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Palladium(II) Complexes of Bicyclic Trienes

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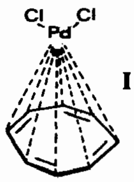
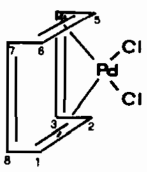
*The reaction of $PdCl_2(C_6H_5CN)_2$ with polyolefins of the type cis-bicyclo[6.1.0]nona-2,4,6-triene and bicyclo[6.2.0]deca-2,4,6-triene gives the expected [(2,3,6,7η^4-polyolefin)$PdCl_2$] (**V**,**VI**), which can be easily converted to the corresponding 3-methoxy substituted derivatives by reaction with methanol. Their reactions with neutral ligands and some preliminary investigations on their thermal rearrangements are also reported. On the basis of the ^1H NMR spectra a qualitative interpretation of the reactivity of these and related iron tricarbonyl complexes towards nucleophilic and electrophilic substitutions is proposed.*

Introduction

The chemistry of cyclic polyolefin metal derivatives has received much attention in the past twenty years, particularly in the field of iron carbonyl complexes[1]. Investigations on polyolefinic complexes of platinum[2] and palladium[3] are however limited to the preparation of complexes of the type (polyolefin)MX_2 {polyolefin = C_7H_8 (cyclohepta-1,3,5-triene), M = Pt[4–6]; C_8H_8 (cycloocta-1,3,5,7-tetraene = COT), M = Pt[7], Pd[8]; and their phenyl-ring substituted derivatives[9]; $C_{13}H_{14}$ (2,4,6-trimethyl azulene), M = Pd[10]; and C_8H_8O (9-oxa-bicyclo[6.1.0]nona-2,4,6-triene), M = Pd[11]}. A series of reactions of $COTPtI_2$ with Grignard reagents have been also reported[12, 13]. Structural studies have been carried out only on $COTPdCl_2$[14], for which a planar configuration (**I**) (C_{4v} symmetry) has been originally proposed, mainly on the basis of the ^1H NMR spectrum[15] (one single, sharp signal at 4.3 τ (DMF) or 4.5 τ (C_6H_5CN)). This spectrum is meaningless and contrasts with the X-ray structural investigation[14], which shows that the $PdCl_2$ unit is bonded to two unconjugated double bonds of the polyolefin (**II**):



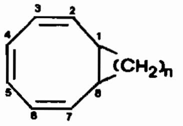
I



II

To account for a single line in the ^1H NMR spectrum one should propose a rapid interconversion between (1,2,5,6-η^4) and (3,4,7,8-η^4) configurations in solution. However, the ^1H NMR spectrum of $C_8H_8PdCl_2$ in $CDCl_3$[**], although of poor quality due to the low solubility of the sample, is consistent with the static configuration (**II**). Therefore the single signal observed by Fritz and Keller[15] in DMF or C_6H_5CN solution is very likely due to decomposition of the complex in those solvents, and must be assigned to the free COT.

In the hope to have more information on the bonding nature of these η^4-polyolefin complexes of palladium we decided to study other similar compounds, substituted in the 1–8 positions of COT, in order to increase their solubility. Here we report the results of an investigation on palladium(II) complexes of *cis*-bicyclo[6.1.0]nona-2,4,6-triene (C_9H_{10}, **III**) and *cis*-bicyclo[6.2.0]deca-2,4,6-triene ($C_{10}H_{12}$, **IV**):



n = 1 **III**
= 2 **IV**

(III) and (IV) have been previously used in several studies with iron[17–21] and ruthenium[22] carbonyls.

Experimental

^1H NMR spectra were recorded in $CDCl_3$ or C_6D_6 (TMS as the internal reference) with a 60 MHz Varian NV-14 spectrometer. IR spectra (nujol mull) were registered on a Perkin–Elmer mod. 457 spectrophotometer in the region 4000–250 cm^{-1}, using CsI plates, and calibrated with a polystyrene film; the accuracy is believed to be within ± 3 cm^{-1}. Molecular weight determinations were performed on a Mechrolab Os-

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[**] That the $C_8H_8PdCl_2$ has the (1,2,5,6-η^4) configuration has been mentioned already on the basis of ^1H NMR spectrum in CD_2Cl_2[16].

TABLE I. Analytical Data.

Complex	Color (yield)[a]	MP (°C, dec.)	Analysis[b] C	H	Cl	M.W.[b]
$C_9H_{10}PdCl_2$ (V)	Yellow (85%)	135–140	36.39 (36.58)	3.43 (3.38)	23.88 (24.00)	297.2 (295.4)
$C_{10}H_{12}PdCl_2$ (VI)	Yellow–Orange (83%)	163–165	38.73 (38.80)	3.89 (3.91)	22.85 (22.91)	312.8 (309.5)
$[C_9H_{10}\cdot OCH_3PdCl]_2$	Pale Yellow (90%)	115–119[c]	41.44 (41.26)	4.52 (4.50)	12.05 (12.18)	576.5 (582.1)
$[C_{10}H_{12}\cdot OCH_3PdCl]_2$	Pale Yellow (92%)	165–170	43.30 (43.30)	4.99 (4.95)	11.49 (11.62)	604.1 (610.1)

[a] After crystallization. [b] Calculated figures in parenthesis. [c] This compound decomposes on melting to an unknown red complex.

mometer model 301 at 37° C, using benzene as the solvent. Melting points were taken on a hot plate apparatus and are incorrect.

Elemental analyses were carried out by the University Analytical Laboratory (Table I). All solvents were dried and purged with nitrogen before use. Other starting materials were used as purchased. Cyclooctatetraene was distilled before use. C_9H_{10}[23] (**III**) and $C_{10}H_{12}$[24] (**IV**) were prepared as described previously[17,20]. $PdCl_2(C_6H_5CN)_2$ was obtained following published procedures[25].

(2,3,6,7-η^4)cis-bicyclo[6.1.0]nona-2,4,6-triene Palladium Dichloride ($C_9H_{10}PdCl_2$) (**V**)

C_9H_{10} (0.7 g, 5.9 mmol) was added to a saturated solution of bis-benzonitrile dichloropalladium (2 g, ≅ 5.2 mmol) in 60 ml of benzene at room temperature with efficient stirring. The red–orange colour of the starting mixture rapidly turned orange–yellow and the yellow micro-crystalline complex (**V**) separated in few minutes. The product was filtered and washed several times with benzene and ethyl ether and then dried in air. The analytical sample was recrystallized from hot benzene. IR and ^1H NMR spectra are reported in Figure 1 and 2; analytical data are summarized in Table I.

(2,3,6,7-η^4)cis-bicyclo[6.2.0]deca-2,4,6-triene Palladium Dichloride ($C_{10}H_{12}PdCl_2$) (**VI**)

This was prepared similarly from $PdCl_2(C_6H_5CN)_2$ (2 g, ≅ 5.2 mmol) in 60 ml of benzene and $C_{10}H_{12}$ (0.8 g, 6 mmol). The orange product (**VI**) was recrystallized from hot benzene. IR and ^1H NMR spectra are reported in Figure 1 and 3.

*Di-μ-chlorodi-{(2,6,7-η^3)cis-3-methoxybicyclo[6.1.0] nona-4,6-dienyl}*dipalladium *($C_9H_{10}OCH_3PdCl)_2$* (**VII**)

$C_9H_{10}PdCl_2$ (**V**) (2 g, ≅ 6.5 mmol) was suspended in 50 ml of methanol and stirred at room temperature. The starting microcrystalline complex became progressively yellow and flocculent. The product was filtered after three hours and crystallized from hot benzene/methanol (10/1). The IR and ^1H NMR spectra are reported in Figure 1 and 4.

Di-μ-chlorodi-{(2,6,7-η^3)cis-3-methoxybicyclo[6.2.0] deca-4,6-dienyl}dipalladium ($C_{10}H_{12}OCH_3PdCl)_2$ (**VIII**)

This was prepared similarly from $C_{10}H_{12}PdCl_2$ (**VI**) (2 g, ≅ 6.5 mmol) and 50 ml of methanol. The reaction is faster and less than one hour is sufficient for the conversion to (**VIII**). The pale yellow product was crystallized as (**VII**). The IR and ^1H NMR spectra are reported in Figure 1 and 4.

Reactions of **V**, **VI**, **VII** and **VIII** with PPh_3 were carried out by mixing the reagents in benzene and are described in the Discussion.

Complexes (**V**) and (**VI**) can be obtained again from (**VII**) and (**VIII**) respectively by stirring them in a saturated solution of HCl gas in benzene.

Thermal rearrangement of (**V**) was carried out in benzene at various temperatures and different reaction times. The reaction mixtures were filtered hot and products precipitated with n-hexane. Attempts to separate the various reaction products by fractional crystallization failed to give pure samples, but only fractions enriched in one of the components (see Discussion).

Results and Discussion

Reaction of equimolecular amounts of the polyolefins (**III**) and (**IV**) with $Pd(C_6H_5CN)_2Cl_2$ in benzene involves rapid substitution of the labile benzonitriles by the polyolefin with precipitation of the corresponding $(C_9H_{10})PdCl_2$ (**V**) and $(C_{10}H_{12})PdCl_2$ (**VI**) complexes (Table I).

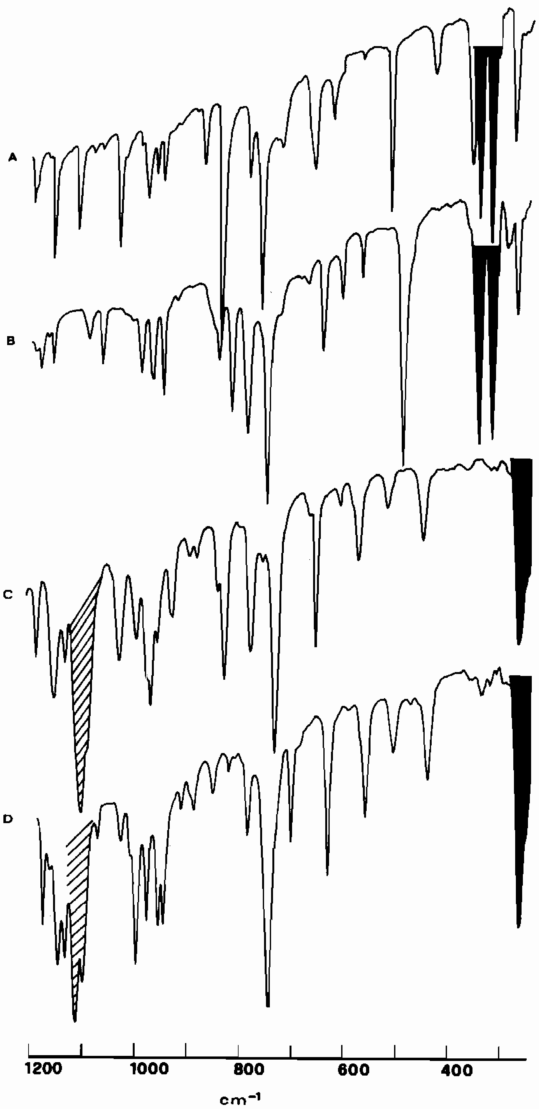
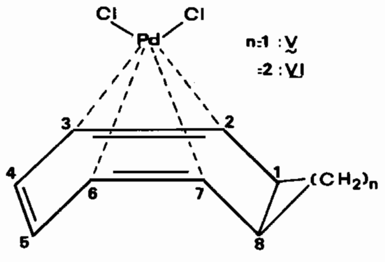


Figure 1. The IR spectrum (nujol mull) in the 1200–250 cm^{-1} region of $C_9H_{10}PdCl_2$ (A), $C_{10}H_{12}PdCl_2$ (B), $[C_9H_{10}OCH_3PdCl]_2$ (C) and $[C_{10}H_{12}OCH_3PdCl]_2$ (D). ν(Pd–Cl) (black peaks) and $\nu(OCH_3)$ are shown.

The IR spectrum of these compounds in the region 400–250 cm^{-1}, excluding bands characteristic of the organic ligands, shows two strong absorptions at 343 and 320 cm^{-1} (**V**) and 345, 322 cm^{-1} (**VI**) respectively (Figure 1) which can be attributed to ν (Pd–Cl)[15,26].

Their monomeric configurations results from molecular weight measurements (Table I). The ^1H NMR spectra (Figures 2, 3) show that both complexes have a plane of symmetry, bisecting the $PdCl_2$ unit and the organic ligands in C_4–C_5, C_1–C_8 and C_9 (**V**) or C_9–H_{10} (**VI**):



While other (2,3,6,7-η^4) complexes of C_9H_{10} (**III**), namely $C_9H_{10}Fe(CO)_3$*[17,18], $[C_9H_{10}RhCl]_2$[27] and $C_9H_{10}RhX$ (X = acac[27] or facac[28]) have been already reported, (**VI**) is the first example of an (2,3,6,7-η^4) $C_{10}H_{12}$ complex. The corresponding $C_{10}H_{12}$ iron tricarbonyl derivative has never been isolated in the reaction of that polyolefin with different sources of $Fe(CO)_3$ and/or in different solvents.[20,29] The patterns of the ^1H NMR spectra of (**V**) and (**VI**) can be compared to that of the C_9H_{10} irontricarbonyl complex.

There are however some interesting differences both between the two palladium complexes (**V** and **VI**) here reported and between (**V**) and the similar iron tricarbonyl derivative. Although (**V**) and (**VI**) show a very similar pattern in the olefinic protons ($H_2 \leftrightarrow H_7$) – which can be assigned as shown in Figures 2 and 3 – the small coupling (<1 Hz)** between the downfield portion of the AB quartet and the singlet due to the free olefinic protons in (**V**), is absent in (**VI**). This is confirmed by simulating the AB portion of the ^1H NMR spectra of (**V**) and (**VI**)***: for (**VI**) the agreement between the calculated and the experimental spectrum is perfect while for (**V**) only the upfield doublet of the AB quartet is superimposable; the experimental downfield one is consistently broader and lower in intensity than in the calculated spectrum. From the above data it appears that in both complexes the H_1–H_2 dihedral angle is *ca.* 90° ($J_{1,2} = J_{7,8} \cong 0$) and therefore coordination of $PdCl_2$ is *endo* with respect to the stereochemistry of the cyclopropane (in **V**) and cyclobutane (in **VI**) rings, as in $C_9H_{10}Fe(CO)_3$[18]. Moreover the small coupling of

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* In our previous work[17] we have reported an impure $C_9H_{10}Fe(CO)_3$ complex without suggesting its configuration. Comparison of the ^1H NMR spectrum of our impure complex with that described by Brookhart[18] as (2,3,6,7-η^4)$C_9H_{10}Fe(CO)_3$ allows us to assign the same configuration to our complex.

** This allows a safe assignment of the broader doublet to H_3 and H_6. By analogy we assign the downfield doublet in (**VI**) to H_3 and H_6.

*** The essential data for the computer program are: (**V**): a = 32.9 Hz, b = 16.0 Hz, Δ = 25.12 Hz, J = 8.5 Hz; (**VI**): a = 21.8 Hz, b = 4 Hz, Δ = 9.43 Hz, J = 8.9 Hz. For the meaning of the symbols see reference 30. We thank Dr. R. Roulet, University of Lausanne, for the calculated spectra described in this paper.

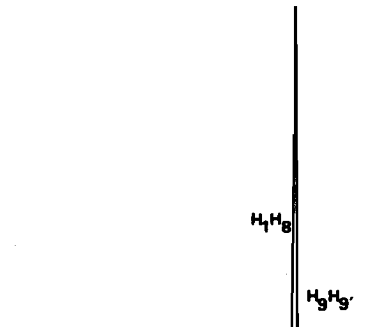

Figure 2. The 60 MHz spectrum of $C_9H_{10}PdCl_2$ (V) in $CDCl_3$ solution. The numbering of hydrogen atoms is the same as in the corresponding schematic representation of V.

$J_{3,4} = J_{5,6} \geqq 1$ Hz in (**V**) suggests that in this complex the H_3–H_4 dihedral angle slightly differs from 90°.

A more important difference is that manifested among the palladium dichlorides (**V** and **VI**) and the iron tricarbonyl complex; although, as pointed out before, the pattern is very similar there is a consistent downfield shift of the peaks due to the coordinated olefinic protons in (**V**) (and in **VI**) on comparison with the free ligand olefinic protons[31] and a more evident one with the corresponding coordinated olefinic protons of the iron tricarbonyl complex*. Several effects may be partially responsible for this shift, such as the different additional ligands and the symmetry of the complexes, but the same electronic configuration (d^8) of the metals suggests that an important part might be due to the formal electron density on the coordinated olefinic carbons. Therefore if due allowance is made for the above considerations, the downfield shifts of H_2, H_3, H_6, and H_7 in (**V**) (and in **VI**) on comparison with the iron analog may indicate a greater electron density on the olefinic carbons of the iron complex, anticipating a different reactivity of the coordinated polyolefinic ligands.

Although the reactivity of $(2,3,6,7\text{-}\eta^4)C_9H_{10}Fe(CO)_3$ is not known, because of the low yield of the preparation[17,18], detailed studies on $(1\text{–}4\text{-}\eta^4)C_7H_8Fe(CO)_3$ (C_7H_8 = cycloepta-1,3,5-triene) and $(1\text{–}4\text{-}\eta^4)C_8H_8Fe(CO)_3$ by Lewis and coworkers[32,33] have shown the possibility of quite a number of electrophilic substitution and addition reactions on the coordinated polyolefins. Comparison of the ^1H NMR spectra of the olefinic protons in the free C_7H_8 and C_8H_8 with those of the corresponding $(1\text{–}4\text{-}\eta^4)$irontricarbonyl complexes shows that the large upfield shift of the protons of the coordinated olefinic carbons is partially compensated by a small downfield shift of

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* $(2,3,6,7\text{-}\eta^4)C_9H_{10}Fe(CO)_3$ shows the following signals in CS_2[18]: 4.52s($H_{4,5}$), 5.92d(H_3, H_6), 6.43d(H_2, H_7) and 8.2–9.05 (H_1, H_8, H_9, $H_{9'}$).

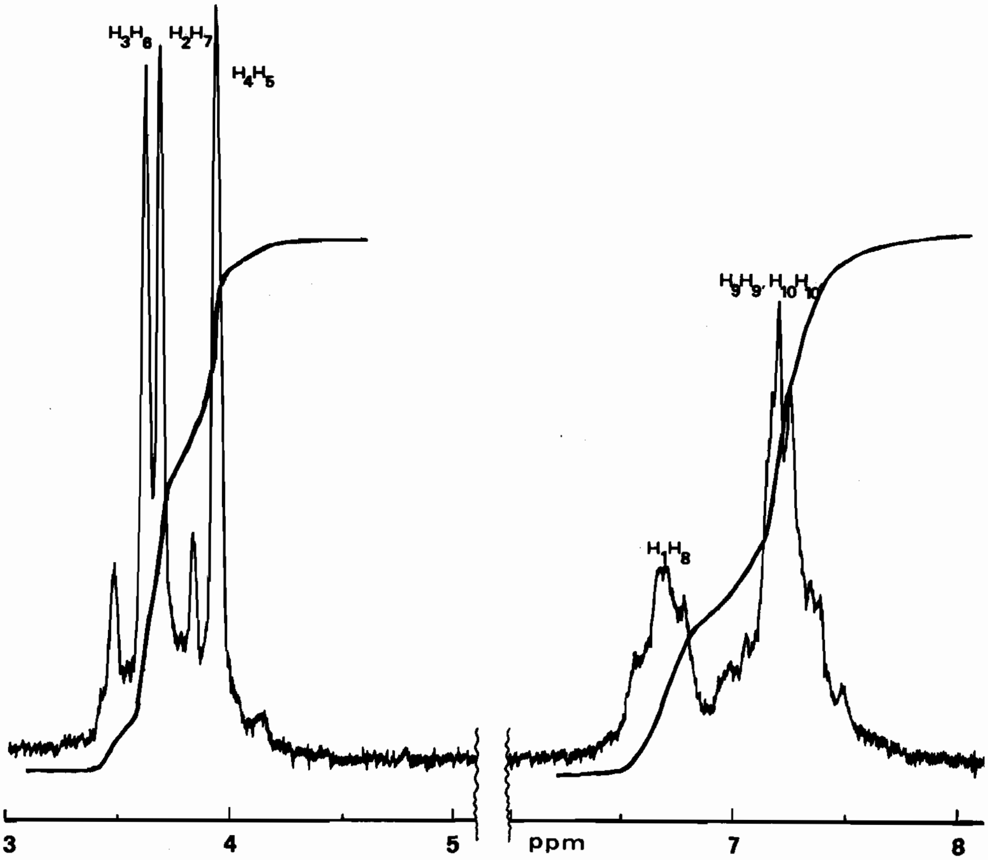

Figure 3. The 60 MHz spectrum of $C_{10}H_{12}PdCl_2$ (VI) in $CDCl_3$ solution. The numbering of hydrogen atoms is the same as for the corresponding carbon atoms in the schematic representation of (VI).

the protons of the non-coordinated olefinic carbons. However it is easy to calculate that the whole effect[*] is an upfield shift of the olefinic protons after coordination. This, we believe, is important to understand the facility of electrophilic reactions on the polyolefinic ring, documented by Lewis' work[32,33]. We can extend this consideration to $(2,3,6,7\text{-}\eta^4)C_9H_{10}Fe(CO)_3$ which also shows in the ^1H NMR spectrum an upfield shift of the olefinic protons with respect to the free C_9H_{10} (τ = 3.9 H_2–H_6)[31]. Although in this case the difference in coordination on comparison with the $(1\text{–}4\text{-}\eta^4)C_7H_8Fe(CO)_3$ and $(1\text{–}4\text{-}\eta^4)C_8H_8Fe(CO)_3$ complexes might activate different centers of the polyolefin, the above considerations suggest a similar facility for electrophilic substitution reactions on the coordinated polyolefin. On the contrary electrophilic substitutions should be very difficult in **(V)** and **(VI)** owing to the decreased electron density on ring carbons upon coordination. Therefore in $PdCl_2$ polyolefin complexes nucleophilic substitution reactions become important; consistently both **(V)** and **(VI)** react easily with methanol to give the corresponding methoxy-substituted complexes **(VII** and **VIII)** which can be in turn converted to the starting monomeric **(V)** and **(VI)** upon treatment of the products with HCl:

$$2C_9H_{10}PdCl_2 \underset{HCl}{\overset{CH_3OH}{\rightleftharpoons}} [C_9H_{10}\cdot OCH_3PdCl]_2 \quad \textbf{(VII)}$$

$$2C_{10}H_{12}PdCl_2 \underset{HCl}{\overset{CH_3OH}{\rightleftharpoons}} [C_{10}H_{12}\cdot OCH_3PdCl]_2 \quad \textbf{(VIII)}$$

These reactions are well known in the chemistry of Pd(II)[36] and Pt(II)[2] complexes of cyclic 1–5 diolefins but they have received less attention in the case of the corresponding polyolefin complexes[*]. In prin-

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[*] The ^1H NMR spectrum of $(1\text{–}4\text{-}\eta^4)C_8H_8Fe(CO)_3$ shows at room temperature one single peak at 4.76 (τ = 4.2 in free C_8H_8) due to the well known fluxionality of the molecule. In the "frozen" configuration the peaks are at τ = 3.6(H_6, H_7), 3.9(H_5, H_8), 4.6(H_2, H_3) and 7.0(H_1, H_4)[35].

[*] Robinson and Shaw[37] have prepared di-μ-chlorodi-[(1,5,6-η^3)2-methoxycycloocta-3,5,7-trienyl]dipalladium and their data for $\nu(OCH_3)$ and τ_{OCH_3} are consistent with our spectroscopic results.

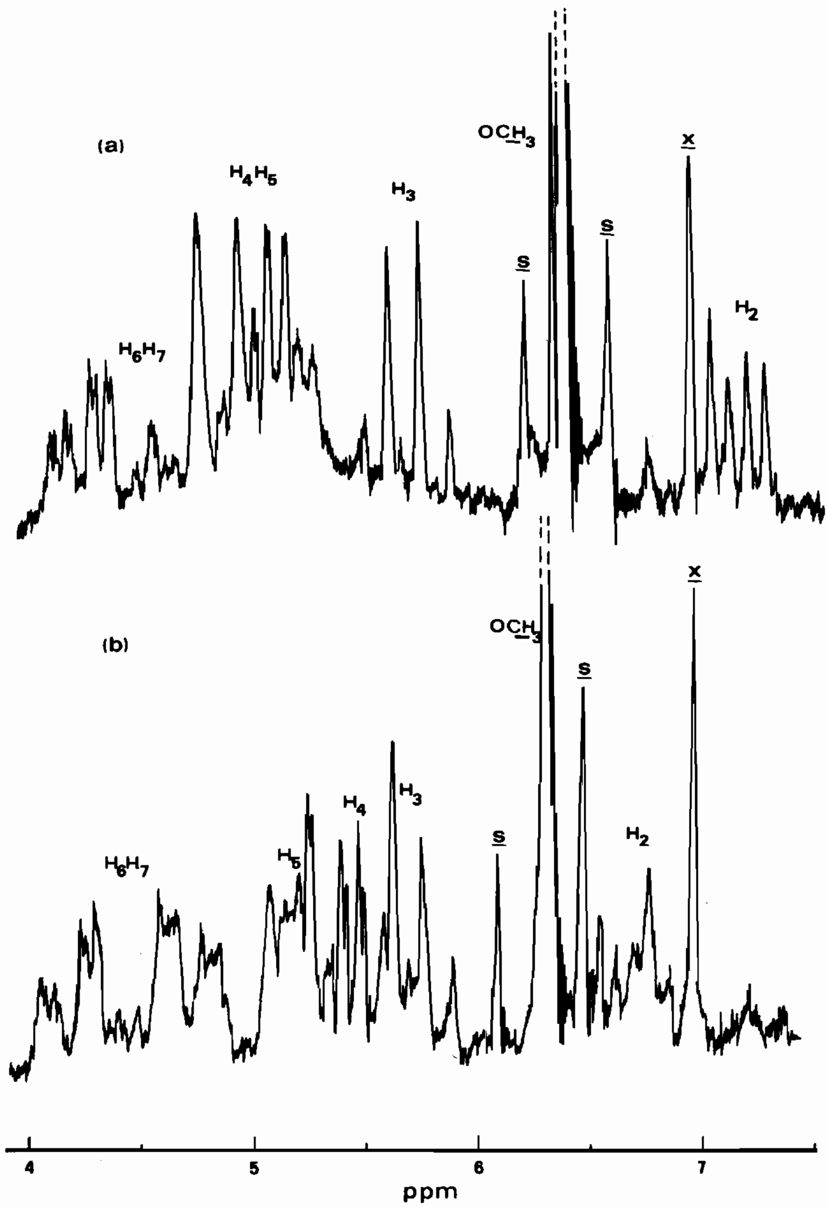
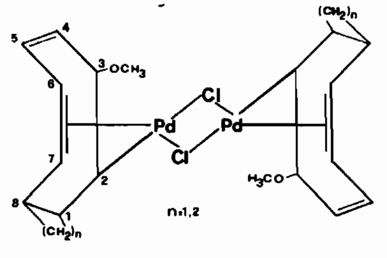
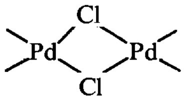


Figure 4. The 60 MHz spectra of $[C_9H_{10}\cdot OCH_3PdCl]_2$ (VII) and $[C_{10}H_{12}\cdot OCH_3PdCl]_2$ (VIII) in C_6D_6 solution. The cyclopropane and cyclobutane protons are omitted (see Discussion). Assignments of H_2, H_3, H_4 and H_5 are tentative. Peaks marked x are due to a solvent impurity; s are spinning side bands. The numbering of hydrogen atoms is the same as in the corresponding schematic representation of VII and VIII.

ciple attack of OCH_3^- can occur on both coordinated and non-coordinated olefinic carbons of (**V**) and (**VI**). The chemical shift arguments suggested above, however, indicate that the most reactive carbons towards a nucleophilic addition are those coordinated to the palladium and specifically C-3 (or C-6). The reaction of (**V**) and (**VI**) with CH_3OH confirms the expectations since (**VII**) and (**VIII**) were isolated in high yield.



The dimeric configurations result from molecular weight determinations (Table I) and from the presence of the characteristic ν(Pd–Cl) stretching frequencies of dimeric



units (Figure 1) at *ca.* 250 cm^{-1}. The OCH_3 band appears in the IR spectrum at 1099 and 1110 cm^{-1} for **(VII)** and **(VIII)**, respectively. The ^{1}H NMR spectra are now more complicated owing to the asymmetry of the substituted polyolefins. However comparison of the two spectra (Figure 4) in the region of the $H_2 \leftrightarrow H_7$ signals, which are presumably very similar in both complexes, allows reasonably safe assignments.

The H_1, H_8, $H_{9,9'}$ protons of **(VII)** appear as a complex multiplet at $\tau = 8.6$–9.3 and H_1, H_8, $H_{9,9'}$, $H_{10,10'}$ protons of **(VIII)** appear as two complex multiplets of intensity 2 and 4 at $\tau = 7.65$–8.0 and 8.1–8.4, respectively. From Figure 4 the presence of further splitting in the $H_{6,7}$ quartet suggests that both the dihedral angles H_5, H_6 and H_7, H_8 are no more 90°.

All the complexes **(V–VIII)** react with neutral ligands **(L)** such as phosphines and amines to give always PdL_2Cl_2. While these products can be easily anticipated for the reaction of **(V)** and **(VI)**, the failure to obtain a simple bridge-splitting reaction from **(VII)** and **(VIII)**, even at low temperature and in stoichiometric ratio, is in contrast with the reactivity manifested by the similar dimeric methoxycyclooctadienyl palladium[36] and platinum[2] chloride complexes. This anomalous behaviour is under further investigation.

The solutions of complexes **(V)** and **(VI)** show a different behaviour on heating. The orange solution of **(V)** turns rapidly red at 60°C in benzene while no change is manifested upon similar treatment of **(VI)**. The products which can be separated from thermolysis of **(V)** are not so far reproducible since slight modifications of reaction temperature and/or reaction time give different ratios of isolated products. Separation of pure samples from the reaction mixture is difficult because of their low solubility. Preliminary results (spectroscopic measurements on different reaction mixtures) suggest that rearrangement of the starting polyolefin occurs together with formation of dimeric chloro-bridged palladium complexes (HCl is evolved). We are now currently investigating these thermal rearrangements with the aim of obtaining different organic moieties from those separated in the thermal rearrangement of (2,6,7-η^3, 3–5-η^3)*cis*-bicyclo[6.1.0]nona-2,4,6-triene hexacarbonyldiiron (Fe–Fe)[37]. The easy displacement of the coordinated polyolefin in these rearranged complexes by neutral ligands **(L)** may be of some utility for the synthesis of new polyolefins.

Acknowledgements

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References

1 For a recent review see: G. Deganello, P. Uguagliati, L. Calligaro, P.L. Sandrini and F. Zingales, *Inorg. Chim. Acta, 13,* 247 (1975).

2 U. Belluco, "Organometallic and Coordination Chemistry of Platinum", Academic Press, New York (1974).

3 P.M. Maitlis, "The Organic Chemistry of Palladium", Academic Press, New York, Vol.1 (1971).

4 R.A. Alexander, N.C. Baenzinger, C. Carpenter and J.R. Doyle, *J. Am. Chem. Soc., 82,* 535 (1960).

5 C.R. Kistner, J.R. Doyle, N.C. Baenzinger, J.H. Hutchinson and P. Kasper, *Inorg. Chem., 3,* 1525 (1964).

6 E.O. Fischer and H.P. Fritz, *Z. Physik. Chem., 17,* 132 (1958).

7 E.O. Fischer, *Z. Naturforsch., 176,* 776 (1953).

8 K.A. Jensen, *Acta Chem. Scand., 7,* 868 (1953).

9 H. Frye, E. Kuljian and J. Viebrock, *Z. Naturforsch., 20b,* 269 (1965).

10 R. Burton, L. Pratt and G. Wilkinson, *J. Chem. Soc.,* 4290 (1960).

11 G. Strukul, P. Viglino, R. Ros and M. Graziani, *J. Organomet. Chem., 74,* 307 (1974).

12 J.R. Doyle, J.H. Hutchinson, N.C. Baenzinger and L.W. Tresselt, *J. Am. Chem. Soc., 83,* 2768 (1961).

13 C.R. Kistner, J.H. Hutchinson, J.R. Doyle and J.C. Storlie, *Inorg. Chem., 2,* 1255 (1963).

14 C.V. Goebel, *Diss. Abstr. B, 28,* 625 (1967).

15 H.P. Fritz and H. Keller, *Ber., 95,* 158 (1962).

16 W. Partenheimer, W. Bennett and J.R. Doyle, *Inorg. Chem.,* in press (quoted by W. Partenheimer, *Inorg. Chem., 11,* 743 (1972)).

17 G. Deganello, H. Maltz and J. Kozarich, *J. Organomet. Chem., 60,* 323 (1973).

18 E.J. Reardon, Jr. and M. Brookhart, *J. Am. Chem. Soc., 95,* 4311 (1973).

19 G. Sholes, C.R. Graham and M. Brookhart, *J. Am. Chem. Soc., 96,* 5665 (1974).

20 F.A. Cotton and G. Deganello, *J. Organomet. Chem., 38,* 147 (1972).

21 F.A. Cotton and G. Deganello, *J. Am. Chem. Soc., 94,* 2142 (1972); *95,* 396 (1973).

22 G. Deganello, P.L. Sandrini, R.A. Michelin and L. Toniolo, *J. Organomet. Chem., 90,* C31 (1975).

23 S.W. Staley and T.J. Henry, *J. Am. Chem. Soc., 91,* 1239 (1969).

24 S.W. Staley and T.J. Henry, *J. Am. Chem. Soc., 93,* 1292 (1971).

25 J.R. Doyle, P.E. Slade and J.B. Jonassen, "Inorganic Synthesis" (E.G. Rochow Editor), Vol. VI, p. 218.

26 W. Partenheimer and E.F. Hoy, *J. Am. Chem. Soc., 95,* 2840 (1973).

27 R. Grigg, R. Hayes and A. Sweeney, *Chem. Comm.,* 1248 (1971).

28 W. Grimme, *J. Am. Chem. Soc., 95,* 2381 (1973).

29 F. A. Cotton and J. M. Troup, *J. Am. Chem. Soc., 95,* 3798 (1973).

30 R. A. Hoffmann, S. Forsén and B. Gestblom, "Analysis of NMR Spectra" in "NMR Basic Principles and Progress", P. Diehl, E. Fluck, R. Kosfeld Editors, Springer–Verlag, Berlin, Heidelberg, New York (1971), p. 56.

31 T. J. Katz and P. J. Garratt, *J. Am. Chem. Soc., 86,* 5194 (1964).

32 B. F. G. Johnson, J. Lewis and G. L. P. Randall, *J. Chem. Soc. (A),* 422 (1971).

33 B. F. G. Johnson, J. Lewis, P. McArdle and G. L. P. Randall, *J.C.S. Dalton,* 456 (1972).

34 See for example C. E. Keller, B. A. Shoulders and R. Pettit, *J. Am. Chem. Soc., 88,* 4760 (1966).

35 R. Grubbs, R. Breslow, R. Herber and S. J. Lippard, *J. Am. Chem. Soc., 89,* 6864 (1967).

36 Ref. 3, p. 163.

37 S. D. Robinson and B. L. Shaw, *J. Chem. Soc.,* 5002 (1964).

38 G. Deganello and L. Toniolo, *J. Organomet. Chem., 74,* 255 (1974).