452. π-*Complexes of Biphenylene.*

By J. Chatt, R. G. Guy, and H. R. Watson.

Biphenylene readily forms co-ordination compounds using one or both of its six-membered rings, but not its four-membered ring.

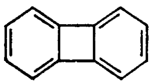
Biphenylene can be written with five Kekulé structures of which one represents it as a cyclobutane derivative (I), two as a cyclobutadiene derivative, and the remaining two as a cyclobutene derivative. In might therefore be expected to form co-ordination compounds by using either of its six-, or its four-membered ring. We have attempted to obtain both types of complex but succeeded in getting only the benzene type.

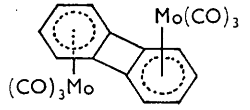
When biphenylene is heated at 130° for 4 hr. with tricarbonyldiglymemolybdenum (4 mols.) [diglyme = $O(CH_2{\cdot}CH_2{\cdot}OMe)_2$] it readily forms scarlet μ-biphenylenebis(tricarbonylmolybdenum) (II). The *trans*-arrangement is implied from the molecular centre of symmetry shown by the *X*-ray crystal data. This substance is stable in air and only sparingly soluble in hot organic solvents, giving solutions which rapidly decompose. Equimolecular proportions of the above reactants, heated at 100° for 6½ hr., form orange tricarbonylbiphenylenemolybdenum, $[C_{12}H_8Mo(CO)_3]$, soluble in organic solvents.

Its solutions slowly deposit molybdenum. The biphenylene can be recovered from both products by reaction with 1,2-bis(diphenylphosphino)ethane:

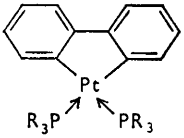
$$[C_{12}H_8\{Mo(CO)_3\}_n] + 2nC_2H_4(PPh_2)_2 \longrightarrow C_{12}H_8 + n[Mo(CO)_2\{C_2H_4(PPh_2)_2\}_2] + nCO$$
$$(n = 1 \text{ or } 2)$$

To see whether the 4-membered ring of biphenylene has sufficient cyclobutadienoid character to react with compounds of metals near the end of the transition series to form such complexes as $[Fe(CO)_3(\text{biphenylene})]$, $[Ni(CO)_2(\text{biphenylene})]$, $[Ni(\text{biphenylene})_2]$, or $[Pt(\text{biphenylene})(PR_3)_2]$ we treated biphenylene with compounds of iron, nickel, and platinum.[1] The iron compound, if it had been obtained, would have been exactly analogous to $[Fe(CO)_3(\text{tetraphenylcyclobutadiene})]$.[2]


(I)



(II)



(III)

No complex was detected on treating biphenylene with (*a*) $Fe(CO)_5$, (*b*) $Ni(CO)_4$, (*c*) $[Ni(CO)_3(PPh_3)]$, or (*d*) nickelocene, $Ni(C_5H_5)_2$, under the conditions given in the Table. However, when biphenylene was treated with $[Ni(CO)_2(PPh_3)_2]$ in a sealed tube at 100°, it gave a small yield of tetraphenylene (1,2:3,4:5,6:7,8-tetrabenzocyclo-octatetraene). This dimerisation may have proceeded through the formation of a biphenylene complex, since it has been suggested[3] that a nickel complex of cyclobutadiene is involved in the analogous formation of cyclo-octatetraene from acetylene.

Attempts to obtain platinum complexes were equally unsuccessful. Biphenylene did not react with *cis*-$[PtCl_2(PPh_3)_2]$ and hydrazine[4] to form a complex of the type $[Pt(\text{biphenylene})(PR_3)_2]$. Attempts to prepare this type of complex from *cis*-$[PtCl_2(PR_3)_2]$ and 2,2′-dilithiobiphenyl or related Grignard reagents (prepared from 2,2′-di-iodobiphenyl) gave products of the type *trans*-$[PtIR'(PR_3)_2]$,[5] where R′ is 2-biphenylyl or 2,2′-iodobiphenylyl. It is interesting that the heterocyclic compound (III) was not obtained.

Reactions of biphenylene with iron, nickel, and platinum complexes.

Reagent			
Formula	Mol.	Conditions *	Substances isolated
$Fe(CO)_5$	5	Benzene soln./80°/250 w u.v. light/20 hr.	Biphenylene
$Ni(CO)_4$	2	Petrol soln./40°/3 hr.	Biphenylene
,,	4	Sealed tube/140°/12 hr.	,,
$Ni(CO)_3(PPh_3)$	1	100°/1 hr. or 16 hr.	Biphenylene, $[Ni(CO)_2(PPh_3)_2]$
$Ni(CO)_2(PPh_3)_2$	1	Benzene soln. in sealed tube/100°/1 hr.	Biphenylene
,,	1	Benzene soln. in sealed tube/100°/7 hr.	Tetraphenylene
$Ni(C_5H_5)_2$	1	Petrol soln./20°/5 days	Biphenylene
,,	0·5	,, ,,	,,
,,	0·5	,, 80°/21 hr.	,,
,,	4	150—160°/1·5 hr.	Biphenylene; & black solid †
cis-$[PtCl_2(PPh_3)_2]$ and N_2H_4,H_2O	0·5	Ethanol soln. at 20°	Biphenylene

* All under nitrogen. † This solid, m. p. 350°, appears to be polymerised nickelocene [Found: C, 64·0; H, 5·05. Calc. for $(C_{10}H_{10}Ni)_n$: C, 63·6; H, 5·35%].

The capacity of biphenylene to form co-ordination compounds using each six-membered ring independently, but not the four-membered ring system, is consistent with the preferred

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[1] For a preliminary account of this work see *Chem. Soc. Special Publ.* No. 12, 1958, p. 65.

[2] Dodge and Schomaker, *Nature*, 1960, **186**, 798.

[3] Longuet-Higgins and Orgel, *J.*, 1956, 1969.

[4] Cf. Chatt, Rowe, and Williams, *Proc. Chem. Soc.*, 1957, **208**.

[5] Cf. Chatt and Shaw, *J.*, 1959, 4020.

bond structure (I),[6] in which there is little or no cyclobutadienoid character in the 4-membered ring.

EXPERIMENTAL

M. p.s were determined on a Kofler hot-stage and are corrected, except those marked with an asterisk which were taken in a nitrogen-filled tube.

Biphenylene was prepared by the method of Baker, Boarland, and McOmie,[7] and had m. p. 112—113°.

The following experiments were carried out under nitrogen.

μ-Biphenylenebis(tricarbonylmolybdenum).—Biphenylene (0·152 g.) and diglymemolybdenum tricarbonyl [8] (0·628 g.) were heated together at 130° for 4 hr.; molybdenum carbonyl sublimed from the fused red mass. The cooled mass was crushed coarsely and extracted with boiling " AnalaR " chloroform (5 × 5 ml.), the hot chloroform then being decanted. This operation removed all the finely divided molybdenum, and there remained the *bis(tricarbonyl)*, m. p.* 204° with prior shrinking and loss of colour at 195° [Found: C, 41·8; H, 1·75; Mo, 37·5%; *M* (by *X*-ray method, density by flotation), 510 ± 5. $C_{18}H_8Mo_2O_6$ requires C, 42·2; H, 1·6; Mo, 37·5%; *M*, 512·2]. Crystal data: monoclinic $2/m$, $a = 10{\cdot}03 \pm 0{\cdot}05$, $b = 11{\cdot}52 \pm 0{\cdot}06$, $c = 7{\cdot}41 \pm 0{\cdot}03$ Å, $\beta \approx 90{\cdot}0°$, $U = 856{\cdot}2$ Å^3, $D_M = 1{\cdot}980 \pm 0{\cdot}005$, $ZM = 1021 \pm 10$, $Z = 2$, $D_O = 1{\cdot}974$, space group $P2_1/c$ (C_{2h}^5, No. 14), molecular symmetry $\bar{1}$. The infrared spectrum has carbonyl stretching bands at 1961 ± 2vs broad, 1942vs, 1923vs, and 1887 ± 2vs broad cm.$^{-1}$. The spectrum due to biphenylene is considerably altered; in particular the broad complex band centred on 734 cm.$^{-1}$ is missing.

A mixture of the bistricarbonyl (0·050 g.) and an excess of 1,2-bis(diphenylphosphino)ethane was heated rapidly from 60° to 140° at 0·05 mm. Biphenylene (0·012 g., 81%) sublimed, and *cis*-dicarbonyldi-1,2-bis(diphenylphosphino)ethanemolybdenum [9] (about 0·005 g.) was extracted from the black residue with acetone.

Biphenylenetricarbonylmolybdenum.—Biphenylene (0·235 g.) and diglymemolybdenum tricarbonyl (0·486 g.) were heated together at 100—103° for 6½ hr. The resulting red-brown mass crystallised from light petroleum (40—60°) to give the *tricarbonyl* (0·111 g., 21·5%), orange needles, m. p.* 163—185° (decomp.) (Found: C, 54·35; H, 2·55%; *M*, ebullioscopic in chloroform, 330. $C_{15}H_8O_3Mo$ requires C, 54·2; H, 2·4%; *M*, 332). The infrared spectrum has carbonyl stretching bands at 1967vs and 1878vs broad cm.$^{-1}$. The portion of the spectrum due to biphenylene is simpler than in the hydrocarbon; the broad band centred on 734 cm.$^{-1}$ is replaced by a sharp band at 752s cm.$^{-1}$. When heated with an excess of 1,2-bis(diphenylphosphino)ethane the compound (0·010 g.) gave biphenylene (0·0030 g.).

Reaction of Biphenylene with $[Ni(CO)_2(PPh_3)_2]$.—Biphenylene (0·10 g., 1 mol.), $[Ni(CO)_2(PPh_3)_2]$ (0·42 g., 1 mol.), and benzene (1·0 ml.) were heated in an atmosphere of nitrogen at 100° in a sealed tube. The clear yellow solution became brown after 3 hr., and was heated for a further 4 hr. After evaporation of the solvent, the yellow-green solid (0·52 g.) was treated with ethanol. The insoluble material was unchanged $[Ni(CO)_2(PPh_3)_2]$ (0·35 g.), m. p. and mixed m. p. 207—210° (decomp.). The ethanol-soluble portion was a sticky solid (0·16 g.); this was washed with light petroleum (b. p. 40—60°), and the residual light yellow solid (0·10 g.), on crystallisation from ethanol, gave 1,2:3,4:5,6:7,8-tetrabenzocyclo-octatetraene (tetraphenylene) as white prisms, m. p. 232—235° (Found: C, 94·9; H, 5·3. Calc. for $C_{24}H_{16}$: C, 94·7; H, 5·3%). Rapson, Shuttleworth, and van Niekerk [10] report m. p. 233°.

Reaction of 2,2′-Dilithiobiphenyl with cis-$[PtCl_2(PEt_3)_2]$.—The dilithio-compound was prepared under nitrogen in ether (25 ml.) from 2,2′-di-iodobiphenyl (1·02 g., 1 mol.) and lithium (0·09 g., 5 g.-atom).[11] A suspension of *cis*-$[PtCl_2(PEt_3)_2]$ (1·25 g., 1 mol.) in ether (10 ml.) was added and the mixture stirred at room temperature for 3 hr. The solution was filtered and evaporation of the filtrate yielded a brown solid which on recrystallisation from ethanol gave [*iodo-(2-biphenylyl)bis(triethylphosphine)platinum*(II)] (0·40 g.) as colourless plates, m. p. 190—195° (Found: C, 40·5; H, 5·55. $C_{24}H_{39}IP_2Pt$ requires C, 40·5; H, 5·5%). The dipole moment (3·0 ± 0·2 D) of this compound shows that it has the *trans*-configuration.[5,12]

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[6] Baker, McOmie, Preston, and Rogers, *J.*, 1960, 414.

[7] Baker, Boarland, and McOmie, *J.*, 1954, 1476.

[8] Werner and Coffield, *Chem. and Ind.*, 1960, 936.

[9] Chatt and Watson, unpublished result.

[10] Rapson, Shuttleworth, and van Niekerk, *J.*, 1943, 326.

[11] Wittig and Herwig, *Chem. Ber.*, 1954, **87**, 1511.

[12] Cf. Chatt and Shaw, *J.*, 1959, 705.

Reaction of the Mono-Grignard Reagent of 2,2′-Di-iodobiphenyl with cis-[PtCl$_2$(PEt$_3$)$_2$].—Magnesium (0·12 g., 2 mol.) in ether (30 ml.) was treated with 2,2′-di-iodobiphenyl (1·02 g., 1 mol.), and the mixture heated under reflux in an atmosphere of nitrogen for 6 hr.[10] *cis*-[PtCl$_2$(PEt$_3$)$_2$] (1·25 g., 1 mol.), suspended in ether (20 ml.), was added and the mixture stirred overnight at room temperature. Dilute hydrochloric acid was then added slowly, with ice-cooling. The insoluble material (0·28 g.) was collected, and on recrystallisation from benzene afforded pale yellow prisms of trans-[*iodo-(2,2′-iodobiphenylyl)bis(triethylphosphine)platinum*(II)], m. p. 270—275° (Found: C, 34·4; H, 4·55. $C_{24}H_{38}I_2P_2Pt$ requires C, 34·4; H, 4·55%). The rather high dipole moment (5·3 ± 0·1 D) indicates that some of the *cis*-isomer may be present. The residue from evaporation of the dried (MgSO$_4$) ether layer afforded *trans*-[PtI$_2$(PEt$_3$)$_2$], m. p. and mixed m. p. 136—137°.

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