Variations in Yields of Di-μ-halogen-bis-[(*trihapto*-cycloalkenyl)palladium(II)] with Ring Size. An Attempted Correlation with the Relative Ease of Hydrogenation of Cyclic Olefins

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The yields for the preparation of a series of di-μ-bromo-bis-(*trihapto*-cycloalkenyl)palladium(II) compounds increase in the sequence $C_9 < C_8 < C_6 < C_7$. In competitive reactions the reactivity of a series of 3-bromoalkenes with solutions containing palladium(II) increases in the order $C_8 < C_6 < C_7$. These results parallel the relative ease of hydrogenation of cyclic olefins. The unusual n.m.r. spectrum of di-μ-halogenobis-[(*trihapto*-cycloheptenyl)palladium(II)] is discussed.

THE relative yields of di-μ-bromo-bis-[(*trihapto*-cycloalkenyl)palladium(II)] compounds (2; X = Br) from reaction of a series of 3-bromocycloalkenes (1; X = Br) with solutions of palladium(II) chloride and sodium chloride in methanol through which carbon monoxide had been passed, increased in the ring size sequence $9 < 8 < 6 < 7$. The preparative procedure based on that described by Dent, Long, and Wilkinson [1] gave significant yields of cyclic π-allylic metal compounds, whereas procedures based on reactions of the appropriate cyclic olefins gave negligible yields. The π-allylic metal compounds from 3-bromocyclohexene and 3-bromocyclo-octene were only formed after the initially precipitated π-allylcarbonyl complexes [1] had been allowed to stand for several hours. Only 3-chlorocycloheptene gave a significant yield of the corresponding chloro π-allylic palladium compounds (2; X = Cl).

Competitive reactions of equimolar amounts of two cycloalkenyl bromides for a deficiency of palladium compound were carried out. In each case only one π-allylpalladium compound was isolated and the reactivity sequence was cycloheptenyl > cyclohexenyl > cyclo-octenyl. It is difficult to draw mechanistic conclusions from such a complicated reaction but it is interesting that the apparent kinetic preference for the formation of π-cycloalkenyl palladium compounds, *i.e.* $C_7 > C_6 > C_8$, is paralleled in the competitive hydrogenation of C_6, C_7, and C_8 cycloalkenes both using homogeneous transition-metal catalysts [2] and heterogeneous palladium metal systems.[3] The common factor in all these systems is probably the initial formation of olefin–metal π-bonds.

The n.m.r. spectra of the π-cycloalkenyl palladium compounds are summarised in the Table. The central proton (2-H) in the π-allyl residue is seen to be at higher field than the two 'outer' protons (1- and 3-H) in the cycloheptenylbromopalladium compound (2; $n = 7$, X = Br) in contrast to the other spectra recorded here and elsewhere. An X-ray structural analysis of this compound showed abnormal features relative to the structures of other π-allylmetal compounds.[4] These features may be associated with crystal packing forces but the n.m.r. data suggest that similar unusual preferred conformations may exist in solution. The 1- and 3-H signals in the cyclo-octenyl compound (2; X = Br, $n = 8$) appeared as a quartet ($J = 8$ Hz) thus showing equal coupling with the 2-H proton and both of the methylene protons on the adjacent carbon atom. This was con-

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[1] W. T. Dent, R. Long, and A. J. Wilkinson, *J. Chem. Soc.*, 1964, 1585.

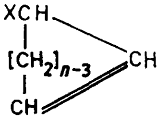
[2] J. P. Candlin and A. R. Oldham, *Discuss. Faraday Soc.*, 1968, **46**, 60.

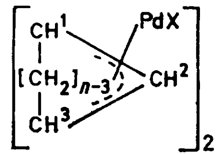
[3] H. A. Quinn, J. H. Graham, and J. J. Rooney, unpublished results.

[4] B. T. Kilbourn, R. H. B. Mais, and P. G. Owston, *Chem. Comm.*, 1968, 1438.

TABLE

N.m.r. spectra of di-μ-halogeno-bis-[(*trihapto*-cycloalkenyl)-palladium(II)] compounds


(1)


(2)

(2, n =)	(2; X =)	τ 1-, 3-H	τ 2-H	$J_{1,2}$/Hz
6	Cl	4·80m	4·45t	7
	Lit. values [a]	4·75m	4·56m	
6	Br	4·80m	4·60t	7
7	Cl	5·09m	5·03t	3
	Lit. values [a]	4·8—5·30m		
7	Br	4·96m	5·20t	8
8	Br	5·14q	4·71t	8
				($J_{3,4}$ = 8 Hz)

[a] From R. Huttel, H. Dietl, and H. Christ, *Chem. Ber.*, 1964, **97**, 2037; H. C. Volger, *Rec. Trav. chim.*, 1969, **88**, 225.

firmed by a decoupling experiment in which it was necessary to irradiate over a frequency range covering both the *cis*- and *trans*-methylene proton absorptions before the 1- and 3-H signal collapsed to a doublet ($J_{1,2}$ 8 Hz). These results suggested a large degree of conformational mobility in the compound which was in accord with inspection of molecular models and with a variable temperature n.m.r. study in which the 2-H absorption was shown to move to lower field on cooling.

EXPERIMENTAL

M.p.s were determined using a Kofler hot stage. N.m.r. spectra were recorded by Mr. R. Spratt for $CDCl_3$ solutions with tetramethylsilane as internal standard using a Varian HA100 spectrometer.

Cyclo-olefins.—Cyclononene was obtained by controlled hydrogenation of cyclonona-1,2-diene prepared from cyclo-octene by the method of Untch *et al.*[5] Commercial samples of the other cyclo-olefins were distilled under nitrogen immediately before use.

3-*Chlorocycloalkenes*.—t-Butyl hypochlorite was prepared by the method of Teeter and Bell[6] and allowed to react with the cycloalkenes[7] to give: 3-chlorocyclohexene, b.p. 38—42° at 20 mmHg, n_D^{20} 1·4870 (lit.,[8] 139—141° at 760 mmHg, n_D^{20} 1·4866); 3-chlorocycloheptene, b.p. 47—48° at 11 mmHg, n_D^{20} 1·4961 (Found: C, 64·2; H, 8·3; Cl, 27·4. $C_7H_{11}Cl$ requires C, 64·4; H, 8·4; Cl, 27·2%).

3-*Bromocycloalkenes*.—The cycloalkenes were treated with *N*-bromosuccinimide and the following bromoalkenes were obtained: 3-bromocyclohexene, b.p. 74° at 28 mmHg, n_D^{20} 1·5231 (lit.,[8] b.p. 80° at 35 mmHg, n_D^{20} 1·5230); 3-bromocycloheptene, b.p. 74° at 14 mmHg, n_D^{20} 1·5306 (lit.,[9] b.p. 67° at 8 mmHg, n_D^{22} 1·5281); 3-bromocyclo-octene, b.p. 95° at 14 mmHg, n_D^{20} 1·5211 (lit.,[10] b.p. 78° at 5 mmHg, n_D^{25} 1·5230); 3-bromocyclononene, b.p. 78—82° at 1 mmHg, n_D^{20} 1·5302.

Reactions of 3-*Halogenocycloalkenes with Palladium Carbonyl Halides*.—Carbon monoxide was passed through a mixture of sodium chloride (0·118 g, 2 mmol) and palladium chloride (0·178 g, 1 mmol) in methanol (3 ml) until the solution became pale yellow (1—1·5 h). An excess of 3-halogenocycloalkene (10 mmol) in methanol (1 ml) was added. A precipitate usually formed within 2 min and was worked up as follows. (i) 3-*Bromocyclohexene*. The initial precipitate was similar to the insoluble materials reported by Dent *et al.*[1] showing i.r. absorption at 1950 cm^{-1}. The precipitate was allowed to stand in contact with the reactants for 0·5 h and diminished in size. The solid was then filtered off washed with methanol, and dried. Attempted recrystallisation led to extensive decomposition, but the solid filtered off analysed correctly for *di-μ-bromo-bis-*[1,2,3-trihapto-*cyclohexenylpalladium*(II)] (2; X = Br, n = 6) (0·130 g 50%), m.p. 130° (dec.) (Found: C, 27·7; H, 3·6; Br, 31·1. C_6H_9BrPd requires C, 26·9; H, 3·4; Br, 29·8%). The filtrate was poured into water and extracted with chloroform, but no more product was obtained on evaporation of the extract.

(ii) 3-*Bromocycloheptene*. Similar reaction of 3-bromocycloheptene gave an immediate precipitate of *di-μ-bromo-bis-*[1,2,3-trihapto-*cycloheptenylpalladium*(II)] (2; X = Br, n = 7) (0·195 g, 70%), m.p. 160—162° (dec.) after crystallisation from ether–chloroform (Found: C, 30·3; H, 4·2. $C_7H_{11}BrPd$ requires C, 29·9; H, 3·9%). The filtrate was poured into water and extracted with chloroform. The extract gave a further small amount (0·01 g, 4%) of the π-allylpalladium compound.

(iii) 3-*Chlorocycloheptene*. The precipitate was filtered off and after recrystallisation from ether–chloroform gave *di-μ-chloro-bis-*[1,2,3-trihapto-*cycloheptenylpalladium*(II)] (0·060 g, 25%) (2; X = Cl, n = 7), m.p. 160° (dec.) [lit.,[11] 137—141° (dec.)] (Found: C, 35·8; H, 4·9; Cl, 15·7. Calc. for $C_7H_{11}ClPd$: C, 35·5; H, 4·7; Cl, 15·0%).

3-*Bromocyclo-octene*.—The initial precipitate showed i.r. absorptions at 1950 cm^{-1} but after standing in contact with the reaction solution for 8 h a small yield (0·060 g, 20%) of *di-μ-bromo-bis-*[1,2,3-trihapto-*cyclo-octenylpalladium*(II)] (2; X = Br, n = 8) was filtered off, m.p. 170° (dec.) (Found: C, 32·8; H, 4·5. $C_8H_{13}BrPd$ requires C, 32·5; H, 4·4%).

3-*Bromocyclononene*.—No initial precipitate was observed but after 0·5 h extensive decomposition occurred to give palladium metal and tarry products.

Di-μ-chloro-bis-[1,2,3-trihapto-*cyclohexenylpalladium*(II)] (2; n = 6, X = Cl), m.p. 85—90° (dec.) was prepared by the method of Shaw[12] who quotes m.p. 80—83° (dec.).

Competitive Reactions.—Equimolar mixtures of 3-bromocycloalkenes (1 mmol each) in methanol (1 ml) were added to the palladium carbonyl halide solution prepared by mixing sodium chloride (0·118 g, 2 mmol) and palladium chloride (0·178 g, 1 mmol) in methanol (1 ml) and passing carbon monoxide as previously described. The solid precipitated was compared (i.r. and n.m.r.) with authentic samples of the possible products. (i) 3-Bromocycloheptene and 3-bromocyclohexene gave (2; n = 7, X = Br) (0·190 g, 70%). (ii) 3-Bromocycloheptene and 3-bromocyclo-octene gave (2; n = 7, X = Br) (0·130 g, 50%). (iii) 3-Bromocyclohexene and 3-bromocyclo-octene gave (2; n = 6, X = Br) (0·130 g, 50%).

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