalt tricarbonyl; B, enlargement of peak in A centered at  $-4.91$  p.p.m.

lated as a pure product because decarbonylation occurred at room temperature. We have prepared II by essentially the same method and have examined its n.m.r. and infrared spectrum. The infrared spectrum of II has the expected absorption at 3086 and 3030  $\text{cm}^{-1}$  for CH stretch, at 2066 and 1984  $\text{cm}^{-1}$  for metal carbonyl groups and a strong band at 1488  $\text{cm}^{-1}$  that we believe to be associated with carbon-carbon stretching of the  $\pi$ -allyl group. Strong bands that have not been assigned are present at 1479, 1387, 1225, 1018, 950, 930 and 771  $\text{cm}^{-1}$ . The relatively few bands are suggestive of a symmetrical structure such as II.

The n.m.r. spectrum of II (Fig. 3) is similar to that of  $\pi$ -allylmanganese tetracarbonyl. In spectrum A, the observed pair of doublets arises from the non-equivalent pairs of *syn* and *anti* hydrogens of the  $\pi$ -allyl group; the splitting in each case is due to coupling with the hydrogen atom on the middle carbon atom. The apparent seven line absorption represents the central hydrogen atom. From first order approximation, the number of lines here should be nine; only seven lines are distinctly observed because of coincidence of two pairs of lines. There is a hint of doubling in peaks 3 and 5. However, in an enlargement of this resonance, spectrum B, peaks 3 and 5 are each resolved into at least six lines and there is evidence of doubling in the other components of the spectrum. This perturbation of the expected simple pattern is due to second order effects.

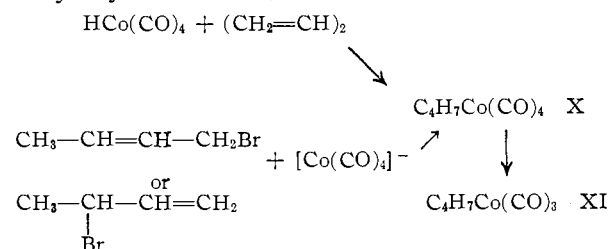
The reaction of 2,3-dichloropropene and lithium cobalt tetracarbonyl gives 2-chloro- $\pi$ -allylcobalt tricarbonyl as a red oil and the n.m.r. spectrum is completely in accord with this structure.

Similarly, 1-chloro- $\pi$ -allylcobalt tricarbonyl is prepared from 1,3-dichloropropene and lithium cobalt tetracarbonyl. The  $H^1$  spectrum of this compound is compatible with either the *syn* or *anti* configuration.

1-Methyl- $\pi$ -allylcobalt tricarbonyl was first prepared by Prichard in this Laboratory<sup>8</sup> but was er-

(8) W. W. Prichard, U. S. Patent 2,600,671, June 17, 1952.

ronously thought to be a butenylcobalt tetracarbonyl  $C_4H_7Co(CO)_4$  (X) on the basis of some misleading analytical data. Further investigation by Jonassen<sup>9</sup> and in this Laboratory<sup>10</sup> established that the correct empirical formula is  $C_4H_7Co(CO)_3$  (XI). Prichard and Jonassen prepared the compound  $C_4H_7Co(CO)_3$  by addition of cobalt carbonyl hydride<sup>11</sup> to 1,3-butadiene.



Later work in this Laboratory and by Heck and Breslow<sup>5a</sup> showed that XI could also be prepared by reaction of 1-bromo-2-butene or 3-bromo-1-butene with a salt of cobalt tetracarbonyl. The first product formed by either route is a butenylcobalt tetracarbonyl (X), which on standing at room temperature loses one mole of carbon monoxide and gives XI. The infrared spectrum of XI has absorption at 2066 and 1984  $cm^{-1}$  for the metal carbonyl groups. The presence of two bands in the carbon-carbon stretching region suggests that XI is a mixture of *syn* and *anti* forms of 1-methyl- $\pi$ -allylcobalt tricarbonyl. On the basis of Lanpher's work<sup>7</sup> on sodium pentenyls, a band at 1505  $cm^{-1}$  was tentatively assigned to the *syn* configuration and a somewhat weaker band at 1495  $cm^{-1}$  assigned to the *anti* configuration. The possible presence of two different methyl groups is also suggested by a shoulder at 1392  $cm^{-1}$  on the stronger band at 1383  $cm^{-1}$ . The n.m.r. spectrum gives further evidence that XI was a mixture of *syn* and *anti* forms.

The  $H^1$  resonance spectrum of 1-methyl- $\pi$ -allylcobalt tricarbonyl, XI, is presented in Fig. 4. The doublets at E and F represent *syn* and *anti* configuration of the  $CH_3$  hydrogen atoms; F probably is the *anti* form. (The relative intensities of the E and F doublets do in fact vary from sample to sample, furthermore, the infrared gives evidence for the presence of two isomers.) Correspondingly the four lines at B represent the two forms of the H on C (see structures IV and V). Doublets at C and at D are due to the *syn* and *anti* hydrogen atoms on  $C_3$ . The doublet in all these cases is due to coupling with the  $H_a$  hydrogen atom. The maximum number of lines predicted for  $H_a$  is 32 for each isomer; only six are observed due to coincidences of lines. In a recent paper,<sup>12</sup> the reaction of butadiene and cobalt carbonyl hydride was reported to yield a mixture of isomeric products with the composition  $C_4H_7Co(CO)_3$ . When this mixture was

(9) H. B. Jonassen, R. I. Stearns, J. Kenttamaa, D. W. Moore and A. G. Whittaker, *J. Am. Chem. Soc.*, **80**, 2586 (1958).

(10) W. W. Prichard, *U. S. Re* 24,853, May 26, 1959.

(11) Jonassen used potassium cobalt tetracarbonyl and acetic acid to generate cobalt carbonyl hydride whereas in Prichard's work the hydride was formed by disproportionation of dicobalt octacarbonyl in methanol.

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

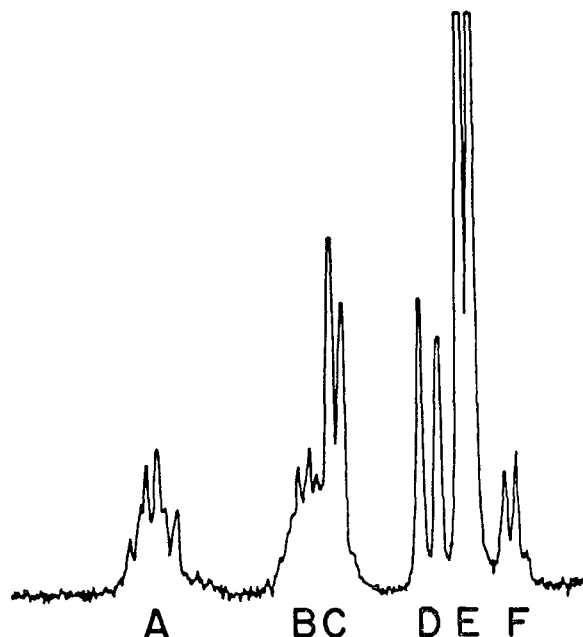
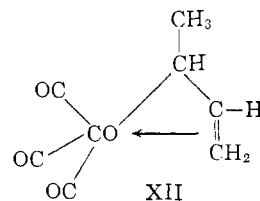


Fig. 4.— $H^1$  magnetic resonance spectrum at 56.4 Mc. of 1-methyl- $\pi$ -allylcobalt tricarbonyl.

heated at 120° for 9 hr. and distilled, the more stable isomer was isolated in 78% yield. The stable isomer was formulated as XII by Aldridge and co-workers<sup>12</sup> on the basis of its infrared spectrum which had



absorption for a "terminal vinyl carbon hydrogen bond and an undisturbed methyl group." The n.m.r. spectrum was said to be consistent with XII.

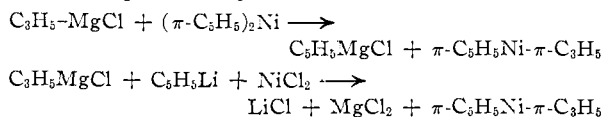
We have heated XI, 1-methyl- $\pi$ -allylcobalt tricarbonyl, for 9 hr. at 120° and recovered 81% of XI unchanged. Thus, we cannot reconcile our results with the preliminary observations reported by Aldridge and co-workers.<sup>12</sup> The work of Heck and Breslow<sup>5a</sup> also suggests that the stable product from the addition of cobalt carbonyl hydride to butadiene is 1-methyl- $\pi$ -allylcobalt tricarbonyl. The data on  $\pi$ -allylcobalt compounds are summarized in Table IB.

**$\pi$ -Allyl Derivatives of Palladium and Nickel.**— $\pi$ -Allyl- $\pi$ -cyclopentadienylpalladium III, where M = Pd, is isolated from the reaction of cyclopentadienyllithium and the dimeric  $\pi$ -allylpalladium chloride<sup>13</sup> that was described by Smidt and Hafner.<sup>6b</sup>  $\pi$ -Allyl- $\pi$ -cyclopentadienylpalladium is an orange red solid, m.p. 60–62°, that readily sublimes at 45–55° (10 mm.). Its n.m.r. spectrum in deuteriochloroform is consistent with the  $\pi$ -allyl- $\pi$ -cyclopentadienyl-

(13) The n.m.r. spectrum of  $(C_2H_5PdCl)_2$  in deuteriochloroform has the typical pattern observed in other  $\pi$ -allyl compounds. The typical multiline pattern for the central hydrogen atom is at -6.11 p.p.m. (center) and the doublets are at -4.70, -4.65 p.p.m. and -3.81, -3.60 p.p.m. with  $J = 3$  and  $J = 12$  c.p.s., respectively.

tadienyl structure and has a peak at  $-6.50$  p.p.m. of relative intensity of 5 for the  $C_5H_5$  hydrogens and the multiline pattern at  $-5.68$  p.p.m. for the central hydrogen atom of the  $\pi$ -allyl group and the doublets at  $-4.41$ ,  $-4.32$  p.p.m. and at  $-3.10$ ,  $-3.28$  p.p.m. with  $J = 5$  c.p.s. and  $J = 10$  c.p.s. respectively.

$\pi$ -Allyl- $\pi$ -cyclopentadienylnickel may be made by the reaction of allylmagnesium chloride with bis-( $\pi$ -cyclopentadienyl)-nickel and by the reaction of equimolar amounts of allylmagnesium chloride and cyclopentadienyllithium with nickel chloride



$\pi$ -Allyl- $\pi$ -cyclopentadienylnickel is a deep-red liquid that was purified by trap to trap distillation at  $\sim 40^\circ$  ( $0.05$ – $0.02$  mm.). Its n.m.r. spectrum is very similar to that of the palladium analog. The spectrum has a peak at  $-5.79$  p.p.m. for the  $C_5H_5$  hydrogens and a poorly resolved multiple peak at  $-3.70$  p.p.m. for the central hydrogen of the  $\pi$ -allyl group. The characteristic doublets for the  $\pi$ -allyl group are present at  $-3.12$ ,  $-3.06$  p.p.m. and at  $-1.98$ ,  $-1.77$  p.p.m. with  $J = 3$  c.p.s. and  $J = 11$  c.p.s., respectively. The poor resolution may have been due to the presence of a paramagnetic species, probably nickelocene.

**Properties of  $\pi$ -Allyl Derivatives of Transition Metals.**—The  $\pi$ -allyl compounds appear to be significantly more stable thermally than the alkyl and aryl derivatives of transition metals. This is particularly true of the  $\pi$ -allyl derivatives of cobalt. They are probably somewhat less stable thermally than the corresponding  $\pi$ -cyclopentadienyl compounds. The oxidative stability varies with the metal.

Allylcobalt tricarbonyl and  $\pi$ -cyclopentadienyl- $\pi$ -allylnickel are very sensitive to oxygen whereas  $\pi$ -allylmanganese tetracarbonyl is relatively stable. No pronounced sensitivity to water was noted in any of the compounds studied.

### Experimental

Melting and boiling points are uncorrected.

Infrared spectra were obtained using a Perkin-Elmer Model 21 Spectrometer.

The n.m.r. spectra were obtained using a Varian Associates High Resolution Nuclear Magnetic Resonance Spectrometer. All  $\sigma$  values are relative to the proton resonance in tetramethylsilane.

**Materials.**—Manganese carbonyl,<sup>14</sup> manganese carbonyl hydride,<sup>15</sup> sodium manganese pentacarbonyl,<sup>15</sup> cobalt carbonyl<sup>16</sup> and cobalt carbonyl hydride<sup>17</sup> were prepared by published procedures.

**Lithium Manganese Pentacarbonyl.**—A solution of 25 g., 0.064 mole, of dimanganese deca-carbonyl in 250 ml. of anhydrous tetrahydrofuran containing 1.4 g., 0.2 g. atom, of short lengths of lithium wire was stirred with a high-speed stirrer for 3 hr. During this time, the reaction mixture was blanketed with argon and a cooling bath was used to prevent the temperature from rising above  $45$ – $50^\circ$ . A stirrer with loose wire ends was used to provide cutting action on the lithium. The deep-green solution of lithium manganese

pentacarbonyl was siphoned from the excess lithium. This solution was assumed to have a lithium manganese pentacarbonyl molarity of 0.51.

**Lithium Cobalt Tetracarbonyl.**—A solution of 34.8 g., 0.10 mole, of dicobalt octacarbonyl in 350 ml. of anhydrous tetrahydrofuran containing 2.65 g., 0.38 g. atom, of short lengths of lithium wire was held in the temperature range of  $-10$  to  $-20^\circ$  while stirring with a high-speed stirrer as described above. The initial vigorous reaction subsided in 20 to 30 minutes, and the solution was then warmed to room temperature while continuing the stirring. The excess lithium pieces were removed and the solution is considered to have a lithium cobalt tetracarbonyl molarity of 0.58.

**Allyl- and  $\pi$ -Allylmanganese Compounds.**—Illustrative procedures for the preparation of allylmanganese pentacarbonyl,  $\pi$ -allylmanganese tetracarbonyl and 2-butenylmanganese pentacarbonyl are given below. The data on other compounds prepared by essentially the same procedure are summarized in Table I.

**Method A. Allylmanganese Pentacarbonyl.**—Allyl chloride (5.7 g., 0.074 mole) was added under a nitrogen atmosphere with stirring to 100 ml. of a 0.65 *M* solution of lithium manganese pentacarbonyl. After stirring for 18 hr., the precipitated lithium chloride was removed by filtration and the tetrahydrofuran was removed by distillation under reduced pressure. Distillation of the yellow residue gave 10.8 g. (71%) of VI, b.p.  $45^\circ$  (15 mm.).

**$\pi$ -Allylmanganese Tetracarbonyl.**—When 12.5 g. (0.053 mole) of allylmanganese pentacarbonyl was heated at  $86^\circ$ , 1160 cc. of carbon monoxide (theoretical = 1200 cc.) was evolved over a 3 hr. period. The yellow residue was distilled to give 9.5 g. (88%) of  $\pi$ -allyl-manganese tetracarbonyl, b.p.  $66^\circ$  (16 mm.); m.p.  $55$ – $56^\circ$ .

**Method B. 2-Butenylmanganese Pentacarbonyl.**—A mixture of 6 g. (0.03 mole) of manganese carbonyl hydride and 13 g. (0.24 mole) of 1,3-butadiene was heated at reflux ( $\sim -3^\circ$ ) for 6 hr. Distillation of the reaction mixture gave 3.5 g. (42%) of 2-butenylmanganese pentacarbonyl, b.p.  $56^\circ$  (4 mm.).

**$\pi$ -Allylcobalt Compounds.**—The preparation of these compounds was very similar to their manganese analogs. However, the intermediate allyl compounds lose carbon monoxide below room temperature and were not isolated. Deoxygenated solvents and a nitrogen atmosphere must be used when working with these compounds because they are oxidized rapidly.

**$\pi$ -Allylcobalt Tricarbonyl.**—A cold trap containing 28 g. (0.16 mole) of cobalt carbonyl hydride was cooled under slight vacuum in liquid nitrogen, and a solution of 10.7 g. of 85% potassium hydroxide in 50 ml. of methanol was added, and the trap was allowed to warm slowly to room temperature. The red solution of potassium cobalt tetracarbonylate was cooled in liquid nitrogen and 12.5 g. (0.16 mole) of allyl chloride was added. As the trap was warmed slowly to room temperature, potassium chloride precipitated and carbon monoxide was evolved rapidly. After gas evolution had ceased, methylene chloride was added and the reaction mixture was filtered under nitrogen. The filtrate was washed twice with oxygen-free water and dried with sodium sulfate. The filtrate was distilled to give 19.8 g. (66%) of  $\pi$ -allyl cobalt tricarbonyl.

**1-Methyl- $\pi$ -allylcobalt Tricarbonyl.**—A 400-ml. pressure vessel was purged with nitrogen and charged with 34.2 g. (0.1 mole) of cobalt carbonyl and 50 g. of glacial acetic acid. The tube was closed immediately, cooled to  $-78^\circ$ , and 20 g. (0.24 mole) of 1,3-butadiene was added to the cold tube. The reaction mixture was shaken for 12 hr. at  $40^\circ$ , then transferred under nitrogen to a separatory funnel and diluted with 750 ml. of deoxygenated water. The heavy, red oil was separated and the aqueous layer extracted with methylene chloride. The oil and methylene chloride solution were combined and dried with sodium sulfate. Distillation gave 8.9 g. (68%) of a mixture of *anti* and *syn* 1-methyl- $\pi$ -allylcobalt tricarbonyl, b.p.  $36^\circ$  (4–5 mm.).

**$\pi$ -Allyl- $\pi$ -cyclopentadienylpalladium.**—A solution of 1.83 g. (0.005 mole) of dimeric  $\pi$ -allylpalladium chloride in 50 ml. of anhydrous benzene was stirred under nitrogen as 25 ml. (0.01 mole) of a 0.386 *M* solution of cyclopentadienyllithium in tetrahydrofuran was added. An exothermic reaction occurred immediately and the reaction mixture became deep red. After stirring for 25 minutes at  $25^\circ$ , the reaction mixture was heated to  $45$ – $50^\circ$  for 10 minutes. After cooling to  $5^\circ$ , 25 ml. of deoxygenated water was added, and the

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benzene layer separated and dried with anhydrous calcium sulfate. The benzene was removed by distillation and the deep-red, semisolid residue was sublimed at 45–55° (10 mm.) to give 1.4 g. (83%) of  $\pi$ -allyl- $\pi$ -cyclopentadienylpalladium, as deep-red needles, m. p. 60–62° (dec.).

*Anal.* Calcd. for  $C_8H_{10}Pd$ : C, 45.2; H, 4.7; mol. wt., 212. Found: C, 45.2; H, 5.0, 4.7; mol. wt., 190, 184.

Its ultraviolet and visible spectra were measured in iso-octane:  $\lambda$  max. 470  $m\mu$  ( $\epsilon$ , 225);  $\lambda$  max. 315  $m\mu$  ( $\epsilon$ , 6,740);  $\lambda$  max. 257  $m\mu$  ( $\epsilon$ , 25,200);  $\lambda$  max. (shoulder) 225  $m\mu$  ( $\epsilon$ , 8,950).

$\pi$ -Allyl- $\pi$ -cyclopentadienylnickel.—A mixture of 10 ml. of freshly prepared cyclopentadiene and 50 ml. of anhydrous pentane was cooled with an ice-bath under an argon atmosphere. The mixture was rapidly stirred as 21 ml. of an 0.24  $M$  ( $\sim$ 0.05 mole) solution of *n*-butyllithium in hexane was slowly added. The solvents were removed *in vacuo* with the exclusion of air and moisture. The resultant cyclopentadienyllithium was dissolved in 100 ml. of anhydrous tetrahydrofuran that had been deoxygenated by purging with nitrogen. The pale yellow solution of cyclopentadienyl-

lithium was stirred under nitrogen and 6.5 g. (0.05 mole) of anhydrous nickel(II) chloride was added. After the characteristic green color of bis-( $\pi$ -cyclopentadienyl)-nickel appeared, 24 ml. (0.05 mole) of a 2.1  $M$  solution of allylmagnesium chloride in tetrahydrofuran was added. A deep red color rapidly formed. The reaction mixture was stirred for 2 days at 0°. Most of the tetrahydrofuran was removed by distillation at 0° (100 mm.). The red residue was purified by trap-to-trap distillation at  $\sim$ 50° (0.45 mm.), and arbitrary cuts were examined by n.m.r. The yield was about 50%. A middle fraction was analyzed.

*Anal.* Calcd. for  $C_8H_{10}Ni$ : C, 58.4; H, 6.1; Ni, 35.5. Found: C, 58.5; H, 6.3; Ni, 32.9.

$\pi$ -Allyl- $\pi$ -cyclopentadienylnickel was also prepared by the reaction of equivalent amounts of bis-( $\pi$ -cyclopentadienyl)-nickel and allylmagnesium chloride in tetrahydrofuran.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE JOHNS HOPKINS UNIVERSITY, AND THE DEPARTMENT OF PHYSIOLOGICAL CHEMISTRY, THE JOHNS HOPKINS SCHOOL OF MEDICINE, BALTIMORE, MARYLAND]

## An Electron Spin Resonance Study of Silver Porphyrin<sup>1</sup>

BY FRITZ K. KNEUBÜHL, W. S. KOSKI AND W. S. CAUGHEY

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The electron spin resonance spectrum of silver(II) deuteroporphyrin IX dimethyl ester has been studied in chloroform solution at ambient temperatures and in castor oil solution at temperatures ranging from  $-128$  to  $+178^\circ$ . The spectra that were obtained could be best interpreted by assuming that the silver isotropic splitting was about twice the nitrogen splitting with overlap of the nitrogen hyperfine lines leading to eleven equally spaced components. The  $g$ -values and the Hamiltonian parameters are evaluated. The significance of the data to the nature of the metal-nitrogen bond is discussed.

### Introduction

The bulk magnetic susceptibility has long been used to study chemical binding in metallic complexes, and in recent years electron spin resonance (e.s.r.) techniques have been brought to bear on the problem. In this Laboratory the latter technique is being used to investigate the metal-nitrogen bond in biologically significant complexes such as the porphyrins. Results of the e.s.r. studies of some vanadyl etioporphyrins<sup>2a</sup> and of copper etioporphyrin<sup>2b</sup> II recently have been published. It is of interest to our program to extend these studies to other porphyrins containing chemically related metals so that the variation of the bonding parameters can be examined as one proceeds through a family of metals in a column of the Periodic Table. This publication gives the result of an e.s.r. study of the  $Ag^{+2}$  complex of deuteroporphyrin IX dimethyl ester. The general procedure used in this paper is the same as that of Roberts and Koski in their study of the corresponding copper complex.<sup>2b</sup> Measurements have been made on solutions of low and high viscosity and in glasses. In the latter two cases the method recently outlined by O'Reilly,<sup>3</sup> Sands<sup>4</sup> and Kneubühl<sup>5</sup> was used to analyze the data.

(1) This investigation was supported in part by research grant RG-5144 from the Division of General Medical Sciences, Public Health Service.

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### Experimental

A Varian Associates Model V 4500 electron paramagnetic resonance spectrometer using 100 kc./sec. modulation was used for the measurements reported here. The microwave frequency was kept constant at 9120 Mc./sec. The magnetic field was monitored with a Harvey-Wells Electronic Inc. Model 501 nuclear magnetic resonance gaussmeter.

The sample of silver(II) deuteroporphyrin IX dimethyl ester (Fig. 1) used in this study was prepared from highly purified deuteroporphyrin IX dimethyl ester and silver carbonate in glacial acetic acid solution. Recrystallization from benzene gave a product melting at 204–205°. Elemental analyses for carbon, hydrogen nitrogen and silver yielded values in close agreement with the theoretically expected values. The detailed experimental procedure for the preparation of this compound will be described in detail elsewhere.<sup>6</sup> The chloroform and castor oil solutions used ranged in concentrations from  $10^{-2}$  to  $10^{-3}$  molar.

### Theory

It will be assumed that the electric field at the silver atom has  $D_{4h}$  symmetry. This assumption appears to be justified since it was shown in the corresponding copper case and in a number of vanadyl porphyrins that substitution on the periphery of the molecule did not noticeably influence the resonance.

The molecular orbitals were constructed only from the atomic orbitals centered on the nitrogen and silver atoms since there were no observable effects of other atoms on the resonance.

If one follows the procedure used in the copper porphyrin case, the odd electron may be placed in the antibonding  $B_{1g}$  orbital.

(6) W. S. Caughey, to be published.