Reactions of Palladium(II) Halides with 7-Methylenebicyclo[2.2.1]hept-2-ene Derivatives; Unique *trans*-Halogenopalladation of the Exocyclic Double Bond

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7-Methylenebicyclo[2.2.1]hept-2-ene and its derivatives are unusual in that the two double bonds are crossed. In contrast to the behaviour of most non-conjugated dienes toward palladium(II), these dienes do not form stable chelated diolefin complexes. Instead, in solvents of low polarity, halogen-bridged dimeric 2—3η-{(bicyclo-[2.2.1]hept-2-en-7-yl)methyl} chelates are formed, in which C(7) is bound to either Cl, Br, or MeO (the latter if methanol is present in the reaction mixture). In the absence of methanol, the very fast overall reactions involve *trans*-addition of palladium and halogen to the exocyclic olefin, with co-ordination of the remaining double bond. The *trans*-addition must occur either by an ionic or a bimolecular path. In any event the facility for *trans*-halogenopalladation observed here suggests that *cis*- and *trans*-halogenopalladations of organic substrates may in general be competitive.

CHLOROPALLADATION of unsaturated organic substrates is an important reaction in organopalladium chemistry. Additions of Pd–Cl to allenes,[1] olefins,[2] acetylenes,[3] methylenecyclopropanes,[4] vinylcyclopropanes,[5] 1,2,3-triphenylcyclopropene,[6] bicyclopropene and dicyclopropylmethane,[7] and spiropentane,[8] conjugated dienes,[9] bicyclo[6.1.0]non-4-ene,[10a] and bicyclo[5.1.0]oct-3-ene [10b]

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[1] R. G. Schultz, *Tetrahedron Letters*, 1964, 301; *Tetrahedron*, 1964, **20**, 2809; M. S. Lupin and B. L. Shaw, *Tetrahedron Letters*, 1964, 883; M. S. Lupin, J. Powell, and B. L. Shaw, *J. Chem. Soc.* (*A*), 1966, 1687.

[2] (*a*) P. M. Henry, *J. Org. Chem.*, 1972, **37**, 2443; (*b*) J. Tsuji, *Accounts Chem. Res.*, 1969, **2**, 144; (*c*) D. Medema, R. van Helden, and C. F. Kohll, *Inorg. Chim. Acta*, 1969, **3**, 255; (*d*) H. Tayim, *Chem. and Ind.*, 1970, 1468.

[3] (*a*) H. Reinheimer, H. Dietl, J. Moffat, D. Wolff, and P. M. Maitlis, *J. Amer. Chem. Soc.*, 1968, **90**, 5321; (*b*) H. Reinheimer, H. Dietl, J. Moffat, and P. M. Maitlis, *ibid.*, 1970, **92**, 2276; (*c*) H. Reinheimer, J. Moffat, and P. M. Maitlis, *ibid.*, p. 2285; (*d*) T. Hosokawa, I. Moritani, and S. Nishioka, *Tetrahedron Letters*, 1969, 3833.

[4] R. Noyori and H. Takaya. *Chem. Comm.*, 1969, 525.

[5] T. Shono, T. Yoshimura, Y. Matsumura, and R. Oda, *J. Org. Chem.*, 1969, **33**, 876; A. D. Ketley and J. A. Braatz, *J. Organometallic Chem.*, 1967, **9**, P5.

[6] P. Mushak and M. A. Battiste, *J. Organometallic Chem.*, 1969, **17**, P46.

[7] A. D. Ketley, J. A. Braatz, and J. Craig, *Chem. Comm.*, 1970, 1117.

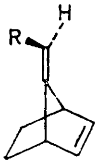
[8] A. D. Ketley and J. A. Braatz, *Chem. Comm.*, 1968, 959.

[9] J. Lukas, P. W. N. M. Van Leeuwen, H. C. Volger, and A. P. Kouwenhoven, *J. Organometallic Chem.*, 1973, **47**, 153; B. L. Shaw, *Chem. and Ind.*, 1962, 1190; M. Donati and F. Conti, *Tetrahedron Letters*, 1966, **11**, 1219.

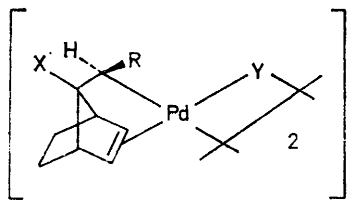
[10] (*a*) G. Albelo and M. F. Rettig, *J. Organometallic Chem.*, 1972, **42**, 183; (*b*) G. Albelo, G. Wiger, and M. F. Rettig, unpublished work.

have been reported. It is generally believed that *cis*-addition of Pd–Cl to the unsaturated substrate occurs in non-polar solvents when excess of halide is absent. Thus, *cis*-addition of Pd–Cl to but-2-yne has been proposed [3b] as a probable first step in its trimerization, and it appears that *cis*-addition of Pd–Cl to olefins is preferred, even in acetic acid containing excess of lithium chloride.[2a] However, in methanolic solutions of lithium chloride–palladium(II) chloride, prop-2-ynyl amines are *trans*-chloropalladated, with the added chlorine attacking from outside the co-ordination sphere.[11]

We report here halogeno- and methoxo-palladation reactions of 7-methylenebicyclo[2.2.1]hept-2-enes (L; R = H, CO·OMe, or CO·OEt) with the complexes $[PdX_2(PhCN)_2]$ (I; X = Cl or Br), using both solvents of low polarity (CH_2Cl_2 and $CHCl_3$) and methanol. The products are the 2—3-η-{(bicyclo[2.2.1]hept-2-en-7-yl)-methyl} complexes, $[L'Pd(\mu\text{-}Y)_2PdL']$ (II; Y = Cl or Br),* which result from overall *trans*-addition of Pd–Cl or Pd–Br (or Pd and –OMe) to the exocyclic double bond. These reactions are the first established instances of *trans*-halogenopalladation of an olefin in the absence of added halide, and are also the first reported halogenopalladations of non-conjugated dienes. The products obtained, (II), are the first stable materials isolated from reactions of palladium(II) with a system of ‘crossed’ double bonds.



(L) R=H, CO·OMe, or CO·OEt

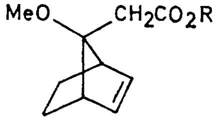


(II) R=H, X=Y=Cl
R=CO·OEt, X=Y=Cl
R=CO·OMe, X=Y=Cl
R=CO·OMe, X=OMe, Y=Cl
R=CO·OEt, X=OMe, Y=Cl
R=H, X=Y=Br
R=CO·OEt, X=Y=Br

RESULTS

Dienes (L) reacted in less than 30 s with solutions of (I; X = Cl) in chloroform or dichloromethane (in such solutions, the predominant Pd^{II} complex is probably $[\{PdCl_2(PhCN)\}_2]$ [12]). The products either precipitated spontaneously as a white powder (II; R = H, X = Y = Cl), or precipitated on addition of diethyl ether–hexane, (II; R = CO·OEt), or diethyl ether–pentane, (II; R = CO·OMe). The yields were practically quantitative. The bromide complexes (II; R = H or CO·OEt) were obtained similarly from (I; X = Br) in 67 and 73% yields, respectively. The formulae $Pd_2X_4L_2$ (X = Cl or Br) were established by elemental analysis and determination of molecular weights in solution. The complexes had no i.r. absorptions in the free-double-bond region (1 680—1 600 cm^{-1}), and did not absorb in the range 1 600—1 475 cm^{-1}, where one normally expects to observe ν(C=C) for a co-ordinated diene.[13] However, it has been observed [10b,14] that absence of absorption in the region 1 600—1 475 cm^{-1} is characteristic of Pd^{II} complexes having both Pd–C σ- and π-bonds. Complexes (II; R = H, CO·OMe, or CO·OEt; X = Y = Cl) exhibited i.r. absorption in the range 580—560 cm^{-1}, assigned to C–Cl stretching vibrations. These peaks were absent in the bromo-derivatives, and in those complexes having X = OMe. Complexes (II; R = H, CO·OMe, or CO·OEt; X = Y = Cl) did not absorb in the terminal Pd–Cl stretching region (370—320 cm^{-1}),[15] and (II; R = CO·OEt, X = Y = Cl) exhibited bands at 272 and 232 cm^{-1} characteristic of a Pd_2Cl_2 bridge with Pd also bound to a σ-η-chelate.[3a,16] In each of the complexes containing an ester function, ν(C=O) occurred very near to 1 700 cm^{-1}, which suggests no unusual involvement of the C=O function.

Treatment of complex (II; R = CO·OEt, X = Y = Cl) with aqueous cyanide, triphenylphosphine, or pyridine yielded quantitatively only the starting diene. (Most of the study was made with this complex and the diene, as the latter is easily accessible.) Attempted reduction of this complex with H_2, $NaBH_4$, or $LiAlH_4$ gave complex mixtures which were intractable. On heating the complex under reflux in benzene–methanol (1 : 1) for 2 d, complex (II; R = CO·OMe, X = OMe, Y = Cl) was obtained in 87% yield.† Treatment of the latter with aqueous cyanide liberated olefin (III) in 82% isolated yield.



(III) R=Me

Addition of (I; X = Cl) to diene (L; R = CO·OEt) dissolved in methanol–chloroform or methanol–benzene gave,

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* The structural formulae of complexes (II), (V), (VIII), and (IX) are not intended to indicate a particular *cis*- or *trans*-isomer.

† The relatively vigorous conditions described above were used to guarantee that both substitution and transesterification were complete. This avoided obtaining any ‘mixed’ complexes. The substitution of CH_3O^- for Cl was independently monitored at room temperature by n.m.r. The results showed that substitution readily occurred at room temperature and that the substitution reaction was essentially complete in *ca.* 1·5 d.

[11] T. Yukawa and S. Tsutsumi, *Inorg. Chem.*, 1968, **7**, 1458.

[12] M. Kubota, B. A. Demechaud, P. M. McKinney, T. E. Needham, and G. P. Spessard, *J. Catalysis*, 1970, **19**; W. Kitching and C. J. Moore, *Inorg. Nuclear Chem. Letters*, 1968, **4**, 691.

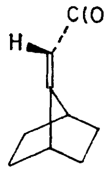
[13] D. B. Powell and T. J. Leedham, *Spectrochim. Acta*, 1972, **A28**, 337.

[14] A. Takahashi and J. Tsuji, *J. Amer. Chem. Soc.*, 1968, **90**, 2387.

[15] D. M. Adams, ‘Metal–Ligand and Related Vibrations,’ E. Arnold, London, 1967; D. M. Adams and P. J. Chandler, *J. Chem. Soc.* (*A*), 1969, 588.

[16] B. Crociani, P. Uguagliati, J. Boschi, and U. Belluco, *J. Chem. Soc.* (*A*), 1968, 2869.

in 3 min, 93% yield of complex (II; R = CO·OEt, X = OMe, Y = Cl). Treatment of the latter with aqueous cyanide gave olefin (III; R = Et) (87%).* The diene reacted with (I; X = Cl) at −45 °C to give the same product, complex (II; R = CO·OEt, X = Y = Cl), as obtained at room temperature. The −45 °C reaction was monitored by n.m.r. spectroscopy and found to have a half-life of *ca.* 2·5 h under the conditions used. During the reaction only resonances attributable to the diene and complex were observed, and no intermediate accumulated.

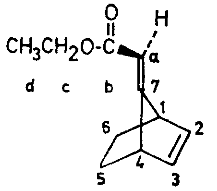


(IV)

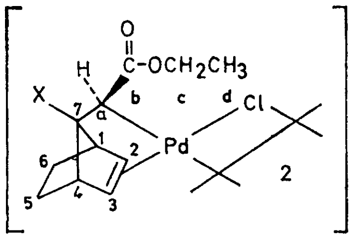
7-(Ethoxycarbonylmethylene)bicyclo[2.2.1]heptane, (IV), did not react with complex (I; X = Cl) in $CDCl_3$ even when the reaction mixture was warmed to 60 °C for 5 h. ^1H and ^{13}C N.m.r. results for the dienes and palladium complexes are presented in Tables 1 and 2.

TABLE 1

^1H N.m.r. results (δ/p.p.m.) [a,b]



(L) R = CO•OEt



(II) X = Cl or OMe

Compound	H_1	$H_{2,3}$	H_4	H_5 (2H)	H_6 (2H)	H_a
(L; R = H)	3·05	6·22 (t, *J* 2·0 Hz)	3·05	1·75	1·15	4·22 (2H, s)
(II; R = H, X = Y = Cl)	2·70	5·41	2·70	1·68	1·10	2·19 (2H, s)
(II; R = H, X = Y = Br)	2·31	5·43	2·31	1·65	1·02	2·05 (2H, s)
(L; R = CO·OEt)	3·05	6·18 (t, *J* 2·0 Hz)	4·20	1·70	1·10	5·12 (1H, s)
(II; R = CO·OEt, X = Y = Cl)	2·82	5·70	3·78	1·90	1·28	3·17 (1H, s)
(II; R = CO·OEt, X = Y = Br)	2·90	5·78	3·82	2·08	1·16	3·33 (1H, s)
(II; R = CO·OEt, X = OMe, Y = Cl)	2·83	5·62	3·57	1·76	1·12	3·28 (1H, s)
(L; R = CO·OMe)	3·15	6·15 (t, *J* 2·0 Hz)	4·10	1·65	1·15	5·12 (1H, s)
(II; R = CO·OMe, X = Y = Cl)	2·82	5·72	3·78	1·95	1·15	3·28 (1H, s)
(II; R = CO·OMe, X = OMe, Y = Cl)	2·97	5·80	3·65	1·87	1·15	3·42 (1H, s)

[a] All spectra in $CDCl_3$ excepting those for complexes (II; R = H, X = Y = Cl or Br) which were run in perdeuteriodimethyl sulphoxide. Chemical shifts are referenced to internal Me_4Si. Subscripts on H correspond to the carbon to which H is bound. All peaks are multiplets unless otherwise specified (s = singlet and t = triplet). [b] For compounds containing ethoxycarbonyl functions, appropriate resonances were observed near 4·13 ($CO·OCH_2$) and 1·25 p.p.m. (CH_3). For compounds containing methoxycarbonyl functions, resonances were observed near 3·78 p.p.m. (CO·OMe). Compounds having the methoxy-function absorbed near 3·2 p.p.m. ($C·OCH_3$).

TABLE 2

^{13}C N.m.r. results (δ/p.p.m.) [a]

Compound	C_1,C_4	C_2,C_3	C_5,C_6	C_7	C_a	C_b	C_c	C_d
(L; R = CO·OEt)	41·7, 46·2	134·6, 135·5	23·9, 23·9	166·4	99·3	174·2	59·5	14·2
(II; R = CO·OEt, X = Y = Cl)	51·7, 54·2	103·5, 105·1	21·8, 23·2	79·4	56·0	171·5	60·3	14·5
(II; R = CO·OEt, X = OMe, Y = Cl) [b]	51·7, 51·7	101·1, 103·4	21·6, 23·4	91·1	49·0	*c*	60·0	14·4

[a] Referenced to Me_4Si. [b] The OMe group appears at δ 47·4 p.p.m. [c] Not observed.

DISCUSSION

Structures of the Complexes.—It is apparent that the Pd^{II} complexes (II) are halogen-bridged dimers in solution of formula $Pd_2X_4L_2$ or $Pd_2X_2(OMe)_2L_2$. The ^1H and ^{13}C n.m.r. spectra are completely consistent with the assigned structures. The cyclic olefin ^1H resonance moves upfield by 0·4—0·8 p.p.m. on complexation, which is typical for Pd^{II} σ,π-complexes,[14] and the H_a resonance moves into the aliphatic region (Table 1) to a position quite reasonable for Pd–C–*H*. Thus, the Pd–CH_2 resonance in complex (V) is found at δ 2·40 p.p.m.[17] ^{13}C N.m.r. studies of various bicyclo[2.2.1]-heptanes and -heptenes have been published,[18] and particular mention is made of the results [18b] for 7-methylenebicyclo[2.2.1]-heptane, (VI), where C_7 and C_a are found at δ 158 and 97

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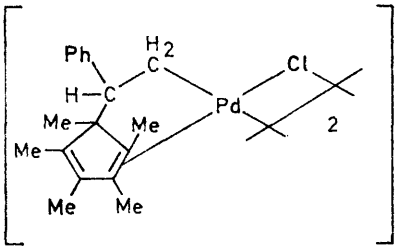
* The available spectral data do not allow us to assign unambiguously the structures of (III) with the OMe group *anti* to the double bond (rather than *syn*).

[17] C. Calvo, T. Hosokawa, H. Reinheimer, and P. M. Maitlis, *J. Amer. Chem. Soc.*, 1972, **94**, 3237.

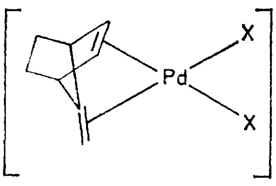
[18] (*a*) J. B. Grutzner, M. Jautelat, J. B. Dence, R. A. Smith, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1970, **92**, 7107; (*b*) R. W. Hoffmann, R. Schuttler, W. Schafer, and A. Schwerg, *Angew. Chem. Internat. Edn.*, 1972, **11**, 512.

p.p.m., respectively. The assignments for (L; R = CO·OEt) (Table 2) are consistent with those for (VI). Chloropalladation of (L; R = CO·OEt) to form complex (II) leads to large shieldings of C_7 and C_a. In addition, both complexes (II; CO·OEt, X = Cl or OMe, Y = Cl) exhibit *ca.* 30 p.p.m. shielding of C_2,C_3 compared to (L; R = CO·OEt), which is quite reasonable for Pd^{II}–olefin binding.[19] On replacing C_7–Cl with C_7–OMe, the resonance assigned to C_7 moves to lower field by *ca.* 12 p.p.m., and that assigned to C_a (β to the point of substitution) moves *ca.* 7 p.p.m. to higher field. These results are expected on substitution of Cl by OMe.[20] The resonance of Pd–C_a at *ca.* 50 p.p.m. is in agreement with results in similar systems,[19b–d] and points to the lack of polarity in the Pd–C σ-bond. Finally, the ^{13}C resonance assigned to Cl–C_7 in complex (II; R = CO·OEt, X = Y = Cl) reveals no ^1H splitting under off-resonance decoupling conditions where '$J(^1H–^{13}C)$ apparent' for each of the other carbons is *ca.* 10 Hz. Further, under off-resonance decoupling conditions, the ^{13}C resonance assigned to Pd–C_a in this complex splits into the expected doublet and the observed multiplicity for each of the other ^{13}C resonances is that expected for the assigned structure.



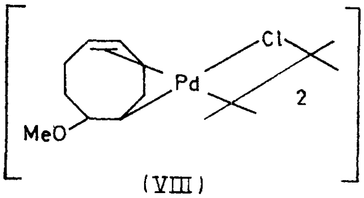
(V)

Mechanism of Complex Formation.—Since (IV) neither forms a π-olefin complex with (I; X = Cl) nor adds Pd–Cl to form a Pd^{II}–alkyl, the *exo*-hydrogen atoms must interfere with approach of Pd^{II} to the exocyclic double bond. That being the case, we expect that initial complexation of dienes (L) occurs on the face where both double bonds may simultaneously interact. The most likely reactive intermediate in these systems would be (VII), a chelated diene complex. The reactivity of (VII) is indicated by the observation that no intermediate [like (VII), for example] accumulates when complex (I; X = Cl) reacts with diene (L; R = CO·OEt) in $CDCl_3$ at −45 °C; only peaks due to the diene and complex (II; R = CO·OEt, X = Y = Cl) were observed in the n.m.r. spectrum. The intermediate (VII) is of course structurally highly unusual, in that the exocyclic olefin lies 'in' the co-ordination plane rather than perpendicular to the plane. Such a geometric arrangement has long been believed to be less stable than, for example, the two 'perpendicular' co-ordinated double bonds in dichloro(η-*cis*,*cis*-cyclo-octa-1,5-diene)palladium(II).[21] In fact, we know of only one stable diene complex where the co-ordinated double bonds are apparently fully crossed (90°), namely dichloro(5-methylenecycloheptene)platinum(II).[22]

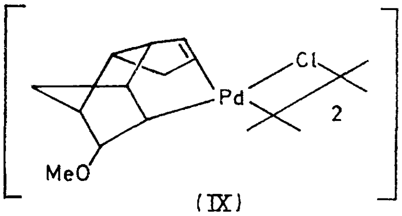


(VII)

The observed reaction products (II) could most reasonably arise by means of ionic dissociation of halogen in (VII), followed by carbon–halogen bond formation (or carbon–oxygen bond formation if methanol is present). A second possibility for the reaction path is bimolecular attack on (VII) by Pd–Cl or by methanol. Direct attack of methanol or other nucleophiles on dienes co-ordinated to Pd^{II} has considerable precedent. For example dichloro(η-*cis*,*cis*-cyclo-octa-1,5-diene)palladium(II) reacts in boiling methanol to give (VIII), but only on addition of base (Na_2CO_3).[23] However, dichloro(η-tricyclo-[5.2.1.0^{2,6}]deca-3,8-diene)palladium(II) reacts in a few hours with methanol in the absence of base to yield (IX).[23] Complex (IX) results from attack on the strained C_8,C_9 double bond;[24] this strain is presumed to be responsible for the greater reactivity of the tricyclo[5.2.1.0^{2,6}]deca-3,8-diene complex toward OMe addition compared to the cyclo-octadiene complex. In our case, the bond-angle strain inherent in the exocyclic double bonds of (L) and the charge polarization $\overset{\delta+}{C_7}{=}\overset{\delta-}{C_8}$, which is inferred from the



(VIII)



(IX)

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[19] (*a*) B. E. Mann, '^{13}C N.m.r. Chemical Shifts and Coupling Constants of Organometallic Compounds,' *Adv. Organometallic Chem.*, 1974, **12**, in the press; (*b*) D. G. Cooper, R. P. Hughes, and J. Powell, *J. Amer. Chem. Soc.*, 1972, **94**, 9244; (*c*) R. P. Hughes and J. Powell, *J. Organometallic Chem.*, 1973, **60**, 387; (*d*) *ibid.*, p. 427.

[20] G. C. Levy and G. L. Nelson, 'Carbon-13 Nuclear Magnetic Resonance for Organic Chemists,' Wiley–Interscience, New York, 1972.

[21] See, for example, W. Partenheimer, *Inorg. Chem.*, 1972, **11**, 743.

[22] C. B. Anderson and J. T. Michalowski, *J.C.S. Chem. Comm.*, 1972, 459.

[23] J. Chatt, L. M. Vallarino, and L. M. Venanzi, *J. Chem. Soc.*, 1957, 3413.

[24] J. K. Stille and R. A. Morgan, *J. Amer. Chem. Soc.*, 1966, **88**, 5135.

^{13}C n.m.r. spectra,[18b] could result in an unusually high reactivity of (VII) to nucleophilic attack. Thus, the direct attack of methanol on (VII) could conceivably be rapid enough to account for the methoxy-product.

We observed in the introduction that chloropalladations of organic substrates are widespread and important reactions. The results of the present work show that *trans*-addition of Pd–Cl and Pd–Br to our olefinic substrates is very fast, even in low-polarity solvents and in the absence of excess of chloride or bromide. It is, therefore, not clear whether one should in general prefer *cis*- to *trans*-halogenopalladation of the substrate, in the absence of structural information. In this connection it is worth noting that Au_2Cl_6 reacts rapidly in dichloromethane with but-2-yne, and *trans*-chloroauration is suggested by thermal decomposition of vinylgold(III) intermediates to *trans*-2,3-dichloro-but-2-ene.[25] The apparent facile *trans*-chloroauration of but-2-yne contrasts with the suggested [3b] *cis*-chloropalladation of the same substrate in the same solvent. These observations together with our own work suggest that the stereochemistries of M-X additions require considerable further study.*

EXPERIMENTAL

Microanalyses for C, H, and Cl were carried out by C. F. Geiger, Ontario, Calif. and Chemalytics, Inc., Tempe, Arizona. Palladium was determined by ignition to constant weight and weighing the residue as Pd. M.p.s are uncorrected. The i.r. spectra were obtained on a Perkin-Elmer 621 grating spectrophotometer. ^{1}H N.m.r. spectra were recorded on a Varian A-60D spectrometer. ^{13}C N.m.r. spectra were obtained at 15 MHz with Fourier-transform techniques. Mass spectra were recorded using a Perkin-Elmer–Hitachi RMU-9D double-focussing spectrometer. Molecular weights were measured with a Mechrolab osmometer, model 301A. Gas–liquid chromatography (g.l.c.) was carried out using an Aerograph model 90P chromatograph with the following columns: (*i*) 2 ft × ¼ in AgNO$_3$ on Carbowax followed by 4 ft × ¼ in SE 30 on Chromosorb P; (*ii*) 5 ft × ¼ in SE 30 on Chromosorb W.

7-Methylenebicyclo[2.2.1]hept-2-ene,[26] 7-(ethoxycarbonylmethylene)bicyclo[2.2.1]hept-2-ene,[27] 7-ethoxycarbonylbicyclo[2.2.1]heptane,[27] dichlorobis(phenyl cyanide)palladium(II),[28] and dibromobis(phenyl cyanide)palladium(II) [28] were prepared by literature methods. The analytical and spectral properties of the dienes are in agreement with the assigned structures and with the literature values. I.r. and mass-spectral data for the dienes and complexes (II) are to be found in Supplementary Publication No. SUP 21077 (5 pp.).†

Preparations.— *7-Methoxycarbonylmethylenebicyclo*[2.2.1]-*hept-2-ene* (L; R = CO·OMe). Diene (L; R = CO·OEt) (600 mg), methanol (10 cm^3), and 1 drop of conc. sulphuric acid were stirred with gentle warming for 24 h. The resulting solution was then poured into water (20 cm^3), extracted with diethyl ether (3 × 10 cm^3), and the ether extracts dried with MgSO$_4$. The drying agent was filtered off and the diethyl ether was removed under reduced pressure. The product was purified by g.l.c. [column (*ii*)], yield 260 mg (47%) (Found: C, 72·6; H, 7·30. Calc. for $C_{10}H_{12}O_2$: C, 73·15; H, 7·35%).

Di-μ-chloro-bis[(2—3-η-{(7-*chlorobicyclo*[2.2.1]*hept-2-en-7-yl)methyl*})*palladium*(II)]. The complex [PdX$_2$(PhCN)$_2$] (I; X = Cl) (45 mg) was added to a solution of (L; R = H) in CHCl$_3$ (1 cm^3). There was an immediate white precipitate which was filtered off, washed with diethyl ether, and dried; yield 32 mg (96%). The white *powder* slowly decomposed above 210 °C (Found: C, 33·35; H, 3·35. Calc. for $C_{16}H_{20}Cl_4Pd_2$: C, 33·9; H, 3·55%).

Di-μ-chloro-bis[(2—3-η-{(7-*chlorobicyclo*[2.2.1]*hept-2-en-7-yl*)(*ethoxycarbonyl*)*methyl*})*palladium*(II)]. Diene (L; R = CO·OEt) (208 mg) in CH$_2$Cl$_2$ (5 cm^3) was added to a solution of complex (I; X = Cl) (400 mg) in CH$_2$Cl$_2$ (5 cm^3). The resulting solution was stirred for 10 min and diethyl ether and hexane were added to precipitate the product. The white *powder* was filtered off, washed with ether, and dried; yield 350 mg (93%), m.p. 175—180 °C (decomp.) (Found: C, 37·0; H, 4·30; Pd, 29·7. Calc. for $C_{22}H_{28}Cl_4O_4Pd_2$: C, 37·1; H, 3·95; Pd, 29·8%). The molecular weight in CHCl$_3$ was 735 (calc. 710).

Di-μ-chloro-bis[(2—3-η-{(7-*chlorobicyclo*[2.2.1]*hept-2-en-7-yl*)(*methoxycarbonyl*)*methyl*})*palladium*(II)]. Diene (L; R = CO·OMe) (220 mg) was added to complex (I; X = Cl) (440 mg) in CHCl$_3$ (2 cm^3). The resulting solution was stirred for 5 min and the product was precipitated by the addition of diethyl ether and pentane. The pale yellow *solid* was filtered off, washed with diethyl ether, and dried; yield 322 mg (95%), m.p. 218—224 °C (decomp.) (Found: C, 35·6; H, 3·50; Pd, 31·25. Calc. for $C_{20}H_{24}Cl_4O_4Pd_2$: C, 35·15; H, 3·55; Pd, 31·15%). The molecular weight in benzene was 692 (calc. 638).

Di-μ-chloro-bis[(2—3-η-{(7-*methoxybicyclo*[2.2.1]*hept-2-en-7-yl*)(*methoxycarbonyl*)*methyl*})*palladium*(II)]. Complex (II; R = CO·OEt, X = Y = Cl) (280 mg) was dissolved in 25 cm^3 of methanol–benzene (1 : 1). The solution was heated under reflux for 2 d, concentrated, and diethyl ether was added to precipitate the product. The pale yellow *solid* was filtered off, washed with diethyl ether, and dried; yield 239 mg (87%), m.p. 190—195 °C (decomp.) (Found: C, 39·45; H, 4·65; Pd, 31·4. Calc. for $C_{22}H_{30}Cl_4O_6Pd_2$: C, 39·2; H, 4·45; Pd, 31·6%). The molecular weight in CHCl$_3$ was 684 (calc. 674).

Di-μ-chloro-bis[(2—3-η-{(*ethoxycarbonyl*)(7-*methoxybicyclo*[2.2.1]*hept-2-en-7-yl*)*methyl*})*palladium*(II)]. Complex (I; X = Cl) (1·65 g) was added to a solution of MeOH (20 cm^3), CHCl$_3$ (5 cm^3), and (L; R = CO·OEt) (900 mg). The resulting solution was stirred for 3 min, then concentrated, and the flocculent yellow *product* was precipitated by addition of diethyl ether and pentane; yield 1·40 g (93%), m.p. 187—192 °C (decomp.) (Found: C, 41·2; H, 4·80. Calc. for $C_{24}H_{24}Cl_2O_6Pd_2$: C, 41·05; H, 4·85%). The molecular weight in benzene was 703 (calc. 701).

Di-μ-bromo-bis[(2—3-η-{(7-*bromobicyclo*[2.2.1]*hept-2-en-7-*

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* *Added at proof:* W. T. Wipke and G. L. Goeke (*J. Amer. Chem. Soc.*, 1974, **96**, 4244) have recently reported on the *trans*-chloropalladation of 5-vinylbicyclo[2.2.1]hept-2-ene in benzene.

† For details see Notice to Authors No. 7, *J.C.S. Dalton*, 1973, Index issue (items less than 10 pp. are supplied as full-size copies).

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yl)methyl})palladium(II)]. Complex (I; X = Br) (40 mg) was added to a solution of diene (L; R = H) (10·5 mg) in $CHCl_3$ (2 cm^3). A pale brown solid precipitated, was filtered off, washed with diethyl ether, and dried; yield 21 mg (67%), m.p. 180—185 °C (decomp.).

Di-μ-bromo-bis[(2—3-η-{(7-*bromobicyclo*[2.2.1]*hept*-2-*en*-7-*yl*)(*ethoxycarbonyl*)*methyl*})*palladium*(II)]. Complex (I; X = Br) (450 mg) was added over 5 min to a rapidly stirred solution of diene (L; R = CO·OEt) (505 mg) in CH_2Cl_2 (5 cm^3). The resulting solution was stirred for 30 min and diethyl ether and pentane were added to precipitate the product. The pale brown *solid* was filtered off, washed with diethyl ether, and dried; yield 310 mg (73%), m.p. 155—157 °C (decomp.) (Found: Pd, 23·8. Calc. for $C_{22}H_{28}Br_4O_4Pd_2$: Pd, 23·95%). The molecular weight in $CHCl_3$ was 860 (calc. 888).

7-*Methoxy*-7-(*methoxycarbonyl*)*methylbicyclo*[2.2.1]*hept*-2-*ene*. Complex (II; R = CO·OMe, X = OMe, Y = Cl) (150 mg) was treated with 1 cm^3 of a saturated solution of NaCN in H_2O. The resulting aqueous solution was extracted with CCl_4 (3 × 2 cm^3) and the extracts were dried with $MgSO_4$. The drying agent was filtered off and the CCl_4 was evaporated. The product was purified by g.l.c. [column (*ii*)] yield 60 mg (82%) (Found: C, 67·9; H, 8·05. Calc. for $C_{11}H_{16}O_3$: C, 67·3; H, 8·2%). ^1H N.m.r. spectrum in $CDCl_3$: 0·95 (2H, m); 1·89 (2H, m); 2·75 (2H, s); 2·77 (2H, m); 3·18 (3H, s); 3·60 (3H, s); and 5·98 p.p.m. (2H, t).

7-(*Ethoxycarbonyl*)*methyl*-7-*methoxybicyclo*[2.2.1]*hept*-2-*ene*.—Compound (IV) (100 mg) was treated as above, yield 52 mg (87%) (Found: C, 68·35; H, 8·70. Calc. for $C_{12}H_{18}O_3$: C, 68·55; H, 8·55%). ^1H N.m.r. spectrum in $CDCl_3$: 0·95 (2H, m); 1·28 (3H, t); 1·92 (2H, m); 2·72 (2H, s); 2·83 (2H, m); 3·24 (3H, s); 4·15 (2H, q); and 6·07 p.p.m. (2H, t).

Reaction of Diene (L; R = CO·OEt) *with Complex* (I; X = Cl) *at Reduced Temperature*.—An n.m.r. tube containing a 0·075M-solution of complex (I) in $CDCl_3$ was thermostatted at −45 °C in the probe of a Varian A-60D n.m.r. spectrometer.* An equimolar quantity of the diene, which had been cooled to −78 °C, was added to the sample tube using a microlitre syringe. The ^1H n.m.r. spectrum of the mixture was recorded at 5 min intervals for 2·5 h. Over this period, the resonances associated with the diene gradually diminished and those corresponding to complex (II; R = CO·OEt, X = Y = Cl) gradually appeared. At the end of 2·5 h, half the diene had been consumed. During the time studied, all observed resonances were assignable to either the diene, complex (II), or phenyl cyanide.

Attempted Reaction of Compound (IV) *with* (I; X = Cl).—A 0·6M-solution of olefin and complex in C_6D_6–$CDCl_3$ (1 : 2) was allowed to stand for 48 h at room temperature during which time its n.m.r. spectrum was recorded frequently. The spectra showed only unco-ordinated olefin at all times. After 48 h at room temperature, the solution was warmed to 60 °C for an additional 5 h. The spectrum still showed only free olefin. Diethyl ether and pentane were then added and a solid precipitated. This was found to be exclusively complex (I).

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* 1M = 1 mol dm^{-3}.