On heating a benzene solution of **6** to 60°, considerable broadening and coalescence and the formation of HMB was observed (Figure 5). When this was cooled to 34°, the resonances of **6** at δ 1.13, 1.36, 1.39, 1.57, 1.86, 2.03, and 2.14 and those of **7** at δ 0.98, 1.03, 1.26 (overlap with **6** resonances at 1.57, 1.86) and that of HMB (2.23) were distinguished.

Reduction of the Mother Liquors from the Precipitation of 6. The solvent was removed from the mother liquors, the oil remaining (*ca.* 13 ml) was stirred with 15 ml of benzene, and an excess of anhydrous hydrazine was added. Metallic palladium precipitated and was removed by filtration. The solvent was removed and the oil remaining was chromatographed over alumina using light petroleum as solvent to remove impurities and HMB. A pale yellow oil (2.0 g) was obtained and was shown to consist of four fractions by vpc. Samples of each of these fractions were collected by preparative vpc using a 5-ft column (0.25 in.) of 20% SE30 at 185°.

Fraction i (*ca.* 10%, 3 min) was identified by its nmr spectrum as vinylpentamethylcyclopentadiene, the product obtained by hydrazine reduction of **6** (see following paper).

Fraction ii (*ca.* 7%, 4.5 min) was obtained in too small amount for complete characterization. From its mass spectrum, it appeared to be an isomer of fraction iv below.

Fraction iii (*ca.* 25%, 13 min) was an oil with analysis corresponding to $C_{16}H_{22}$. *Anal.* Calcd for $C_{16}H_{22}$: C, 89.75; H, 10.25; mol wt, 214. Found: C, 89.27; H, 10.55; mol wt, 214 (mass spectroscopic).

Fraction iv (*ca.* 55%, 19 min) was a yellow oil with molecular formula corresponding to $C_{16}H_{25}Cl$. *Anal.* Calcd for $C_{16}H_{25}Cl$: C, 76.01; H, 9.97; Cl, 14.02; mol wt, 252. Found: C, 75.91; H, 9.99; Cl, 14.26; mol wt, 252 (mass spectroscopic), 258 (osmometric in benzene).

The pmr spectra of iii and iv were recorded but were very complex, showing a large number of resonances in the methyl region.

Formation of $[Cl(MeC_2Me)_3PdCl\cdot PdCl_2]_n$ (7) from 2-Butyne and $(PhCN)_2PdCl_2$ in $CDCl_3$. Solutions were made up containing 228 mg (0.6 mmol) of $(PhCN)_2PdCl_2$ in 10 ml of $CDCl_3$ and 108 mg (2.0 mmol) of 2-butyne in 10 ml of $CDCl_3$. The solutions were cooled to −78° and four mixtures were made up in nmr tubes each containing 0.3 ml of the solution of $(PhCN)_2PdCl_2$ and (A) 0.03 ml, (B) 0.1 ml, (C) 0.3 ml, and (D) of 0.6 ml of the 2-butyne solution. The tubes were shaken at −78° to ensure mixing and then allowed to come to equilibrium in the probe of the 60-MHz nmr spectrometer. Spectra were drawn out at regular intervals, and after completion of the runs the peaks corresponding to $[Cl(MeC_2Me)_3PdCl\cdot PdCl_2]_n$ (**7**) were cut out and weighed. In this case this method was preferable to integration since the peaks were rather small and broad, particularly at the beginning of the run. Mixtures A and D were allowed to react at −21° and the peak weights (mg) obtained were (time in minutes in parentheses): (A) 9.8 (3), 13.1 (6), 17.8 (9), 14.5 (12), 18.2 (15), 18.9 (18), 18.2 (27), 19.4 (39); (D) 10.8 (6), 14.0 (10), 14.8 (14), 15.7 (20), 15.9 (30), 16.9 (50), and 17.3 (60). Similar results but rather slower rates were observed for B and C at −27°.

Acknowledgment. We thank the National Research Council of Canada for supporting this work and Johnson, Matthey, and Mallory for the loan of palladium chloride.

Reactions of Acetylenes with Noble-Metal Halides. IX.[1] The Decomposition of the Complex $[Cl(Me_2C_2)_3PdCl]_2$, Particularly to Vinylpentamethylcyclopentadiene

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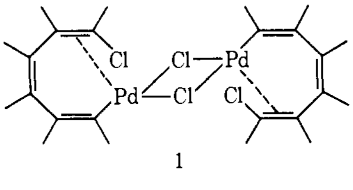
Contribution from the Department of Chemistry, McMaster University, Hamilton, Ontario, Canada. *Received October 20, 1969*

Abstract: The reaction of the previously reported complex $[Cl(MeC_2Me)_3PdCl]_2$ (**1**) with triphenylphosphine, -arsine, and -stibine gave hexamethylbenzene (HMB), vinylpentamethylcyclopentadiene (VCP), and 1-chlorovinylpentamethylcyclopentadiene (CVCP). The CVCP was formed at higher temperatures; below 0°, VCP, together with a small amount of HMB, was the only organic product. The reaction of **1** with triphenylphosphine was studied by nmr from −60 to +30°. Two reaction paths were found. One, at a phosphine:palladium ratio of 2, involved (i) cyclization to a five-membered ring, (ii) an averaging of five methyl groups by a "cyclopropane merry-go-round" process, and (iii) decomposition of this to VCP and HMB. The second path predominated at phosphine:palladium ratios of 4 and over. Step i is the same as above, but no averaging process occurred on raising the temperature. Instead, a new species stable to −10° was detected in step ii. This species, identified as 1-[chloro-*cis*-bis(triphenylphosphine)palladium]vinyl-1,2,3,4,5-pentamethylcyclopentadiene (**4**), arose from the five-membered ring intermediate in (i) by loss of a proton. In step iii at higher temperatures, **4** reacted with the proton to give VCP and HMB again. The reaction with triphenylarsine (and probably that with triphenylstibine) proceeded in a similar fashion to the first reaction path. *o*-Phenanthroline reacted with **1** to give a stable complex identified as 1-[chloro(*o*-phenanthroline)palladium]vinyl-1,2,3,4,5-pentamethylcyclopentadiene. Complex **1** was decomposed by halogens to HMB; hydrazine gave VCP; lithium aluminum hydride gave largely ethylpentamethylcyclopentadiene; and ethanol or dimethyl sulfoxide gave acetylpentamethylcyclopentadiene. The mechanisms of some of these reactions are discussed.

In the preceding paper[1] we reported on the synthesis of a novel type of complex, $[Cl(Me_2C_2)_3PdCl]_2$ (**1**), from the trimerization of 2-butyne by palladium chloride (as its bis(benzonitrile) complex) in benzene. From its mode of formation, analysis, and spectroscopic properties, as well as its ready decomposition to hexamethylbenzene (HMB) in halogenated solvents, we concluded that its structure was best formulated as



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[1] Part VIII: H. Dietl, H. Reinheimer, J. Moffat, and P. M. Maitlis, *J. Amer. Chem. Soc.*, 92, 2276 (1970).

[2] Fellow of the Alfred P. Sloan Foundation and author to whom any correspondence should be addressed.

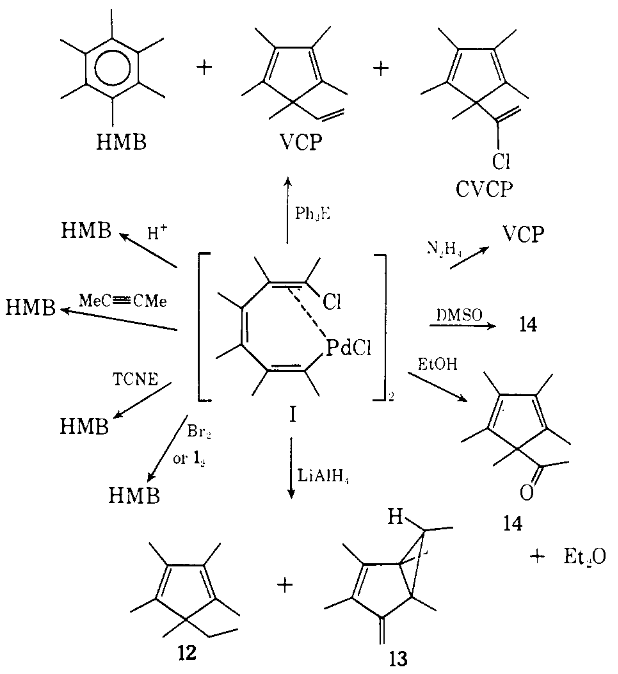
When the reaction of 2-butyne and bis(benzonitrile)-palladium chloride was carried out in chloroform at low temperatures, a new product (**2**) was obtained. This was also formed during the chloroform-induced decomposition of **1** to HMB and could also be prepared by addition of 2 mol of palladium chloride (as the bis-(benzonitrile) complex) to **1**. Although we were unable to isolate **2**, we suggest that its structure is closely related to that of **1** and is best represented as $[Cl(MeC_2Me)_3PdClPdCl_2PdCl_2PdCl(MeC_2Me)_3Cl]$.[1] As far as we examined it, **2** reacted entirely analogously to **1**, both in the reactions described previously and in those described here.

This paper reports the reactions of complex **1** with a number of reagents, in particular Lewis bases. These reactions were originally undertaken with the aim of preparing a simple derivative of **1** which would be susceptible to X-ray analysis. In fact it was found that **1** was so labile that no derivative of it with the basic structure still intact could be isolated.

Results and Discussion

The reactions of $[Cl(MeC_2Me)_3PdCl]_2$ (**1**) investigated here are summarized in Scheme I. Unlike the decomposition of **1** in halogenated solvents or on heating, hexamethylbenzene (HMB) was only a minor product from many of these reactions. The major products were derivatives of pentamethylcyclopentadiene.[3] One set of reactions, with triphenylphosphine, -arsine, and -stibine, proved amenable to a detailed study.

Scheme I. Reactions of Complex **1**



Reactions of $[Cl(MeC_2Me)_3PdCl]_2$ (1) with Ph_3P, Ph_3As, and Ph_3Sb. When the reaction of **1** with triphenylphosphine was carried out at 20° or above, the products were bis(triphenylphosphine)palladium chloride, a small amount, usually about 10%, of HMB, and two new organic compounds, 5-vinyl-1,2,3,4,5-pentamethylcyclopentadiene (VCP) and 5-(1-chlorovinyl)-1,2,3,4,5-pentamethylcyclopentadiene (CVCP).

$$[Cl(Me_2C_2)_3PdCl]_2 + PPh_3 \longrightarrow$$
$$(Ph_3P)_2PdCl_2 + \underset{(HMB)}{C_6Me_6} + \underset{(VCP)}{C_5Me_5CH{=}CH_2} + \underset{(CVCP)}{C_5Me_5CCl{=}CH_2}$$

The two compounds, VCP and CVCP, were isolated by preparative vpc and were identified as such by analyses, molecular weights, infrared, mass-spectroscopic cracking patterns, and particularly their pmr spectra. VCP has also been prepared by Criegee and Grüner,[4] and the reported properties correspond with ours. CVCP also took up 3 mol of hydrogen when hydrogenated over a platinum catalyst and formed a tetracyanoethylene (TCNE) adduct.[5]

A series of reactions was carried out in which excess (*ca.* 4 mol) triphenylphosphine, -arsine, and -stibine were added to a solution of **1** in both chloroform and benzene at different temperatures. In each case an essentially similar reaction occurred, with formation of HMB, VCP, and CVCP as well as $(Ph_3E)_2PdCl_2$ (E = P, As, Sb). The relative proportions of HMB, VCP, and CVCP were estimated by nmr.

An interesting feature of the results presented in Table I is that CVCP was a significant product only at higher temperatures, particularly in the reaction with triphenylphosphine in benzene, where it was the major product. The "normal" decomposition reaction of **1** to give HMB had been largely suppressed in most of these reactions, except those with triphenylarsine, and it appeared that CVCP was largely formed at the expense of VCP at higher temperatures.

Table I. Decomposition Products of $[Cl(Me_2C_2)_3PdCl]_2$ (**1**) with Ph_3E (E = P, As, Sb)

Base	Temp, °C	% in chloroform HMB	% in chloroform VCP	% in chloroform CVCP	% in benzene HMB	% in benzene VCP	% in benzene CVCP
Ph_3P	0	25	65	10	10	60	30
	20	15	65	20	10	45	45
	40	15	60	25	10	25	65
	50	15	60	25			
	65				15	5	80
Ph_3As	0	15	80	5	35	45	20
	20	25	70	5	40	40	20
	40	30	60	10	45	30	25
	50	30	50	20			
	65				45	30	25
Ph_3Sb	0	15	85	0	10	90	0
	20	10	90	Trace	10	85	5
	40	15	80	5	20	75	5
	50	15	80	5			
	65				30	55	15

At low temperatures, particularly in those reactions described below, VCP and about 10% HMB were the only products and formation of CVCP had been completely suppressed. The reaction leading to $(Ph_3E)_2PdCl_2$, HMB, and VCP here was quantitative.

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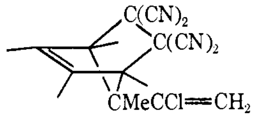
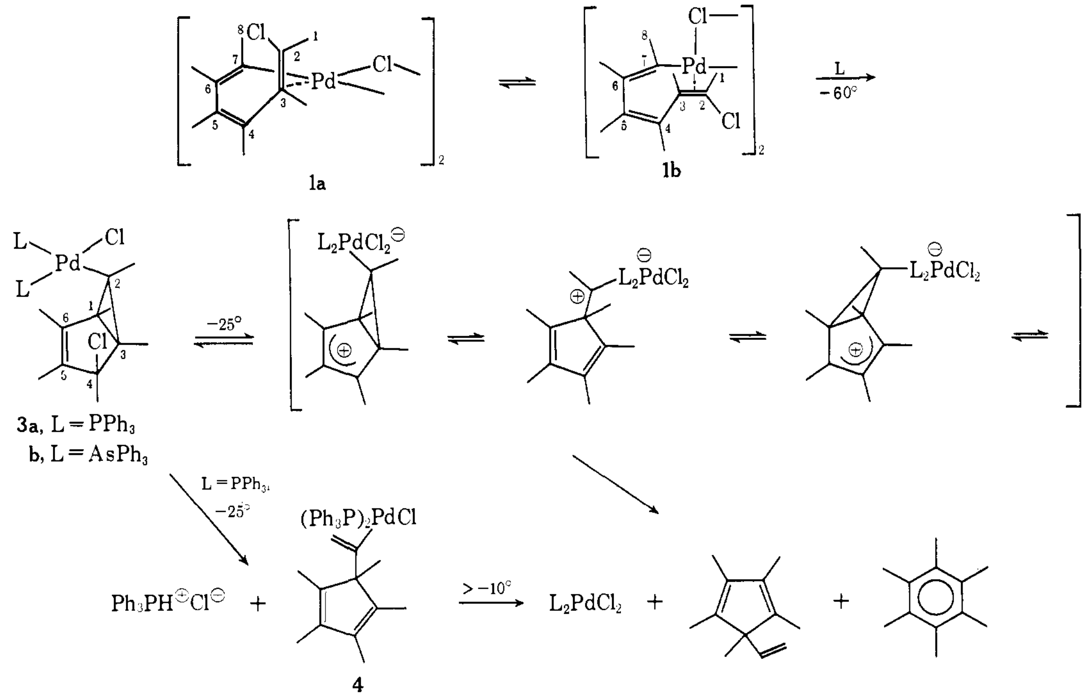
(3) Some of this work was mentioned in a communication: H. Reinheimer, H. Dietl, J. Moffat, D. Wolff, and P. M. Maitlis, *J. Amer. Chem. Soc.*, **90**, 5321 (1968).

(4) R. Criegee and H. Grüner, *Angew. Chem. Int. Ed. Engl.*, 7, 468 (1968).

(5) This was not readily purified from excess TCNE, but its pmr spectra agreed with its formulation as



Scheme II



The reactions of **1** with triphenylphosphine and -arsine were investigated by nmr at low temperatures. Four sets of conditions were particularly studied: (i) with a Ph_3P:Pd molar ratio of 2:1, (ii) with a large Ph_3P:Pd ratio (minimum, 4:1, usually 5 or 6:1), (iii) with Ph_3As:Pd ratio 2:1, and (iv) with Ph_3As:Pd 5:1. Runs iii and iv gave identical results. The results are presented in Figures 1–3. Spectra were taken at 5 or 10° intervals over as short a time span as was practicable (1.5–2.5 hr for a complete run). Only significant changes in the spectra are shown in the figures, and spectra run at intermediate temperatures showed intermediate behavior. No intermediates other than those described were detected.

The processes which were observed can be interpreted in terms of the reactions depicted in Scheme II.

Structure of the Complexes 3a and 3b. At the lowest temperatures investigated (−60°) with PPh_3:Pd ratios of between 1[6] and 6, it was found that a reaction had already occurred. The new product, **3a**, showed six resonances of approximately equal intensities due to six inequivalent methyl groups (Figure 1A).[7] Small peaks arising from the further products of reaction were also visible even at these low temperatures.

This new complex, **3a**, was very labile and could not be isolated. Our formulation of it is based on the following considerations.

(i) The presence of six inequivalent methyl groups in the nmr spectrum indicates a high asymmetry of the ligand.

(ii) The highest field peak (δ 0.51) was a broad doublet at these temperatures. The position of this methyl implied that it was highly shielded. Reaction of **1** with triphenylarsine at −60° gave a species, **3b**, with a very similar pmr spectrum[8] (Figure 2A). Here, however, the highest field peak was not split into a doublet, and there-

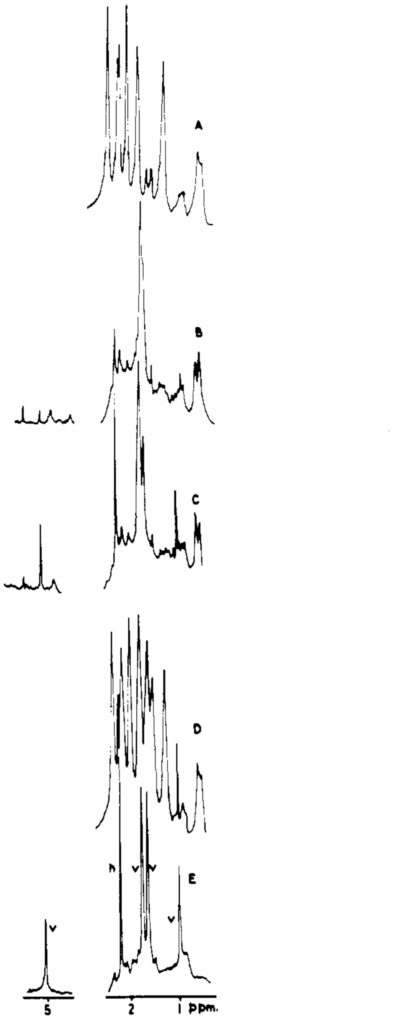


Figure 1. Nmr spectra (100 MHz) of the reaction of complex **1** with triphenylphosphine (Ph_3P:Pd = 2:1) in $CHCl_3$: (A) at −60°, after mixing at −78°; (B) at −25°; (C) at −10°; (D) sample cooled to −50° again; (E), at +10° (h = HMB, v = VCP).

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[6] Reactions with Ph_3P:Pd = 1 were not very informative. HMB and VCP were formed but the final spectrum indicated the presence of large quantities of starting complex. Intermediate spectra were complex as a result.

[7] At δ 2.36, 2.15 (doublet, J = 3 Hz), 1.98, 1.76, 1.24, and 0.51 (doublet, J = 6 Hz) (Figure 1A).

[8] At δ 2.37, 2.19, 1.99, 1.71, 1.23, and 0.72 (all singlets) (Figure 2A).

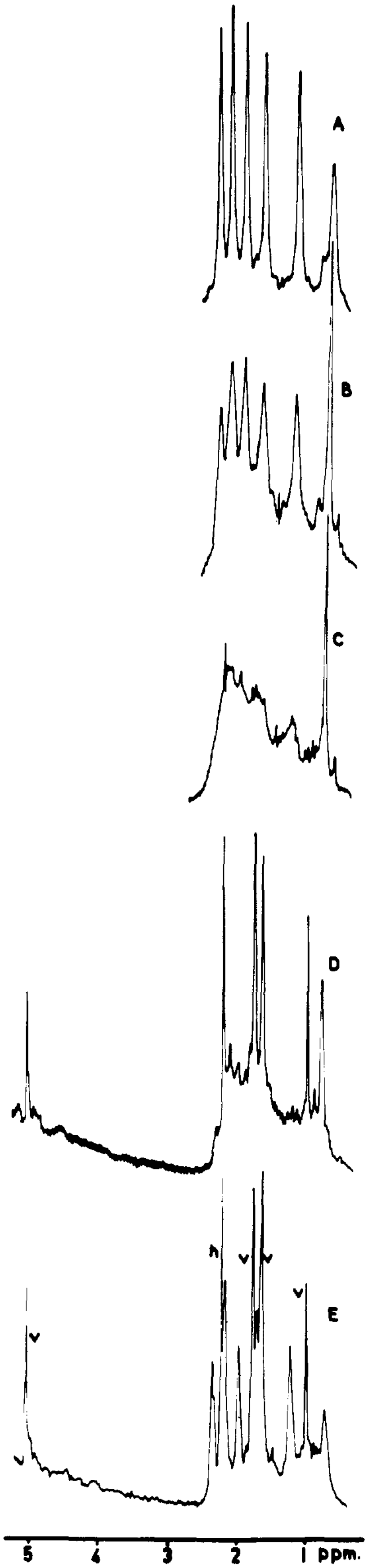

Figure 2. Nmr spectra (100 MHz) of the reaction of complex **1** with triphenylarsine (Ph_3As:Pd = 5:1) in $CHCl_3$: (A) at −50°, after mixing at −78°; (B) at −30°; (C) at −15°; (D) at 0°; (E) sample cooled to −50° again (h = HMB, v = VCP, remaining peaks due to complex **3b** as in A above).

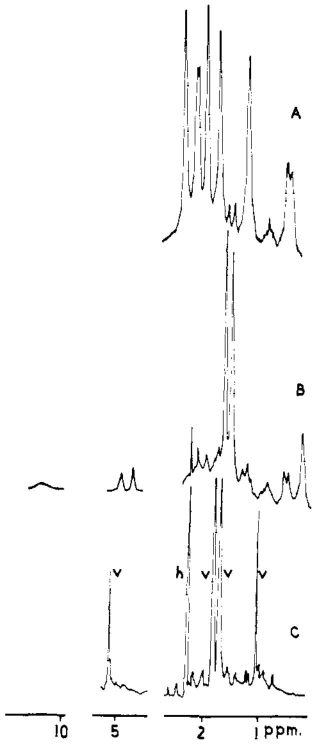

Figure 3. Nmr spectra (100 MHz) of the reaction of complex **1** with triphenylphosphine (Ph_3P:Pd = 5:1): (A) at −50°, after mixing at −78°; (B) at −25°; (C) at +18° (h = HMB, v = VCP).

fore we conclude that the δ 0.51 doublet in the spectrum of **3a** arises from methyl–phosphorus coupling. Similarly, in the spectrum of **3a** the peak at δ 2.15 is split, whereas in **3b** this is a singlet. It is possible that some of the other peaks in **3a** may also be coupled to the phosphorus but with unresolved splittings. The coupling to phosphorus of the high-field methyl is characteristic of the presence of the grouping P–Pd–C–Me in the molecule, with the phosphorus *trans* to the C methyl.[9]

(iii) In the *absence* of a large excess of the phosphine, this spectrum changed on raising the temperature until, at −25°, the five lower field methyls had almost averaged to one singlet. This was observed at δ *ca.* 1.70 (Figure 1B).[10]

In contrast, the high-field doublet for **3a** sharpened considerably on raising the temperature to −25°, without appreciable change in chemical shift or coupling constant. The same behavior was noted for the arsine analog **3b** (Figure 2B). In this case, however, the averaging process was slower, and no cleanly averaged singlet could be observed at −25°. Here too the high-field methyl resonance (singlet) sharpened quite remarkably.

In both the arsine and the phosphine reactions, decomposition to the final products occurred fairly rapidly above −25°. However, on lowering the temperatures of samples which had been above −25° back

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(9) E. O. Greaves, R. Bruce, and P. M. Maitlis, *Chem. Commun.*, 860 (1967).

(10) The position of this singlet is considerably upfield from the averaged positions of the five methyls (δ 1.91). There are two reasons why this may be so. (i) The peak is quite broad and certainly already contains significant contributions from the VCP product peaks at δ 1.67 and 1.79. (ii) Even at this temperature the singlet is not fully established and there is still a high "proton density" at lower field (Figure 1C).

down to $-50°$, the spectra of **3a** and **3b**, together with decomposition products (HMB and VCP), were clearly reestablished (Figures 1D, 2E). This shows that the process leading from **3** to the averaged spectrum is reversible, allowing for the irreversible decomposition.

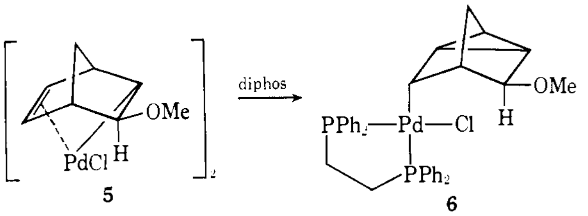
Thus a structure for the organic ligand in **3a** (or **3b**) must be such that a very easy *reversible* formation of a fluxional molecule, in which five methyl groups become equivalent on the nmr time scale, can occur. Since the major final product here is VCP, the most reasonable structure for this low-temperature intermediate is based on a bicyclo[3.1.0]cyclohexene skeleton, with a methyl and L$_2$PdCl attached to C$_2$. The geometry about C$_2$ and C$_4$ is not known, but other considerations (see below) suggest both the metal and the C$_4$ chlorine to be in the *endo* positions.

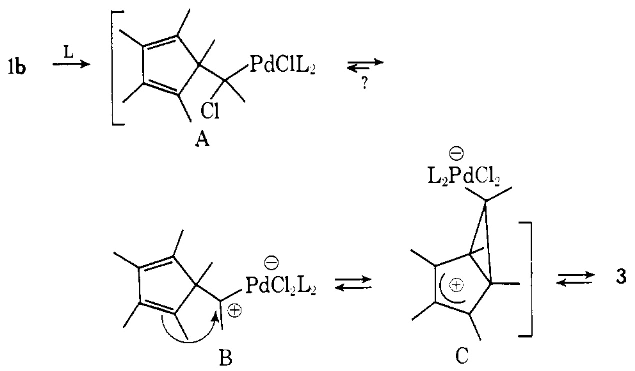
Our observation of P–Pd–C–Me coupling implies further that the two ligands (L) in **3** must be *cis* to each other. Models of **3** also indicate that nonbonded interactions are less for the *cis* than for the *trans* configuration; but even here considerable crowding occurs. In particular, the C$_2$ methyl is close to a phenyl ring of a triphenylphosphine or -arsine. This probably accounts for the high shielding observed and also for the broadness of this resonance, arising from restricted rotation, at low temperatures.

The other (smaller) coupling to phosphorus observed in 3a is probably of a methyl at C$_1$ or C$_3$. As these are in quite different stereochemical relationships to the *trans*-phosphine, significant coupling to only one of them is not surprising. The formation of **3** from [Cl(MeC$_2$Me)$_3$PdCl]$_2$ (**1**) arises by a "*cis* insertion" of C$_2$C$_3$ into the Pd–C$_7$ bond to give A, followed by rearrangement.

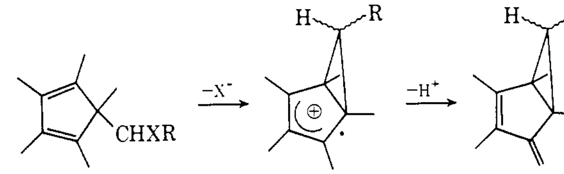
There has been considerable discussion about *cis*-insertion mechanisms,[11] and it seems agreed that for this to occur the coordinated double bond, and the M–X bond into which it is inserted, must be coplanar.[12] This condition is met with in conformer **1b**, as discussed in the preceding paper, and hence it is not surprising that pentamethylcyclopentadienyl products arise so easily.

Perhaps the most convincing analogy to this reaction is that recently described by Coulson,[13] who observed that the norbornenylpalladium complex **5** reacted with the chelating phosphine 1,2-bis(diphenylphosphino)-ethane (diphos) to give the nortricyclenylpalladium complex **6**.





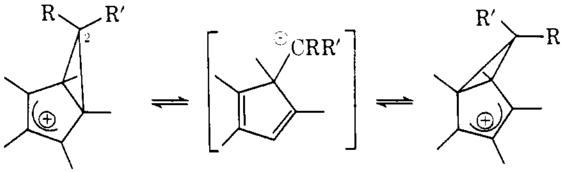
In our case the reaction **1b** → A is as usual, solvent or ligand assisted, and the intermediate A (not detected) now contains a very active chlorine which is able to ionize easily (B). Ring closure to C, which is in equilibrium with **3** at low temperatures, can then occur. A number of authors[4,14,15] have shown that 5-substituted pentamethylcyclopentadienes of type **7** rearrange readily to the cations **8**, which can further yield the 4-methylenebicyclo[3.1.0]hexenes **9**. Our reactions bear an obvious analogy to these, except that elimination of a proton does not occur.



7, X = OTs; R = H
X = Cl; R = Me
8
9

Further Reactions of Complexes 3a and 3b. Two different types of behavior were found on raising the temperature. The first type, described above, occurred when the triphenylphosphine complex **3a** was allowed to warm up in the *absence* of a large excess of triphenylphosphine. Very similar behavior was found for the triphenylarsine complex **3b**, but here additional triphenylarsine made no difference.

This process is very similar to that described by Childs and Winstein[16] and by Koptyug *et al.*,[15] for the bicyclo[3.1.0]hexenyl cations, **10**, where this effect has been observed at low temperatures for R = R′ = Me, and R(*endo*) = H, R′(*exo*) = Me. Childs and Winstein have termed this suprafacial concerted 1,4-sigmatropic shift of CRR′ a "cyclopropane merry-go-round," and have shown that no inversion occurs at C$_2$ during this process. They also gave evidence favoring the accumulation of positive charge at the C$_2$ carbon in the transition state since the cation with a C$_2$ dimethyl underwent this transformation faster than a C$_2$ monomethyl cation which was in turn faster than the pentamethyl cation **10** (R = R′ = H).[17] The main differences between this and our system is that an extra



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10

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(11) P. Cossee, *Rec. Trav. Chim. Pays-Bas*, **85**, 1151 (1966).

(12) B. L. Shaw, *Chem. Commun.*, 464 (1968).

(13) D. P. Coulson, *J. Amer. Chem. Soc.*, **91**, 200 (1969).

(14) S. Winstein and M. Battiste, *ibid.*, **82**, 5244 (1960).

(15) V. A. Koptyug, L. I. Kuzubova, I. S. Isaev, and V. I. Mamatyuk, *Chem. Commun.*, 389 (1969); see also L. A. Paquette and G. R. Krow, *Tetrahedron Lett.*, 2139 (1968); L. A. Paquette, G. R. Krow, J. M. Bollinger, and G. A. Olah, *J. Amer. Chem. Soc.*, **90**, 7147 (1968); H. Hogeveen and H. C. Volger, *Rec. Trav. Chim. Pays-Bas*, 87, 1042 (1968); **88**, 353 (1969).

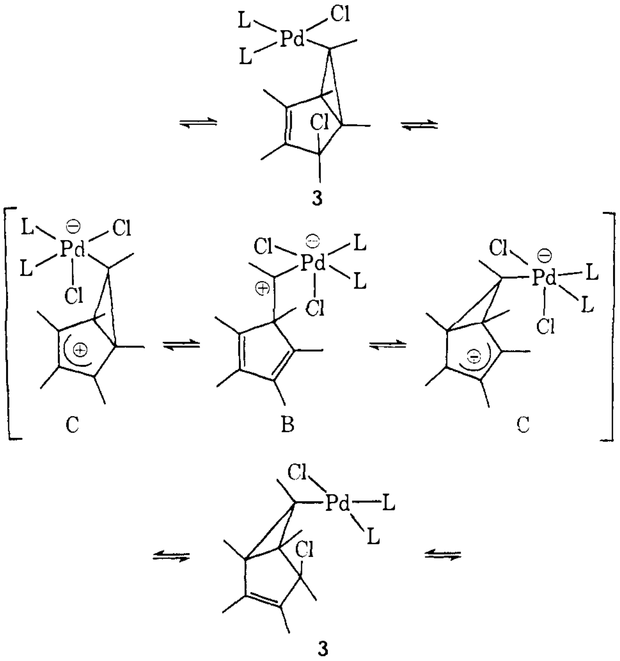
(16) (a) R. F. Childs, M. Sakai, and S. Winstein, *J. Amer. Chem. Soc.*, **90**, 7144 (1968), (b) R. F. Childs and S. Winstein, *ibid.*, **90**, 7146 (1968).

(17) R. F. Childs, personal communication.

chlorine is present at C_4 in **3**, which has to come off before the averaging can occur, and that the metal is attached at C_2. If the stereochemistry of **3** is as depicted, with both the metal and C_4 chlorine *endo*, then models show the chlorine to be close to the fifth coordination site of the metal and almost within bonding distance of it. The metal is well placed to assist the removal of the chlorine, and the facility with which the averaging occurs suggests this stereochemistry indeed to be correct.

The transition state for this averaging process, B, also probably has the positive charge on C_2 stabilized by back-bonding from the metal. From the position of the (incompletely) averaged signal of the cyclopentenyl methyls, it does not appear that a large positive charge is generated on the ring.[10] The proposed averaging process is depicted in Scheme III.[18]

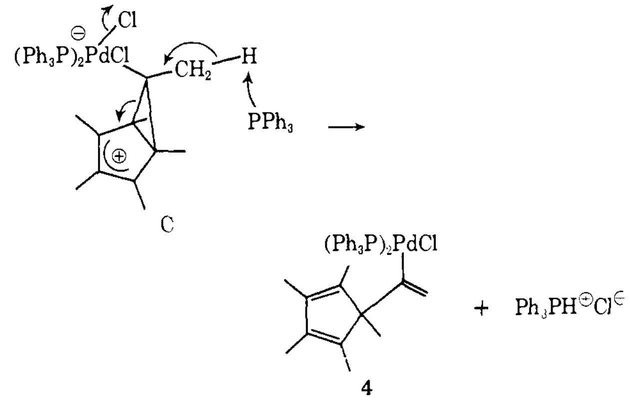
Scheme III



Experiments carried out with triphenylarsine showed no difference in spectra obtained with different ratios of reactants, and the fluxional behavior was always found. In the reactions with triphenylphosphine, a ratio of phosphine to palladium greater than about 4 gave totally different spectra at −25°. The spectrum at −50° under these conditions was identical with that obtained at lower Ph_3P:Pd ratios (Figure 3A). On warming up this solution, however, a change began to occur which was largely complete by −25° and which could *not* be reversed on cooling again. The major characteristics of the spectrum at this temperature included a singlet at δ 0.25 (intensity 3), two singlets each of intensity 6 at δ 1.52 and 1.64, and two broader peaks each of intensity 1 at δ 4.72 and 4.93 (Figure 3B). With the exception of the highest field peak, this spectrum was remarkably similar to that of VCP or CVCP, except that the peaks were all shifted downfield by a small amount of 0.1–0.2 ppm. The absence of any visible coupling (*i.e.*, <2 Hz) in the vinylic proton resonances (δ 4.72, 4.93) implies that these protons must be geminal.[20] Hence the palladium must be σ-bonded to the vinyl group in the α position.[21] The highest field peak, at δ 0.25, was very high for a methyl, probably owing to considerable shielding by one or more phenyls of the triphenylphosphine ligands. The other peaks were not so shielded. For these reasons, we suggest that the complex responsible for this spectrum was 1-(chloro-*cis*-bis(triphenylphosphine)palladium)vinyl-1,2,3,4,5-pentamethylcyclopentadiene (**4**) (Scheme II).[22]

The most interesting feature of the spectra of solutions containing **4** was the observation of a small very broad resonance at δ *ca.* 10.5 (Figure 3B). This sharpened up a little on cooling the solution down to −50°, and appears to be due to H^+. The spectra of solutions of triphenylphosphonium chloride ($Ph_3PH^+Cl^-$) in chloroform under as nearly similar conditions as could be achieved also showed a resonance which appeared as a singlet at δ 10.8 at −40° and which varied considerably in position with temperature. Unfortunately, owing to solubility problems, good resolution of this low-field peak in solutions of **4** was not possible.

The presence of H^+ is in agreement with the remainder of the spectrum which shows that a proton has been removed from the original $C_{12}H_{18}$ ligand. We propose that this proton arises from a species such as C in the *presence of a base* and that triphenylphosphine, but *not* triphenylarsine,[23] is a strong enough base to abstract H^+ from the (C_2) methyl. This is favored by contributions from structures such as B (Scheme III). The proton was



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[18] It is interesting that in this system we have no evidence for fluxional behavior involving migration of the metal atom.[19] Our observation of phosphorus–methyl coupling throughout indicates that the metal–carbon bond remains unbroken.

[19] See, for example, the review by F. A. Cotton, *Accounts Chem. Res.*, 1, 257 (1968).

[20] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution NMR Spectroscopy," Vol. 2, Pergamon Press, Oxford, 1966, p 711.

[21] Alternatives, such as the palladium being bonded to the ring, either π or σ, can be ruled out: the first, because it is most unlikely for the metal to be π-complexed in the presence of such a large excess of phosphine; and the second, because of the symmetry of the molecule implied by the simple pmr spectrum. Such structures would not agree either with the ratio of vinylic protons to other protons (1:1:6:6:3) found.

[22] There is a suggestion in the olefinic region of the spectrum (Figure 1B) of a species which may be due to **4** in the Ph_3P:Pd 2:1 reaction. However, this may be caused by another species or may even be spurious. This was not observed in any of the arsine experiments.

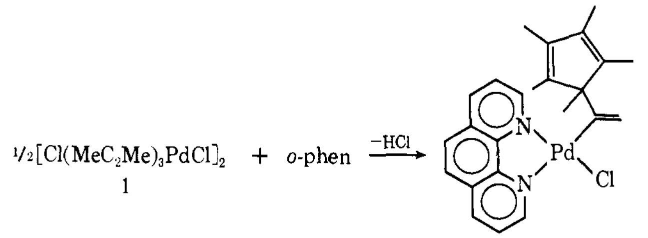
[23] There is little information in the literature about the relative base strengths of group V compounds. Peach and Waddington[24] have measured the conductivities of Ph_3N, Ph_3P, Ph_3As, and Ph_3Sb in liquid hydrogen chloride in the presence of BCl_3, but it is not clear just what their results mean in terms of relative basicities. We prefer to use the criterion that triphenylphosphine is soluble in acids and that salts of the type $Ph_3PH^+X^-$ are readily isolated whereas that is not the case for triphenylarsine.[25]

[24] M. E. Peach and T. C. Waddington, *J. Chem. Soc.*, 1238 (1961).

[25] Beilstein's "Handbuch der organischen Chemie," Vol. XVI, pp 759, 828.

probably present as Ph_3PH^+, but the resolution, even at −50°, was too poor to observe coupling to the phosphorus. This resonance was not seen in experiments with a Ph_3P:Pd ratio of 2:1.

Supporting evidence for the structure of complex **4** comes from reactions with other bases, notably chelating diamines such as *o*-phenanthroline. When *o*-phenanthroline was allowed to react with **1**, a complex, to which we ascribe the structure **11**, based on analysis and spectroscopic data, was isolated in good yield. Similar materials were obtained from bipyridyl and, in an impure state, from pyridine. The detailed chemistry of these complexes is presently under investigation, but their close relationship to complexes such as **4** is apparent. This result indicates that when a strong enough base is present, proton abstraction and formation of a σ-vinylpalladium(II) complex always occurs.



11

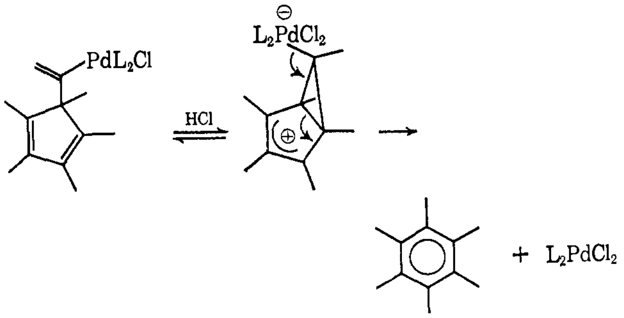
Decomposition of the Intermediates to HMB and VCP. Even at the temperature where the averaged spectrum in the reactions with Ph_3P:Pd of 2:1 was first seen (Figure 1B), peaks due to the final products, VCP and HMB, could be clearly discerned. On warming up the solution these peaks grew until at +10° no trace of the averaging process could be seen. The same was true of the reactions of $[Cl(MeC_2Me)_3PdCl]_2$ with Ph_3As (Figure 2), except that the decomposition to VCP and HMB may have been fractionally slower. In neither case were other intermediates detectable.

In the reactions where an excess of PPh_3 was used and the σ-vinyl complex **4** was generated, this complex was stable up to *ca.* −10°. On further warming, to +10°, very little change occurred in the positions and shapes of the most intense peaks (δ 1.52 and 1.64). However, both the high-field singlet and the low-field vinylic proton resonances sharpened and moved to lower and higher field, respectively, until at +10° they appeared at δ 0.56, 4.40, and 4.83.[26a] This can be interpreted most readily in terms of a change in the stereochemistry about the metal, involving rearrangement of the triphenylphosphines from *cis* to *trans*. This would alter the relative shieldings of the high-field methyl (bridgehead on the cyclopentadiene ring) and of the vinylic protons most, and also allow a greater freedom of rotation to the bridgehead methyl.

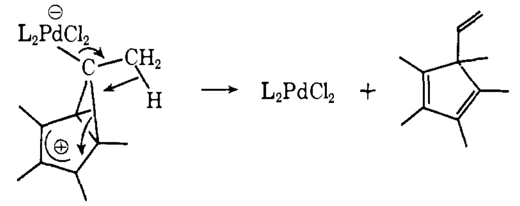
From +10 to +18° another irreversible change in the spectrum occurred. This was seen most dramatically in the continuing downfield shift of the highest field singlet and in the replacement of the lower field vinylic protons by a sharp resonance at δ 5.05. In addition, a sharp singlet at δ 2.23 grew rapidly in intensity. The spectrum at +18° corresponded exactly to a mixture of HMB and VCP, and it appeared that both arose from **4** (Figure 3C).

Since C (or, possibly, B) and the complex **4** are related by an acid–base equilibrium, it seems plausible that they both decompose by the same route. The same consideration also applies to the Ph_3As reaction. Here the arsine analog of **4**, while not present in high enough concentrations for detection, may nevertheless play an important role in the reactions.

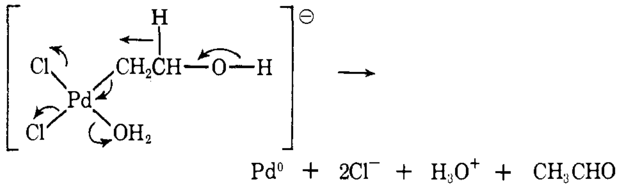
The decomposition to **HMB** is suggested to proceed as follows



while that to VCP can be thought of as proceeding by a 1,2-hydride shift.[26b]



1,2-Hydride shifts are well known, if not very well understood, in many palladium-catalyzed reactions. For example, in the formation of acetaldehyde from ethylene, water, and $PdCl_2$, it is generally agreed that the intermediate β-hydroxyethylpalladium complex decomposes by just such a 1,2-hydride shift.[27]



Alternatively, it is conceivable that VCP is formed from complex **4** by oxidative addition of HCl to the metal, followed by a rearrangement. This is the mode by which platinum(II)–carbon bonds are broken,[28] and similar mechanisms may well be possible for palladium, even though Pd(IV) is a less favored oxidation state.

Formation of 1-Chlorovinylpentamethylcyclopentadiene, CVCP. It is not appropriate at this time to speculate at length on the route by which the higher tem-

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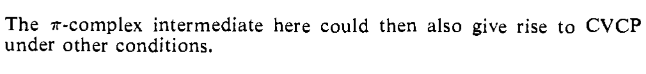
(26) (a) The vinylic resonances did not move to the same extent; that originally at δ 4.77 moved further (to *ca.* 4.40) than the one at δ 4.92 which only moved slightly, to 4.83. (b) A variant of this, which we suggested earlier,[3] involves the isomerization of A, followed by elimination of PdCl.



$$C_5Me_5CCl\cdot Me(PdClL_2) \longrightarrow \underset{\displaystyle HPdClL_2}{C_5Me_5CCl{=}CH_2} \longrightarrow$$

$$C_5Me_5CHCl\cdot CH_2PdClL_2 \longrightarrow VCP + L_2PdCl_2$$

The π-complex intermediate here could then also give rise to CVCP under other conditions.

(27) A. Aguilo, *Advan. Organometal. Chem.*, **5**, 330 (1967); P. M. Henry, *J. Amer. Chem. Soc.*, **86**, 3246 (1964); **88**, 1595 (1966).

(28) V. Belluco, M. Giustiniani, and M. Graziani, *ibid.*, **89**, 6494 (1967); V. Belluco, U. Croatto, P. Ugualiati, and R. Pietropaolo, *Inorg. Chem.*, **6**, 718 (1967).

perature product, CVCP, arises from reaction of $[(Cl(MeC_2Me)_3PdCl]_2$ and triphenylphosphine, -arsine, or -stibine. One possibility, as already mentioned,[3] is that CVCP arises by a Pd–H β elimination from an intermediate such as A ($C_5Me_5CMeCl(PdClL_2)$).[26b] Alternatively a complex such as **4** may decompose thermally, in the presence of excess PPh_3, *e.g.*

$$\underset{\mathbf{4}}{C_5Me_5C({=}CH_2)(PdCl(PPh_3)_2)} \xrightarrow[\Delta]{PPh_3} \underset{\text{CVCP}}{C_5Me_5CCl{=}CH_2} + (Ph_3P)_nPd$$

Analysis of the inorganic product of the reaction of **1** with PPh_3 at 65° indicated the formation of some zerovalent palladium complex, $(Ph_3P)_4Pd$, but this could arise equally well by decomposition of the hydride, $(Ph_3P)_2PdHCl$, in the presence of PPh_3.

Other Reactions of $[Cl(MeC_2Me)_3PdCl]_2$ (1) Leading to Cyclopentadienes. A number of other reagents reacted with complex **1** to give organic products containing a five-membered ring (Scheme I). These include hydrazine, $LiAlH_4$, ethanol, and dimethyl sulfoxide.

(i) **Hydrazine.** Anhydrous hydrazine was added to a solution of complex **1** in benzene at 5°. Metal was precipitated; the nmr spectrum of the organic product showed it to be composed entirely of VCP.

This reaction may proceed *via* a hydrazine complex similar to **11**, *e.g.*, $(N_2H_4)_2PdCl(CH_2{=})CC_5Me_5$; further reaction of this, *via* a hydride intermediate, generates VCP.

(ii) **Lithium Aluminum Hydride.** Complex **1** was allowed to react with lithium aluminum hydride in ether at −40°. Metal separated out immediately; the organic products were isolated by preparative vpc and identified as ethylpentamethylcyclopentadiene (**12**, 90%) and the known hydrocarbon 4-methylene-1,2,3,5,6-pentamethylbicyclo[3.1.0]hex-5-ene (**13**, 5%);[4] 5% of another unknown material and a trace of HMB were also obtained.

(iii) **Ethanol.** The complex decomposed in ethanol at 20° during the course of a day to give metal. The organic products were examined by nmr and found to contain HMB (*ca.* 8%), the remainder being acetylpentamethylcyclopentadiene (**14**). In addition, a small amount of diethyl ether was formed in the reaction. Compound **14** had the same nmr spectrum as reported by Junker, *et al.*[29] It formed a dinitrophenylhydrazone and gave a positive iodoform reaction. The formation of the ketone was accelerated by the presence of sodium carbonate.

(iv) **Dimethyl Sulfoxide.** The reaction with d_6-DMSO in deuteriochloroform was studied briefly by nmr; the only product, apart from a trace of HMB, was again C_5Me_5COMe (**14**).

The ethylpentamethylcyclopentadiene (**12**) from the lithium aluminum hydride reduction can arise in a number of ways, for example, by reduction of an intermediate, D, analogous to A (S = solvent).

$$\underset{\text{D}}{C_5Me_5CClMePdCl(S_x)} + LiAlH_4 \longrightarrow \underset{\mathbf{12}}{C_5Me_5Et} + Pd^0$$

This same intermediate may also be implicated in the reaction of **1** with ethanol, *e.g.*

$$D + EtOH \longrightarrow C_5Me_5C(OEt)MePdCl(S_x) \xrightarrow{EtOH} C_5Me_5COMe + Et_2O + HCl + Pd^0$$

The DMSO reaction may follow a similar path, as water (indicated by the pmr spectrum) was present. In that case DMSO merely functions as a solvent here.

Other Reactions of $[Cl(MeC_2Me)_3PdCl]_2$ (1) Leading to HMB. A number of other reactions were tried with the aim of removing the acyclic ligand from **1**. These all gave HMB.

(i) **Trifluoroacetic Acid and Hydrogen Chloride.** The complex reacted with both of these in benzene and chloroform to give largely HMB. Some unidentified material was formed in small amounts in the reaction of HCl with **1** in chloroform.

(ii) **Halogens.** Complex **1** was treated with both iodine and bromine in chloroform at −50° and the solutions were allowed to warm up. The reactions were followed by nmr, and the only product obtained in each case was HMB.[30] It began to form at *ca.* −15°. The lower temperature spectra were not readily interpretable.

(iii) **Tetracyanoethylene.** Attempts to cause the free double bonds in **1** to react with a twofold excess of TCNE were unsuccessful. In benzene only HMB, together with unchanged TCNE and inorganic material ($PdCl_2$), was obtained.

It is very tempting to suggest that all the reactions to give HMB from **1**, particularly those where it is the sole or major product, go by the same paths, and that this is related to the route by which HMB arises from the intermediate σ-vinyl complex **4** or the cyclopropane merry-go-round system. The evidence we have at the moment is quite insufficient for us to discuss this possibility more closely. However, it is interesting in this respect to note that, as mentioned in the preceding paper,[1] decomposition of the complex $[Cl(CH_3C_2CD_3)_3PdCl]_2$ (from $CH_3C_2CD_3$) gave HMB-d_9 containing *ca.* 10% of the 1,2,3-tris(trideuteriomethyl)-4,5,6-trimethylbenzene. This could arise by an averaging involving a bicyclo[3.1.0]hexene intermediate and a cyclopropane merry-go-round. The nmr of $[Cl(MeC_2Me)_3PdCl]_2$ in benzene at 60° suggests that a fluxional molecule is also being reversibly created here.[1]

The possibility that complex **1**, in the conformation **1a**, undergoes a Woodward–Hoffmann allowed disrotatory cyclization to a *cis*-cyclohexadiene, which then eliminates $PdCl_2$ to leave HMB, is rather unlikely. It does not explain the observed solvent and reagent effects or the formation of the "abnormal" isomer, above.

Miscellaneous Reactions of $[Cl(MeC_2Me)_3PdCl]_2$ (1).

(i) **Ethylene.** Complex **1** did not react with ethylene at 20° and 1 atm in either chloroform or benzene.

(ii) **2-Butyne.** As discussed in the previous paper, complex **1** (and **2**) could be used to trimerize 2-butyne to HMB if the reaction was carried out under carefully controlled conditions.

(iii) **Carbon Monoxide.** The complex reacted with carbon monoxide in benzene only in the presence of a small amount of methanol and sodium carbonate, to give a red solid. This material is still under investigation, but preliminary studies indicate it to contain a

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(29) H. Junker, W. Schäfer, and H. Neiderbruck, *Chem. Ber.*, **100**, 2508 (1967).

(30) It is interesting to note that Hübel and his coworkers found that the cobalt complexes $(RC_2R')_3Co_2(CO)_4$ also gave the benzenoid trimers on reaction with bromine in carbon tetachloride, and in rather higher yield than on heating.[31]

(31) See, for example, the review by W. Hübel, "Organic Syntheses via Metal Carbonyls," I. Wender and P. Pino, Ed., Interscience Publishers, New York, N. Y., 1968, p 312.

metal-bonded carbonyl. It decomposed on heating to give HMB and VCP.

Experimental Section

The complex **1** was prepared as described previously.[1] All reagents were of AR quality; solvents were dried and distilled before use. All reactions were carried out under dry nitrogen. Pmr spectra were measured using a Varian HA-100 spectrometer; hexamethylbenzene (δ 2.23) was usually used as internal reference and this was calibrated against solvent (benzene, chloroform) or tetramethylsilane. Low-temperature nmr studies were conducted by mixing solutions containing the stoichiometric amounts of the reactants in an nmr tube at −78° and allowing the tube to warm up to the required temperature in the probe of the spectrometer. The temperature was determined by measuring the separation of methanol peaks. Organic products were analyzed by vpc using a Varian A90-P3 gas chromatograph and columns of 5% SE30 on 60–80 Chromosorb W and 5% Carbowax on 60–80 Chromosorb W. The materials were collected by preparative vpc with a Varian Aerograph on larger columns of the same materials. Mass spectra were determined using a Hitachi Perkin-Elmer RMU-6A and a CEC 110B high-resolution mass spectrometer.

Reaction of Complex 1 with Triphenylphosphine. Triphenylphosphine (1.05 g, 4 mmol) dissolved in 2 ml of benzene was added to a stirred solution of 0.34 g (0.5 mmol) of complex **1** in 15 ml of benzene at 20°. The color lightened immediately and after 3 min a precipitate began to form. The stirring was continued for a further 30 min, and the yellow solid (0.31 g) was filtered off. This was shown to be bistriphenylphosphinepalladium(II) chloride by its infrared spectrum and analysis. *Anal.* Calcd for $C_{36}H_{30}Cl_2P_2Pd$: C, 61.60; H, 4.31; Cl, 10.10; P, 8.83; Pd, 15.16. Found: C, 61.02; H, 4.46; Cl, 10.40; P, 9.07; Pd, 15.54.

The filtrate was evaporated to low volume on a rotary evaporator, and the resultant greasy solid was stirred with 20 ml of light petroleum. A pale yellow solid (0.67 g), containing the above, as well as triphenylphosphine and tetrakis(triphenylphosphine)palladium (see below) were left.

The light petroleum mother liquor was taken to dryness, dissolved in 1 ml of light petroleum, and chromatographed on alumina. A colorless oil and a white solid were separated and collected, but the excess triphenylphosphine was not collected. The white solid was identified as hexamethylbenzene (HMB) by nmr (singlet at δ 2.23) and by its melting point, 164°. The oil was separated into its two components by preparative vpc at 140°. The first fraction, *ca.* 25%, was a colorless oil, identified as vinylpentamethylcyclopentadiene (VCP) by analysis and nmr, mass, uv, and ir spectra. *Anal.* Calcd for $C_{12}H_{18}$: C, 88.82; H, 11.18; mol wt, 162.140844. Found: C, 89.05; H, 11.16, mol wt, 162.139930 (mass spectroscopic). Nmr spectrum, in $CDCl_3$:[4] δ 1.01 (s, 3 H), 1.67 (d,[32] 6 H), 1.79 (d,[32] 6 H), 5.04 (m,[33] 3 H); in C_6H_6 (at 60 MHz): δ 1.24 (s, 3 H), 1.90 (s, 12 H), 5.34 (m, 3 H).[34] Uv in hexane, λ_{max} 2400 Å (ϵ 3780). Ir (liquid film): 3080 (m), 3050 (w), 1655 (w), 1625 (s), 1440 (s), 1400 (w), 1375 (m), 1078 (s), 1000 (s), 906 (s), 775 (w), 680 (m), 585 (m), 550 (m) cm^{-1}.

Attempts to hydrogenate VCP in the presence of a PtO_2 catalyst were unsuccessful, and a polymer was the only product.

The second fraction from the vpc separation (*ca.* 75%)[35] was a pale yellow oil which was identified as 1-chlorovinylpentamethylcyclopentadiene (CVCP) by analysis and nmr, mass, uv, and ir spectra. It also took up 3 mol of hydrogen on catalytic hydrogenation. *Anal.* Calcd for $C_{12}H_{17}Cl$: C, 73.26; H, 8.71; Cl, 18.02; mol wt, 196.101872 ($C_{12}H_{17}{}^{35}Cl$), 198.098922 ($C_{12}H_{17}{}^{37}Cl$). Found: C, 79.92; H, 8.64; Cl, 17.80; mol wt, 196.103268, 198.100317 (mass spectroscopic). Nmr spectrum, in $CDCl_3$: δ 1.11 (s, 3 H); 1.68 (d,[32] 6 H), 1.79 (d,[32] 6 H), 5.24 (d, $J_{HH} = 1.3$ Hz, 1 H), and 5.29 (d, $J_{HH} = 1.3$ Hz, 1 H); in C_6H_6 (at 60 MHz): δ 1.21 (s, 3 H), 1.90 (s, 12 H), 5.39 (dd, 2 H).[34] Uv in hexane, λ_{max} 2500 Å (ϵ 4750). Ir (liquid film): 3110 (w), 1660 (m), 1625 (s), 1620 (sh), 1440 (s) 1375 (m), 1350 (w), 1174 (s), 1138 (s), 1078 (s), 1050 (w), 882 (vs), 790 (m), 760 (m), 738 (m), 708 (ν_{C-Cl}, s), 650 (m), 610 (s), 530 (m), 512 (m) cm^{-1}.

A sample of CVCP was hydrogenated at 3.2 atm and 20° over a PtO_2 catalyst in methanol. After removal of solvent an oil was obtained. This was shown to be a saturated chloro compound by its mass spectrum. The molecular ion peaks were observed at *m/e* 204 ($C_{12}H_{23}{}^{37}Cl$) and 202 ($C_{12}H_{23}{}^{35}Cl$). In addition, peaks corresponding to the cleavage at the quaternary carbon involving (i) loss of methyl (giving $C_{11}H_{20}Cl$, *m/e* 187,189) and (ii) loss of C_2H_4Cl (giving $C_{10}H_{19}$, *m/e* 139) were found.

A solution of 0.04 g of CVCP was stirred in benzene at 45° for 18 hr with a solution of 0.03 g of tetracyanoethylene. The solvent was removed to leave a violet solid. All attempts to purify this adduct from excess TCNE failed. However, the pmr spectrum (60 MHz) clearly showed that a 1:1 adduct had been formed. The nmr spectrum in $CDCl_3$ had peaks at δ 1.62 (s, 3 H), 1.73 (s, 6 H), 1.88 (s, 6 H), 4.87 (d, $J_{HH} = 3$ Hz, 1 H), 5.52 (d, $J_{HH} = 3$ Hz, 1 H).[5]

In another reaction, complex **1** was allowed to react with triphenylphosphine in a nitrogen-filled glove box, to avoid the presence of even traces of air. Carefully degassed solvents were also used here. Complex **1** (0.34 g, 0.5 mmol) was added to a solution of 1.05 g (4 mmol) of triphenylphosphine in 25 ml of benzene at 65°. The light yellow solution was stirred for 10 min and then cooled to 20°. A bright yellow precipitate (0.14 g) was filtered off and was found to be largely bis(triphenylphosphine)palladium chloride. *Anal.* Calcd for $C_{36}H_{30}Cl_2P_2Pd$: C, 61.60; H, 4.31; Cl, 10.10. Found: C, 64.41; H, 4.39; Cl, 8.02.

A second and a third crop of crystals also precipitated from the solution upon standing; these were collected and washed with light petroleum. Their infrared spectra were identical with the above and their analyses showed them to be largely $(Ph_3P)_2PdCl_2$. *Anal.* Found: C, 62.34, 62.05; H, 4.45, 4.82; Cl, 9.31, 9.79. The coprecipitation of some triphenylphosphine probably accounts for differences from theoretical in these three samples.

The orange filtrate was concentrated to 5 and 15 ml of carbon disulfide added. This was done to convert the remaining product, presumed to be largely tetrakis(triphenylphosphine)palladium, into the more stable CS_2 adduct, $(Ph_3P)_2PdCS_2$.[36] A number of fractions of this product were again collected and analyzed. Most were contaminated, either with $(Ph_3P)_2PdCl_2$ or with triphenylphosphine. One of them (0.09 g) gave an analysis in fair agreement with $(Ph_3P)_2PdCS_2$. *Anal.* Calcd for $C_{37}H_{30}P_2S_2Pd$: C, 62.82; H, 4.27; S, 9.07. Found: C, 62.62; H, 4.59; S, 10.68.

On evaporation of the mother liquors, an oil was obtained which contained (by nmr analysis), in addition to some triphenylphosphine, 15% HMB, 5% VCP, and 80% CVCP.

Reactions of Complex 1 with Triphenylphosphine, -arsine, and -stibine at Different Temperatures. (a) Above 0°. A solution of **1** (0.025 g, 0.037 mmol) and triphenylphosphine (0.077 g, 0.29 mmol) in deuteriochloroform (total volume, *ca.* 0.5 ml) was allowed to react at 0° for 15 min. The solution was decanted from a small amount of precipitated $(Ph_3P)_2PdCl_2$ and analyzed for HMB, VCP, and CVCP quantitatively by pmr.

Similar experiments were carried out in benzene and also with triphenylarsine (0.090 g, 0.29 mmol) and triphenylstibine (0.10 g, 0.29 mmol), in place of triphenylphosphine, in both benzene and chloroform, at a variety of temperatures. The results are presented in Table I.

(b) Below 0°. A solution containing complex **1** dissolved in chloroform in an nmr tube was cooled to −78°. To this was added a solution containing the appropriate amount of triphenylphosphine or -arsine also at −78°. The solution was shaken briefly. The tube was put into the probe of the spectrometer at −60° and allowed to reach equilibrium for *ca.* 10 min. The spectra were recorded and are presented in Figures 1A and 2A.[7,8]

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(32) The peaks are seen as clearly resolved doublets (splitting, 0.9 Hz) with unresolved wings on either side. This arises from homoallylic coupling between two inequivalent methyls and would probably be resolved into a quartet at a resolution greater than was possible with the instrument at our disposal.

(33) At 100 MHz this appeared as a poorly resolved central triplet with two other smaller peaks on each side. The spectrum contained insufficient information for unambiguous assignments of either coupling constants or chemical shifts.

(34) As we noted previously,[1] considerable solvent shifts of methyl protons, even of uncomplicated organic molecules, occur between benzene and chloroform. In general, benzene gave better resolution of lower field protons and chloroform of higher field protons.

(35) The amounts isolated from the vpc separation bear no relation to the amounts of VCP and CVCP determined by nmr. Part of this is probably due to decomposition of VCP during the alumina chromatography used for primary purification of the reaction mixture. The products were monitored by nmr throughout the purification procedure, and, apart from some loss of VCP, no change occurred.

(36) T. Kashiwagi, N. Yasuoka, T. Ueki, N. Kasai, M. Kakudo, S. Takahashi, and N. Hagihara, *Bull. Chem. Soc. Jap.*, **41**, 296 (1968).

Reaction of Complex 1 with Lithium Aluminum Hydride. Complex **1** (2.55 g, 3.8 mmol) was added to a stirred suspension of 1.10 g (30 mmol) of lithium aluminum hydride in 30 ml of dry ether at −40°. Black palladium metal separated immediately. After 10 min the solution was allowed to warm to 20° and filtered; when the solvent was removed a pale yellow oil remained. This was analyzed by vpc and found to contain, in addition to a little HMB, one major component (*ca.* 90%) and two minor ones (*ca.* 5%). The mixture was separated by preparative vpc on a column of 20% SE-30 at 120°. The major product eluted first (retention time 19 min) and was identified as ethylpentamethylcyclopentadiene (**12**) by analysis and nmr. *Anal.* Calcd for $C_{12}H_{20}$: C, 87.73; H, 12.27; mol wt, 164. Found: C, 87.81; H, 12.15; mol wt, 164 (mass spectroscopic). Nmr in $CHCl_3$; δ 0.26 (t, $J_{HH} = 6.5$ Hz, 3 H), 0.87 (s, 3 H), 1.40 (q, $J_{HH} = 6.5$ Hz, 2 H), 1.66 (d,[32] 6 H), 1.77 (d[32], 6 H).

The second fraction was a colorless oil of insufficient quantity for analysis. The third fraction was also obtained in minute yield, but its nmr spectrum was similar to that reported[4] for *endo*-H-4-methylene-1,2,3,5,6-pentamethylbicyclo[3.1.0]hex-5-ene (**13**). Nmr in $CHCl_3$: δ 0.67 (q, $J_{H-Me} = 6$ Hz, 1 H, *endo*-H at C_2), 0.95 (d, $J_{Me-H} = 6$ Hz, 3 H, *exo*-methyl at C_2), 1.05 (s, 3 H), 1.14 (s, 3 H), 1.59 (q,[32] 3 H), 1.75 (q,[32] 3 H), 4.64 (d?, 1 H), 4.67 (d? 1 H).

Reaction of Complex 1 with Hydrazine. A solution of complex **1** (0.68 g, 1 mmol) in 25 ml of benzene at 5° was treated with 0.64 ml (20 mmol) of anhydrous hydrazine. Metal was precipitated immediately; this was filtered off and the solvent removed. The resultant oil (crude) was found to contain only VCP by nmr.

Reaction of Complex 1 with Bromine. A solution of 0.1 mmol of bromine in chloroform at −78° was added to a solution of 0.05 mmol of complex **1** in chloroform at −78°. The resultant solution was studied by nmr over the temperature range −50 to +20°. At −50° six broad peaks at δ 1.29, 1.55, 1.71, 1.81, 1.97, and 2.03 were observed. These underwent little change up to *ca.* −15° when a sharp singlet, at δ 2.23, due to HMB began to appear. This grew rapidly with increase in temperature, until by +20° this was the only remaining resonance. A small amount of brown solid precipitated slowly during the course of reaction. Iodine reacted entirely analogously.

Reaction of Complex 1 with Ethanol. A solution of **1** was allowed to decompose in ethanol over 24 hr. Metal was formed and was filtered off. The solvent was removed to leave an oil. Nmr analysis showed the presence of HMB (*ca.* 8%) and 1-acetylpentamethylcyclopentadiene (**14**) only. The latter was identified by a positive iodoform reaction, its nmr spectrum,[29] and that of its 2,4-dinitrophenylhydrazone. Nmr of **14** in $CDCl_3$ (60 MHz): δ 1.09 (s, 3 H), 1.59 (s, 3 H), 1.61 (d,[32] 6 H), 1.87 (d,[32] 6 H). *Anal.* Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.58; H, 10.13.

The dinitrophenylhydrazone showed resonances ($CDCl_3$, 60 MHz) at δ 1.26 (s, 3 H), 1.45 (s, 3 H), 1.69 (d, 6 H), 1.88 (d, 6 H), as well as aromatic protons at δ 8.14 (s, 1 H), 8.26 (d, $J_{HH} = 2.5$ Hz, 1 H), 9.13 (d, $J_{HH} = 2.5$ Hz, 1 H).

An entirely analogous reaction occurred when complex **1** was stirred with methanol.

Reaction of Complex 1 with *o*-Phenanthroline. *o*-Phenanthroline (0.36 g, 2 mmol) was added to a solution of 0.34 g (0.5 mmol) of complex **1** in 10 ml of benzene. A bright yellow precipitate formed immediately. Stirring was continued for 30 min; the precipitate was filtered off and washed with benzene. After drying, 0.58 g of a yellow powder, containing the complex **11** and *o*-phenanthroline hydrochloride, was obtained. This was carefully recrystallized several times from benzene to give the pure complex, 1-(chloro-(*o*-phenanthroline)palladium)vinylpentamethylcyclopentadiene as small crystals, mp 200–210° dec. *Anal.* Calcd for $C_{24}H_{25}ClN_2Pd$: C, 59.64; H, 5.21; Cl, 7.34; N, 5.80; Pd, 22.02. Found: C, 58.63; H, 5.19; Cl, 7.48; N, 5.91; Pd, 21.85. Nmr in $CDCl_3$: δ 1.38 (s, 3 H), 1.64 (s, bd, 6 H), 1.82 (s, bd, 6 H), 4.70 (d, $J_{HH} = 1.5$ Hz, 1 H), 4.89 (d, $J_{HH} = 1.5$ Hz, 1 H).

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Carbon Dioxide Catalysis of Reactions of Chromium(III). I. Oxygen Exchange of Hydroxopentaamminechromium(III) Ion

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Abstract: Carbon dioxide catalyzes the exchange of oxygen between $Cr(NH_3)_5OH^{2+}$ and solvent water. At 25° in buffered perchlorate solutions of ionic strength 0.1, the rate of exchange is rate $= k_1[Cr(NH_3)_5OH_2{}^{3+}] + (k_2 + k'''[CO_2])[Cr(NH_3)_5OH^{2+}]$, where k_1 is 6.3×10^{-5} sec^{-1}, k_2 is 17×10^{-5} sec^{-1}, and k''' is 7 M^{-1} sec^{-1}. Also, ^{18}O introduced as $HCO_3{}^{*-}$ rapidly appears in $Cr(NH_3)_5OH^{2+}$. These results require a mechanism involving formation of a carbonato–Cr(III) complex and quite rapid scrambling of the oxygen atoms of this complex.

Carbonato species of Co(III) are well known[1] and stable but no authenticated carbonato complex of Cr(III) has been described.[2] Attempts to prepare such complexes generally produce Cr_2O_3. CO_2 is an efficient catalyst for decomposition of chromium–ammine complexes, but also catalyzes other substitution reactions on Cr(III).

In a study of Cr(III) substitution reactions[3] an unusual pH dependence of the rate of oxygen exchange of $Cr(NH_3)_5OH^{2+}$ was noted. This was traced to CO_2 catalysis and we now report a study of this catalytic reaction. This provides a mechanism which unifies otherwise puzzling aspects of Cr(III) chemistry.

Experimental Section

Water triply distilled from quartz was employed. $NaClO_4$ solutions, prepared by neutralization of $HClO_4$, were digested at 80° and pH 8 for several hours, thereby coagulating a fine precipitate (probably SiO_2), which was removed by filtration. CO_2 was purified prior to mass spectrometric analysis by gas chromatography. Solutions were protected from atmospheric CO_2 by "Lithasorb" contained in drying tubes connected to air vents.

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