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The Preparation and Characterization of Substituted Pentaphenylcyclopentadienyl Ligands, Their Precursors, and Complexes of Iron

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Abstract

The synthesis and characterization by infrared, ^1H and ^{13}C n.m.r. and mass spectroscopy of the compounds $C_5Ph_4(p\text{-}C_6H_4R)X$ (R = H, Me, Et, Bu^t; X = OH, Br, H), $C_5Ph_{4-n}(p\text{-}C_6H_4Me)_nO$ (n = 1, 2, 4), $C_5Ph_{5-n}(p\text{-}C_6H_4Me)_nX$ (n = 2, 3; X = OH, Br) and $C_5Ph_4(p\text{-}C_6H_4R)Fe(CO)_2Br$ (R = H, Me, Et, Bu^t) are described.

Introduction

The study of complexes of the cyclopentadienyl ligand and its substituted analogues has been a major theme in organometallic chemistry since the discovery of ferrocene some 40 years ago.[1,2] Ring-substituted cyclopentadienyl ligands have received considerable attention in the search for compounds with different stabilities, solubilities, steric or electronic properties or reactivity patterns. In particular, the $C_5Me_5^-$ ligand[3] has found extensive application because of its electron-donating and steric properties, and its lack of α-hydrogen atoms.

By contrast, complexes of the pentaphenylcyclopentadienyl ligand have received surprisingly little attention, although the ligand precursors were first reported in 1925,[4] and the first transition metal complexes in 1965.[5] The $C_5Ph_5^-$ ligand appears to be more electron withdrawing than the $C_5H_5^-$ ligand, and its large volume is reported to confer enhanced kinetic stability to organometallic derivatives.[6] Certainly, isolated examples of complexes of the $C_5Ph_5^-$ ligand exhibiting dramatic structural and electronic differences from their $C_5H_5^-$ and $C_5Me_5^-$ analogues have already been described.[7,8]

The low solubility of many of the complexes of $C_5Ph_5^-$ has been a significant impediment to the development of the chemistry of this ligand. However, the

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[2] Miller, S. A., Tebboth, T. A., and Tremaine, J. F., *J. Chem. Soc.*, 1952, 632.
[3] Threlkel, R. S., and Bercaw, J. E., *J. Organomet. Chem.*, 1971, **136**, 1.
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[7] Heeg, M. J., Janiak, C., and Zuckerman, J. J., *J. Am. Chem. Soc.*, 1984, **106**, 4259.
[8] Schott, A., Schott, H., Wilke, G., Brandt, J., Hoberg, H., and Hoffman, E. G., *Justus Liebigs Ann. Chem.*, 1972, 508.

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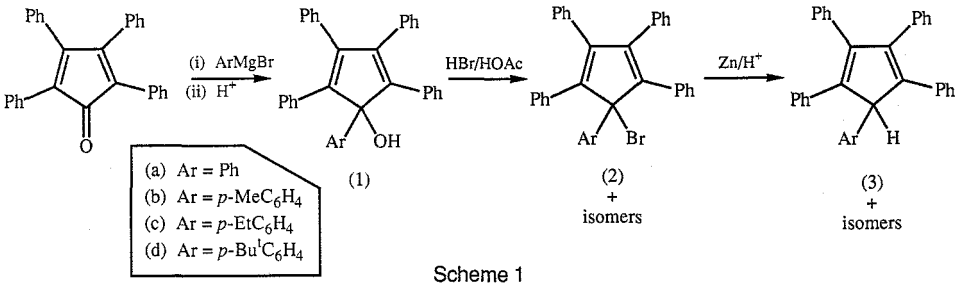
pentaphenylcyclopentadienyl ligand system offers the potential to introduce readily substituents on the phenyl rings so as to modify the steric and electronic properties of organometallic derivatives as well as solubilizing the metal complexes.

We have examined a range of new phenyl-substituted pentaphenylcyclopentadienyl ligands, and report here the syntheses and characterization of their precursors and selected metal complexes. We have recently reported the structural characterization of $Fe(C_5Ph_5)(CO)_2Br$, the first structurally characterized iron derivative of the $C_5Ph_5^-$ ligand.[9]

Synthesis of 1,2,3,4,5-Pentaarylcyclopentadienes and Complexes

(a) Pentaphenylcyclopentadiene

The preparation of the ligands was based on the procedure of Ziegler and Schnell.[4] This involves the reaction of an aryl Grignard reagent with an appropriately substituted tetracyclone to produce the pentaarylcyclopentadien-1-ol (1) which can be converted into the corresponding pentaarylcyclopentadiene (3) via the 1-bromopentaarylcyclopentadiene (2) (Scheme 1).



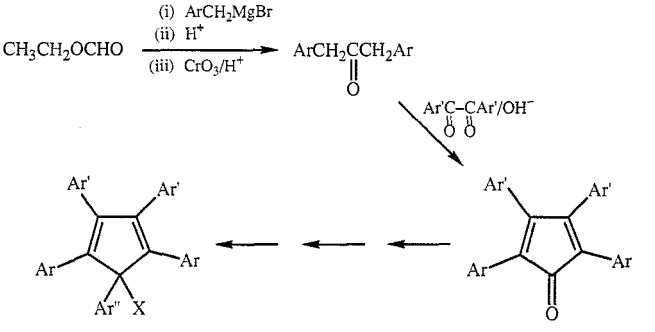
Scheme 1

This route has been employed previously by Heeg *et al.*,[7] Chambers *et al.*,[10] Schumann *et al.*[11] and Slocum[12] in the synthesis of pentaphenylcyclopentadiene (3a) and 4-(t-butylphenyl)tetraphenylcyclopentadiene (3d). Conversion of the pentaarylcyclopentadien-1-ols into the corresponding 1-bromopentaarylcyclopentadienes can be effected with HBr in glacial acetic acid. Isolation of the intermediate 1-bromopentaarylcyclopentadiene is not necessary, as the pentaarylcyclopentadiene can be produced from the pentaarylcyclopentadien-1-ol in a single step by reduction of the alcohol in glacial acetic acid with H_3PO_2/HI, zinc/HBr or zinc/HCl, although the preparation using hypophosphorous acid generally resulted in higher yields. The 1-bromopentaarylcyclopentadienes are, however, ligand precursors of considerable synthetic utility, and these have been routinely isolated in our work.

[9] Field, L. D., Hambley, T. W., Lindall, C. M., and Masters, A. F., *Polyhedron*, in press.
[10] Chambers, J. W., Baskar, A. J., Bott, S. G., Atwood, J. L., and Rausch, M. D., *Organometallics*, 1986, **5**, 1635.
[11] Schumann, H., Janiak, C., and Zuckermann, J. J., *Chem. Ber.*, 1988, **121**, 207.
[12] Slocum, D. W., Duraj, S., Matusz, M., Cmarik, J. L., Simpson, K. M., and Owen, D. A., in 'Metal Containing Polymeric Systems' (Eds J. E. Sheats, C. E. Carraher Jr and C. V. Pittman) (Plenum: New York 1985).

(b) 1-(p-Alkylphenyl)-2,3,4,5-tetraphenylcyclopenta-2,4-diene Derivatives

The route outlined in Scheme 1 can be readily extended for the synthesis of 1-(*p*-alkylphenyl)-2,3,4,5-tetraphenylcyclopenta-2,4-diene derivatives by reaction of 4-R-phenylmagnesium halides with tetracyclone. Using this approach, we have prepared a number of 1-(4′-R-phenyl)-2,3,4,5-tetraphenylcyclopenta-2,4-dien-1-ols and 1-bromo-1-(4′-R-phenyl)-2,3,4,5-tetraphenylcyclopenta-2,4-dienes (R = H, Me, Et and Bu^t). These derivatives are white or yellow crystalline materials, generally with significantly higher solubilities than the parent derivatives (R = H). All of the 1-bromo-1-(4′-R-phenyl)-2,3,4,5-tetraphenylcyclopenta-2,4-dienes and 1-(4′-R-phenyl)-2,3,4,5-tetraphenylcyclopenta-2,4-dienes (R ≠ H) were obtained as constituents of mixtures of isomers, consistent with the formation of a delocalized cationic intermediate in the reaction of the alcohol with HBr. The formation of pentaarylcyclopentadienyl carbocations from the corresponding alcohols under acidic conditions has been studied in depth,[13] and mixtures of isomeric products have been reported on quenching of unsymmetrical pentaarylcyclopentadienyl cations. The presence of isomers in the bromo derivatives (2b–d) is apparent from their n.m.r. spectra; the ^{1}H n.m.r. spectrum of 1-bromotetraphenyl(*p*-tolyl)cyclopenta-2,4-diene (2b) shows three methyl resonances in approximately the statistical ratio 1 : 2 : 2. For the range of *p*-alkyl substituents examined, approximate statistical isomer distributions were obtained. The presence of the isomers does not affect the subsequent reaction chemistry and ligand formation, and no attempt at separation was made.



	Ar	Ar′	Ar″	X
(5a)	Ph	*p*-MeC$_6$H$_4$	Ph	OH
(5b)	Ph	*p*-MeC$_6$H$_4$	*p*-MeC$_6$H$_4$	OH
(6a)	Ph	*p*-MeC$_6$H$_4$	Ph	Br
(6b)	Ph	*p*-MeC$_6$H$_4$	*p*-MeC$_6$H$_4$	Br

	Ar	Ar′
(4a)	*p*-MeC$_6$H$_4$	*p*-MeC$_6$H$_4$
(4b)	Ph	*p*-MeC$_6$H$_4$

Scheme 2

(c) Pentaarylcyclopentadienes with Substituents on More than One Phenyl Ring

Cyclopentadienes substituted with different groups at positions 2, 3, 4 and 5 can be synthesized by initial formation of the appropriate aryl-substituted tetracyclones (4). A most convenient route to tetracyclones is by base-catalysed

[13] For example: Saunders, M., Berger, R., Jaffe, A., McBride, J. M., O'Neill, J., Breslow, R., Hoffman, J. M., Jr, Perchonock, C., Wasserman, E., Hutton, R. S., and Kuck, V. J., *J. Am. Chem. Soc.*, 1973, **95**, 3017; Breslow, R., Chang, H. W., Hill, R., and Wasserman, E., *J. Am. Chem. Soc.*, 1967, **89**, 1112, and references therein.

condensation of disubstituted benzil and disubstituted 1,3-diphenylacetone in absolute alcohol.[14] The required diphenylacetone derivatives were prepared by chromic acid oxidations of the corresponding alcohols which were synthesized by condensation of a Grignard reagent, derived from an alkyl-substituted benzyl halide, with ethyl formate[15] (Scheme 2). Tetracyclones (4) formed in this way enter directly into the reaction sequence described in Scheme 1 to give (5) and (6). In the first instance, we have concentrated on the introduction of methyl substituents at the 4-position of the phenyl rings. However, the approach is general and clearly applicable to the introduction of various substituents and substitution patterns on the phenyl rings.

(d) Metal Complexes of Pentaarylcyclopentadienes

The 1-bromopentaarylcyclopenta-2,4-diene derivatives are useful precursors to substituted cyclopentadiene ligands since there are a number of approaches to the formation of metal complexes. They can react directly with low-valent transition metal species:

$$C_5Ar_5Br + M^{n+}L_n \rightarrow (\eta^5\text{-}C_5Ar_5)M^{n+2}L_{n-x}Br + xL$$

Alternatively they can be converted into the corresponding pentaarylcyclopenta-2,4-diene derivatives, which on deprotonation, react with metal salts:

$$C_5Ar_5Br \xrightarrow{Zn/H^+} C_5Ar_5H \xrightarrow{base} C_5Ar_5^- \xrightarrow{MXL_n} (\eta^5\text{-}C_5Ar_5)M^{n+2}L_{n-x} + X^- + xL$$

Low-valent metal complexes can also react with the radical generated by treatment of the substituted 1-bromopentaarylcyclopenta-2,4-diene with zinc:

$$2C_5Ar_5Br + Zn \longrightarrow 2C_5Ar_5^{\bullet} + ZnBr_2 \xrightarrow{ML_n} (C_5Ar_5)_2M + nL$$

The oxidative addition route is particularly useful, as a wide range of potential metal precursors with a variety of coligands is available. The oxidative additions of 1-bromopentaphenylcyclopenta-2,4-dienes to iron pentacarbonyl and dicobalt octacarbonyl serve to demonstrate the ligand chemistry of the substituted pentaphenylcyclopentadienyl ligands.

1-Bromo-1-(*p*-alkylphenyl)-2,3,4,5-tetraphenyl-2,4-cyclopentadienes (2a–d) react smoothly with iron pentacarbonyl or dicobalt octacarbonyl to give the expected substituted pentaarylcyclopentadienyl bromodicarbonyliron(II) or dicarbonylcobalt(I) derivatives in reasonable yields (Scheme 3).

$$C_5Ph_4(Ar)Br + Fe(CO)_5 \longrightarrow [\eta^5\text{-}C_5Ph_4(Ar)]Fe(CO)_2Br \quad (7)$$

$$C_5Ph_4(Ar)Br + {}^1/_2\,Co_2(CO)_8 \xrightarrow{Zn} [\eta^5\text{-}C_5Ph_4(Ar)]Co(CO)_2 \quad (8)$$

(a) Ar = Ph	(c) Ar = *p*-EtC_6H_4
(b) Ar = *p*-MeC_6H_4	(d) Ar = *p*-$Bu^tC_6H_4$

Scheme 3

[14] Furniss, B. S., Hannaford, A. J., Rogers, V., Smith, P. W. G., and Tatchell, A. R., 'Vogel's Textbook of Practical Organic Chemistry' 4th Edn (Longmans: New York 1978).
[15] Kharasch, M. S., and Reinmuth, O., 'Grignard Reactions of Nonmetallic Substances' (Prentice Hall: New York 1954).

We have recently reported the crystal structure of bromodicarbonyl(pentaphenylcyclopentadienyl)iron(II) (7a).[9] Other iron compounds in this series have been characterized by ^1H and ^{13}C n.m.r., infrared and mass spectroscopy. The reaction of C_5Ph_5Br with $Co_2(CO)_8$ in the presence of zinc dust has been reported[16] to yield $(\eta^5\text{-}C_5Ph_5)Co(CO)_2$ (8a). Preliminary studies[17] show that the compounds (8b–d), identified by their infrared spectra, can also be prepared as shown in Scheme 3. The introduction of substituents onto one of the phenyl rings does not markedly alter the spectroscopic properties of the metal complexes, but significantly improves their solubilities. Table 1 lists the carbonyl stretching frequencies of various iron derivatives.

Table 1. Infrared CO stretching frequencies (cm^{-1}) for $[C_5(p\text{-}R\text{-}C_6H_4)Ph_4]Fe(CO)_2Br$ complexes (7a–d)

Compound	R	KBr discs		CH_2Cl_2 solutions	
(7a)	H	2031·0	1987·6	2037·6	1996·3
(7b)	Me	2024·3	1980·0	2036·8	1994·4
(7c)	Et	2028·1	1986·7	2036·8	1994·4
(7d)	Bu^t	2033·0	1989·6	2036·8	1994·4

Conclusions

A variety of precursors of substituted pentaphenylcyclopentadienyl ligands can be prepared in high yields, the purity depending on the formation of isomers. Substituents can be introduced on any of the phenyl rings, and a range of multiply substituted pentaphenylcyclopentadienyl ligand precursors is available. The synthetic procedures are in principle appropriate for the syntheses of an extensive range of multiply substituted ligand precursors. Metal complexes of these ligands can be prepared either from the 1-bromopentaphenylcyclopenta-2,4-dienes by an oxidative addition route, or by deprotonation of the pentaphenylcyclopentadiene.

Experimental

All manipulations involving Grignard reagents and metal carbonyls were carried out under argon by using standard inert-atmosphere techniques.[18] Tetracyclone (Aldrich), iron pentacarbonyl (Aldrich) and 4,4′-dimethylbenzil (Aldrich) were used as received. All solvents were dried and distilled under nitrogen prior to use unless otherwise stated. Dioxan, benzene, tetrahydrofuran and diethyl ether were distilled from sodium benzophenone ketyl. Pentane, n-hexane, n-heptane, benzene, toluene, xylenes and 1,2-dimethoxyethane were distilled from sodium wire. Dichloromethane and acetone were distilled from phosphorus pentoxide. Acetic acid, acetic anhydride and ethanol were A.R. grade and were used as received. HBr was used as a 48% solution in acetic acid. *p*-Bromotoluene, *p*-bromoethylbenzene and *p*-bromo-t-butylbenzene were used as received. Melting points were recorded on a Kofler hot stage in air and are uncorrected.

60-Mz ^1H n.m.r. spectra were recorded on a Hitachi Perkin–Elmer R-24B high-resolution n.m.r. spectrometer. 400-MHz ^1H and 100-MHz ^{13}C n.m.r. spectra were recorded on a Bruker WM 400 n.m.r. spectrometer; 15-MHz ^{13}C n.m.r. spectra were recorded on a JEOL FX-60Q

[16] Broadley, K., Lane, G. A., Connelly, N. G., and Geiger, W. E., *J. Chem. Soc., Dalton Trans.*, 1986, 373.
[17] Lindall, C. M., B.Sc.(Hons) Thesis, University of Sydney, 1988.
[18] Shriver, D. F., 'The Manipulation of Air-Sensitive Compounds' (McGraw-Hill: New York 1969).

spectrometer. Spectra were obtained at room temperature unless otherwise noted and were referenced to solvent resonances. Infrared spectra were recorded on a Digilab 20/80 FTS infrared spectrophotometer as solids supported in compressed KBr discs or in solution. Mass spectra were recorded on a modified MS-9 mass spectrometer at 70 eV.

1-(4′-Alkylphenyl)-2,3,4,5-tetraphenylcyclopenta-2,4-dien-1-ol Derivatives

General procedure.—A solution of a Grignard reagent was made by the reaction of an ether solution (250 ml) of the appropriate *p*-alkylbromobenzene (0·25 mol) with magnesium turnings (6·0 g, 0·25 mol) suspended in dry ether (50 ml) under an argon atmosphere. The solution of the Grignard reagent was added slowly, through a catheter over 30 min, to a well-stirred, degassed solution of tetraphenyl-2,4-cyclopentadien-1-one (61·70 g, 0·16 mol) in dry benzene (300 ml) in a 1-litre Schlenk flask sealed with a septum. The dark purple colour of the solution changed to translucent orange after the addition was complete. Stirring was continued for 1 h at room temperature, and the solution left to stand for 16 h. The solution was transferred to a separating funnel, and washed with 1 M H_2SO_4 (300 ml) and water (4×200 ml). The solution was concentrated under vacuum until solid began to precipitate, and the remaining product was precipitated by addition of n-heptane (200 ml) and cooling. The product was collected by filtration, washed with n-heptane until the washings were colourless, and dried under high vacuum. The 1-(4′-alkylphenyl)-2,3,4,5-tetraphenylcyclopenta-2,4-dien-1-ols were obtained as pale pink solids (crude yield typically >90%), and used without further purification for the preparation of the corresponding bromides. Samples were purified by column chromatography on silica (230–400 mesh) with 30% hexane in dichloromethane as eluent. The alcohols were recrystallized by dissolving the chromatographed material in a minimum of dichloromethane, slowly adding 2 vol. of n-heptane, and leaving the solution to stand at room temperature (with slow solvent evaporation) until the alcohol crystallized.

1,2,3,4,5-Pentaphenylcyclopenta-2,4-dien-1-ol (1a) was obtained as a yellow crystalline solid, m.p. 177° (lit.[10] 175–176°). I.r.: ν_{max} (KBr, cm^{-1}) 3542s, 3539s, 3059w, 3021w, 1483m, 1441m, 1154m, 1139m, 1064m, 1056m, 1024m, 967m, 925m, 920m, 809m, 778m, 764m, 746m, 737s, 711m, 689s, 682s. ^1H n.m.r. (60 MHz, $CDCl_3$): δ 2·69–2·71, br s, 1H, OH; 7·28–7·53, m, 25H, ArH. ^{13}C n.m.r. (15 MHz, $CDCl_3$): δ 90·2 (Cp COH), 125·0, 126·9, 127·0, 127·0, 127·7, 127·9, 128·4, 129·5, 129·9, 133·9, 135·1, 140·2, 142·5, 148·0 (Ar C and Cp C). M.s.: *m/z* 462 (M, 100%), 446 (13), 279 (15), 267 (10), 178 (30), 165 (13), 105 (21), 77 (27).

*2,3,4,5-Tetraphenyl-1-(*p*-tolyl)cyclopenta-2,4-dien-1-ol* (1b) was obtained as a white crystalline solid, m.p. 183–186° (Found: C, 90·6; H, 5·6. $C_{36}H_{28}O$ requires C, 90·7; H, 5·9%). I.r.: ν_{max} (KBr, cm^{-1}) 3577s, 3563m, 3556–3536s, 3077m, 3067m, 3023s, 1599w, 1494m, 1435m, 1081s, 1029m, 1022m, 923m, 793s, 757s, 743s, 711–687s. ^1H n.m.r. (60 MHz, $CDCl_3$): δ 2·25–2·26, s, 3H, CH_3; 2·42–2·43, br s, 1H, OH; 6·95–7·45, m, 24H, ArH. ^{13}C n.m.r. (15 MHz, $CDCl_3$): 21·1 (CH_3), 90·2 (Cp COH), 125·0, 126·9, 127·0, 127·7, 127·8, 129·2, 129·6, 129·9, 134·0, 135·2, 136·3, 137·1, 142·3, 148·0 (Ar C and Cp C). M.s.: *m/z* 476 (M, 100%), 460 (43), 399 (10), 355 (12), 278 (16), 264 (13), 191 (12), 177 (27), 164 (16), 104 (17), 90 (17), 77 (13), 57 (12).

*1-(*p*-Ethylphenyl)-2,3,4,5-tetraphenylcyclopenta-2,4-dien-1-ol* (1c) was obtained as pale yellow rhombic plates after slow crystallization, m.p. 170–170·5° (Found: C, 90·5; H, 6·0. $C_{37}H_{30}O$ requires C, 90·6; H, 6·2%). I.r.: ν_{max} (KBr, cm^{-1}) 3538m, 3076w, 3054w, 3020w, 2961w, 1594w, 1496m, 1487m, 1441m, 1077m, 1028m, 805m, 758m, 737m, 696s. ^1H n.m.r. (400 MHz, $CDCl_3$): δ 1·17–1·21, t, 3H, CH_3; 2·56–2·62, q, 2H, CH_2; 2·45, br s, 1H, OH; 6·96–7·47, m, 24H, ArH. ^{13}C n.m.r. (15 MHz, $CDCl_3$): δ 15·2 (CH_3), 28·4 (CH_2), 90·3 (Cp COH), 125·1, 126·4, 126·9, 127·7, 127·8, 128·2, 128·6, 129·0, 129·6, 129·9, 134·1, 135·4, 137·3, 142·3, 142·7, 148·2 (Ar C and Cp C). M.s.: *m/z* 490 (M, 100%), 178 (15), 105 (16), 71 (9), 57 (9), 43 (19).

1-(*p*-t-Butylphenyl)-2,3,4,5-tetraphenylcyclopenta-2,4-dien-1-ol (1d) was obtained as pale yellow needles after slow crystallization, m.p. 182–183° (lit.[12] 175–176°). I.r.: ν_{max} (KBr, cm^{-1}) 3561m, 3052m, 2957s, 2922m, 2900m, 2869m, 2855m, 1486m, 1442m, 1073m, 1026m, 923m, 801m, 765m, 746m, 720m, 704s, 698s. ^1H n.m.r. (400 MHz, $CDCl_3$): δ 1·27, s, 9H, $(CH_3)_3C$; 2·51, br s, 1H, OH; 6·96–7·48, m, 24H, ArH. ^{13}C n.m.r. (15 MHz, $CDCl_3$): δ 31·4, 31·9 [($\mathbf{C}H_3)_3C$], 34·4 [$(CH_3)\mathbf{C}$], 90·3 (Cp COH), 124·8, 125·2, 126·9, 127·7, 127·8, 129·6, 129·9, 134·1, 135·4, 137·0, 142·3, 148·2, 149·7 (Ar C and Cp C). M.s.: *m/z* 518 (M, 100%), 502 (18), 384 (10), 178 (21), 105 (18), 91 (13), 71 (22), 57 (46), 43 (57).

*1-Bromo-1-(4'-alkylphenyl)-2,3,4,5-tetraphenylcyclopenta-2,4-diene Derivatives**

General procedure.—The 1-(*p*-alkylphenyl)-2,3,4,5-tetraphenylcyclopenta-2,4-dien-1-ol (0·039 mol) was suspended and partly dissolved in glacial acetic acid (250 ml) in a round-bottom flask fitted with a reflux condenser, a drying tube and a dropping funnel. The solution was heated, with stirring, to approximately 80° and a solution of HBr (48%, 22 ml) in glacial acetic acid (30 ml) was added dropwise over 45 min. The colour changed from yellow/orange to a dark orange/red almost immediately. After the addition was complete, stirring was continued for 2 h at approximately 70° before the solution was cooled to room temperature and left to stand for 16 h. The precipitated bromide was collected by filtration and dried under high vacuum over potassium hydroxide. The product was recrystallized from a mixture of dichloromethane and n-hexane (*c.* 1 : 3 v/v). Analytical samples were obtained by chromatography on a silica column (230–400 mesh) with 30% hexane in dichloromethane as eluent, followed by recrystallization from dichloromethane/hexane. Yields were 85–95%.

1-Bromo-1,2,3,4,5-pentaphenylcyclopenta-2,4-diene (2a) was obtained as a yellow crystalline solid, m.p. 184–186° (lit.[11] 188–189°). I.r.: ν_{max} (KBr, cm^{-1}) 3004w, 2990w, 2956w, 2928w, 2920w, 1951w, 1805w, 1593s, 1576m, 1494w, 1483w, 1444w, 1438w, 1338m, 1335m, 1329m, 1326m, 1314w, 1183m, 1072w, 1028w, 915s, 911s, 832s, 808s, 780s, 584s, 563s. ^{1}H n.m.r. (400 MHz, $CDCl_3$): δ 6·94–7·49, m, ArH. ^{13}C n.m.r. (15 MHz, $CDCl_3$): δ 127·1, 127·2, 127·4, 127·5, 127·7, 127·8, 128·3, 130·0, 130·4, 134·1, 134·7, 135·8, 141·8, 148·3 (Ar C and Cp C). M.s.: *m/z* 527 (20%), 526 (55), 525 (35), 524 (M, 57), 523 (24), 522 (11), 447 (33), 446 (100), 445 (85), 367 (27), 365 (16), 363 (16), 352 (10), 289 (33), 267 (16), 265 (21), 183 (12), 182 (11), 181 (11), 176 (18), 175 (17), 167 (22), 165 (19), 78 (24), 57 (12), 43 (34), 42 (24), 41 (17).

*1-Bromotetraphenyl(*p*-tolyl)cyclopenta-2,4-diene* (2b) (mixture of isomers) was obtained as a fine yellow crystalline solid, m.p. 167–168° (Found: C, 79·9; H, 4·9. $C_{36}H_{27}Br$ requires C, 80·2; H, 5·0%). I.r.: ν_{max} (KBr, cm^{-1}) 3050w, 3023w, 1509w, 1486m, 1435m, 1021w, 834w, 764m, 715m, 700m, 690s. ^{1}H n.m.r. (400 MHz, $CDCl_3$): δ 2·15, 2·19, 2·25, 3xs, CH_3; 6·79–7·49, m, ArH. ^{13}C n.m.r. (15 MHz, $CDCl_3$): δ 21·0, 21·1, 21·2 (CH_3), 127·1, 127·4, 127·5, 127·7, 127·8, 128·2, 128·3, 128·5, 129·1, 130·0, 130·1, 130·2, 130·5 (Ar CH), 131·1, 131·6, 132·7, 134·2, 134·4, 134·8, 135·0, 136·0, 136·6, 136·8, 137·4, 141·5, 141·7, 141·8, 141·9, 142·0, 148·0, 148·5 (Ar C_{quat}). M.s.: *m/z* 538 (M, 3%), 461 (32), 460 (100), 459 (91), 458 (37), 381 (23), 367 (13), 366 (12), 365 (15), 364 (11), 289 (18), 265 (14), 183 (13), 182 (18), 181 (16), 167 (13), 165 (12).

*1-Bromo(*p*-ethylphenyl)tetraphenylcyclopenta-2,4-diene* (2c) (mixture of isomers) was obtained in >90% yield as a fluffy yellow solid, m.p. 147–149° (Found: C, 79·6; H, 5·3. $C_{37}H_{29}Br$ requires C, 80·3; H, 5·3%). I.r.: ν_{max} (KBr, cm^{-1}) 3050w, 3022w, 2963w, 1596w, 1571w, 1486m, 1435m, 1182w, 1066w, 1027w, 1021w, 916w, 844m, 834m, 803w, 790w, 759m, 733m, 707m, 699s, 697s, 612w. ^{1}H n.m.r. (400 MHz, $CDCl_3$): δ 1·13, 1·16, 1·20, 1·24, 4xt, $CH_2C\mathbf{H}_3$; 2·51, 2·53, 2·54, 2·61, 4xq, $C\mathbf{H}_2CH_3$; 6·84–7·49, m, ArH. ^{13}C n.m.r. (15 MHz, $CDCl_3$): δ 14·9, 15·1 ($CH_2\mathbf{C}H_3$), 28·4, 28·4, 28·5 ($\mathbf{C}H_2CH_3$), 126·9, 127·0, 127·1, 127·2, 127·4, 127·6, 127·7, 127·8, 128·3, 129·9, 130·1, 130·2, 130·5, 130·6 (Ar CH), 134·4, 134·9, 135·0, 135·2, 136·1, 136·1, 148·4 (Ar C_{quat} and Cp C_{quat}). M.s.: *m/z* 552 (M, <1%), 475 (40), 474 (100), 473 (53), 472 (24), 444 (13), 367 (18), 366 (10), 365 (12), 289 (18), 265 (13), 165 (10).

*1-Bromo(*p*-t-butylphenyl)tetraphenylcyclopenta-2,4-diene* (2d) (mixture of isomers) was obtained as a dark yellow-orange crystalline solid after two slow recrystallizations from CH_2Cl_2/hexane, m.p. 145–148° (lit.[11] 80–130°) (Found: C, 80·5; H, 5·6. $C_{39}H_{33}Br$ requires C, 80·5; H, 5·7%). I.r.: ν_{max} (KBr, cm^{-1}) 3056w, 3029w, 2958m, 2949m, 1506w, 1498w, 1490m, 1441m, 1397w, 1070w, 1026w, 916w, 850w, 842w, 833m, 794m, 773w, 768m, 757m, 734m, 703s, 699s, 696s, 692s. ^{1}H n.m.r. (400 MHz, $CDCl_3$): δ 1·23, 1·25, 1·27, 3xs, $(CH_3)_3C$; 6·85–7·50, m, 24H, ArH. ^{13}C n.m.r. (15 MHz, $CDCl_3$): δ 31·2, 31·3, 31·4 (CH_3),

* IUPAC rules A-11.3 and C-15.11(*c*) require compounds (2), (3) and (6) to be named as cyclopenta-1,3-dienes, e.g., 5-bromo-1,2,3,4,5-pentaphenylcyclopenta-1,3-diene (2a). The numbering of the cyclopentadiene ring for such compounds in this paper, however, has been chosen for the sake of consistency with the IUPAC numbering of the cyclopenta-2,4-dien-1-ols (1) from which these compounds are derived.

34·4 [(CH_3)**C**], 124·3, 124·6, 125·2, 127·0, 127·1, 127·3, 127·5, 127·6, 127·7, 127·9, 128·3, 129·7, 129·8, 130·1, 130·5, 130·7, 130·9 (Ar CH), 131·6, 134·2, 134·4, 134·7, 134·8, 135·2, 136·0, 136·2, 141·5, 141·6, 141·8, 141·9, 142·0, 142·6, 147·8, 147·9, 148·3, 148·5, 149·8, 150·3, 151·0 (Ar C_{quat}). M.s.: *m/z* 580 (M, <1%), 503 (32), 502 (100), 501 (70), 500 (10), 487 (15), 445 (12), 444 (33), 368 (12), 367 (34), 365 (10), 289 (16), 265 (13), 167 (15), 57 (51), 44 (38), 43 (26), 41 (15).

(p-Alkylphenyl)tetraphenylcyclopenta-2,4-diene Derivatives

General procedure.—The preparations followed that reported by Chambers *et al.*[10] for the preparation of pentaphenylcyclopenta-2,4-diene. The 1-(4′-alkylphenyl)-2,3,4,5-tetraphenylcyclopenta-2,4-dien-1-ol (16 mmol), was dissolved in glacial acetic acid (100 ml), and stirred vigorously at 75° for 30 min. A mixture of hydrobromic acid (48%, 10 ml) and glacial acetic acid (20 ml) was added over a period of 30 min by means of a pressure-equalizing dropping funnel, and the suspension was stirred for 2 h at 80°. Zinc dust (4·2 g, 65 mmol) was added and the temperature maintained at 100° for 2 h. The reaction mixture was allowed to cool, and the product was filtered off from the solution as a pale yellow solid. The crude product was recrystallized from boiling xylenes, washed with pentane, and dried under high vacuum, to yield the 1-(4-alkylphenyl)-2,3,4,5-tetraphenylcyclopenta-2,4-diene as a yellow to white powder.

1,2,3,4,5-Pentaphenylcyclopenta-2,4-diene (3a) was obtained in 57% yield as a white powder, m.p. 259–261° (lit.[10] 248–256°). I.r.: ν_{max} (KBr, cm^{-1}) 3076w, 3022w, 1490m, 1483m, 1439w, 764s, 710s, 684s. ^1H n.m.r. [400 MHz, $(CD_3)_2SO$, at 80°]: δ 6·8–7·85, m, ArH. ^{13}C n.m.r. [15 MHz, $(CD_3)_2SO$, at 80°]: δ 126·0, 126·4, 126·9, 127·3, 127·5, 128·0, 128·4, 129·1, 129·5. M.s.: *m/z* 447 (36%), 446 (M, 100), 291 (14), 165 (14), 91 (12), 55 (10), 44 (92), 40 (48).

Tetraphenyl(p-tolyl)cyclopenta-2,4-diene (3b) (mixture of isomers).—Hydrochloric acid (10 M) was used instead of hydrobromic acid. The compound (mixture of isomers) was obtained in 20% yield as a white *powder*, m.p. 155–160° (Found: C, 94·0; H, 6·1. $C_{36}H_{28}$ requires C, 93·9; H, 6·1%). I.r.: ν_{max} (KBr, cm^{-1}) 3048m, 1672m, 1500w, 1487w, 1451m, 1445w, 1019m, 988m, 861w, 762m, 755m, 698m, 690s. ^1H n.m.r. (400 MHz, $CDCl_3$): δ 2·15, 2·23, 2·26, 3×s, CH_3; 5·05, 5·06, 2×s, CpH; 6·81–7·45, m, 24H, ArH. ^{13}C n.m.r. (15 MHz, $CDCl_3$): δ 21·0, 21·1, 21·2 (CH_3), 62·7, 62·8 (Cp CH), 125·0, 126·2, 126·4, 126·6, 126·9, 127·0, 127·6, 127·7, 127·8, 128·3, 128·5, 128·6, 128·8, 129·1, 129·2, 129·3, 129·6, 129·9, 130·1, 130·7, 132·9, 133·1, 134·0, 135·9, 136·0, 136·1, 136·2, 136·3, 136·5, 138·2, 138·4, 143·5, 144·1, 146·3, 146·6, 148·0 (Ar C and Cp C). M.s.: *m/z* 460 (M, 100%), 289 (10), 165 (12), 105 (13), 44 (70), 40 (29).

(p-Ethylphenyl)tetraphenylcyclopenta-2,4-diene (3c) (mixture of isomers) was obtained as a yellow solid on recrystallization from ethanol, m.p. 60–65° (Found: C, 93·8; H, 6·4. $C_{37}H_{30}$ requires C, 93·7; H, 6·3%). I.r.: ν_{max} (KBr, cm^{-1}) 3054w, 3025m, 2957m, 2927w, 1492m, 1440m, 1228m, 1071m, 1027m, 841w, 760m, 697s. ^1H n.m.r. [400 MHz, $(CD_3)_2SO$]: δ 1·10, 1·11, 1·13, 3×t, CH_2CH_3; 2·46, 2·47, 2·50, 3×q, CH_2CH_3; 6·8–7·85, m, Ph. ^{13}C n.m.r. [15 MHz, $(CD_3)_2SO$]: δ 15·0, 15·1, 15·4, 15·5 (CH_2CH_3), 28·3, 28·4 (CH_2CH_3), 58·9, 60·1, 60·3, 60·5, 60·6, 60·7, 60·8, 61·0, 63·8, 64·4 (Cp CH), 125·9, 126·0, 126·1, 126·2, 126·3, 126·4, 126·5, 126·6, 126·7, 126·8, 126·9, 127·1, 127·2, 127·3, 127·4, 127·5, 127·6, 127·7, 127·8, 127·9, 128·0, 128·1, 128·2, 128·3, 128·4, 128·5, 128·6, 128·7, 128·8, 128·9, 129·1, 129·2, 129·3, 129·4, 129·6, 129·8, 130·1, 130·2, 130·3, 130·5, 136·1, 137·1, 137·2, 139·2, 139·6, 139·7, 140·6, 141·1, 142·0, 142·4, 142·5, 142·7 (Ar C and Cp C). M.s.: *m/z* 474 (M, 40%), 400 (20), 133 (16), 105 (100), 91 (10), 77 (33), 51 (10).

(*p*-t-Butylphenyl)tetraphenylcyclopenta-2,4-diene (3d) (mixture of isomers) was obtained in approximately 15% yield as a white powder on recrystallization from pentane, m.p. 201–203° (lit.[11] 202–204°) (Found: C, 93·3; H, 6·8. Calc. for $C_{39}H_{34}$: C, 93·2; H, 6·8%). I.r.: ν_{max} (KBr, cm^{-1}) 3078w, 3056w, 3024m, 2959m, 2899w, 2865w, 1597w, 1491m, 1449w, 1440m, 1363w, 1269w, 1072m, 1028m, 845m, 798w, 785m, 768m, 742m, 717m, 697s. ^1H n.m.r. (400 MHz, $CDCl_3$): δ 1·18, 1·23, 1·25, 3×s, $(CH_3)_3C$; 5·08, s, CpH; 5·10, s, CpH; 6·90–7·30, m, ArH. ^{13}C n.m.r. (15 MHz, $CDCl_3$): δ 31·20, 31·27, 31·30 (CH_3), 34·39 [(CH_3)**C**], 62·3, 62·5, 62·9 (Cp CH), 124·6, 125·4, 126·2, 126·4, 126·6, 127·6, 127·7, 127·8, 127·9, 128·0, 128·4, 128·5, 129·1, 129·6, 129·7, 129·9, 130·1, 132·8, 135·8, 136·0, 136·3, 136·4, 136·7,

138·3, 138·6, 143·9, 144·0, 145·9, 146·3, 146·6, 149·1 (Ar C and Cp C). M.s.: *m/z* 502 (M, 100%), 487 (20), 367 (5), 165 (5), 91 (5), 57 (14), 41 (7).

*2,3,4,5-Tetra(*p*-tolyl)cyclopenta-2,4-dien-1-one (4a)*

A Grignard reagent was prepared by the addition of a solution of α-bromo-*p*-xylene (25 ml, 135 mmol) in dry ether (200 ml) to magnesium turnings (3·3 g, 136 mmol) suspended in dry ether (50 ml) activated with a crystal of iodine. After the addition was complete, the solution was stirred for 16 h at room temperature, then cooled in ice. A solution of ethyl formate (4·85 ml, 60 mmol) in dry ether (40 ml) was added to the Grignard reagent with stirring. The mixture was stirred vigorously at 0° for 2 h and then refluxed gently for 30 min. The mixture was filtered; the filtrate was washed with a saturated aqueous ammonium chloride solution (200 ml), then with water (5×200 ml). The solvent was removed to yield a yellow oil (13·4 g) which was predominantly the required product, 1,3-di(*p*-tolyl)propan-2-ol, containing a small amount of 1,2-di(*p*-tolyl)ethane. The crude alcohol was taken up in acetone (120 ml) at 0°. Chromic acid (20 ml) was added dropwise to the well stirred solution until a persistent brown colour was achieved. Ethanol was added to decompose excess chromic acid. The solution was transferred to a separating funnel and diluted with saturated aqueous sodium chloride (200 ml), and the product was extracted into ether (3×200 ml). The organic solvents were removed on a rotary evaporator, leaving a yellow oily solid (15·6 g), which was used without further purification.

Crude 1,3-di(*p*-tolyl)acetone (9·83 g, 41 mmol) and 4,4′-dimethylbenzil (8·88 g, 37 mmol) were dissolved in absolute ethanol (30 ml) at 60°, and a solution of potassium hydroxide (1·5 g, 33 mmol) in absolute ethanol (10 ml) was added. The colour of the solution rapidly changed to red and the solution was left to stand for 16 h. Ethanol (20 ml) was added and the solution cooled in ice. The precipitate was collected and purified by chromatography on silica gel (230–400 mesh) with dichloromethane as eluent. The purple *product* was recrystallized from dichloromethane/hexane, triturated with hot hexane, filtered off, washed with cold hexane and dried (Found: C, 89·7; H, 6·3. $C_{33}H_{28}O$ requires C, 90·0; H, 6·4%). ^{1}H n.m.r. (400 MHz, $CDCl_3$): δ 2·29, 12H, s, 4×CH_3; 6·79–7·14, 16H, 2×AA′XX′, ArH. ^{13}C n.m.r. (100 MHz, $CDCl_3$): δ 21·33 (CH_3), 21·35 (CH_3), 124·95 (C_{quat}), 128·28 (C_{quat}), 128·60 (Ar CH), 128·70 (Ar CH), 129·38 (Ar CH), 129·68 (C_{quat}), 130·00 (CH), 130·51 (C_{quat}), 136·97 (C_{quat}), 138·19 (C_{quat}), 153·97 (**C**CO), 200·78 (CO). M.s.: *m/z* 441 (20%), 440 (M, 90), 412 (14), 206 (45), 119 (100), 105 (18), 91 (24), 86 (20), 84 (26), 65 (14), 57 (12), 51 (18), 49 (51).

*2,5-Diphenyl-3,4-di(*p*-tolyl)cyclopenta-2,4-dien-1-one (4b)*

Diphenylacetone (5·68 g, 27 mmol) and 4.4′-dimethylbenzil (6·44 g, 27 mmol) were dissolved in absolute ethanol (35 ml) under gentle reflux. A solution of potassium hydroxide (0·87 g, 15·5 mmol) in absolute ethanol (7 ml) was slowly added to the well stirred solution. The colour of the solution was dark red when the addition was complete and heating was continued for a further 15 min. The solution was cooled in ice, and the product was collected by filtration, washed with cold ethanol, and dried in vacuum. *2,5-Diphenyl-3,4-di(*p*-tolyl)cyclopenta-2,4-dienone* was obtained as a dark black/purple microcrystalline solid (10·0 g, 90%), m.p. 220–221° (Found: C, 90·1; H, 5·6. $C_{31}H_{24}O$ requires C, 90·3; H 5·9%). ^{1}H n.m.r. (400 MHz, $CDCl_3$): δ 2·31, 6H, s, CH_3; 6·70–7·0, 8H, AA′XX′, tolyl ArH; 7·23, 10H, m, ArH. ^{13}C n.m.r. (100 MHz, $CDCl_3$): δ 21·4 (CH_3), 125·2 (C_{quat}), 127·3 (Ar CH), 127·9 (Ar CH), 128·6 (Ar CH), 129·4 (Ar CH), 130·2 (C_{quat}), 131·2 (C_{quat}), 138·4 (C_{quat}), 154·6 (**C**CO), 200·3 (CO). M.s.: *m/z* 412 (M, 100%), 384 (30), 206 (30), 193 (11), 192 (70), 191 (29), 189 (13), 165 (12), 59 (20).

*1,2,5-Triphenyl-3,4-di(*p*-tolyl)cyclopenta-2,4-dien-1-ol (5a)*

A Grignard reagent, prepared from bromobenzene (3·14 g, 20 mmol) in diethyl ether (50 ml) as described above, was added slowly to a well stirred solution of 2,5-diphenyl-3,4-di(*p*-tolyl)cyclopenta-2,4-dien-1-one (4·50 g, 11 mmol) in dry degassed benzene (100 ml). The colour changed from an intense red/purple to translucent orange when the addition was complete. The solution was stirred for 16 h at room temperature, then washed with a saturated aqueous ammonium chloride solution (200 ml), followed by water (4×200 ml). The solvent was removed on a rotary evaporator to give a crude product which was recrystallized

from propan-1-ol/dichloromethane/n-heptane (150 : 30 : 100 v/v/v). *1,2,5-Triphenyl-3,4-di(p-tolyl)cyclopenta-2,4-dien-1-ol* was obtained as a pale yellow crystalline solid (5·1 g) as a propan-1-ol solvate. The compound becomes opaque at 110° and melts sharply at 215–216°. The propan-1-ol is not removed in vacuum (Found: C, 87·3; H, 6·7. $C_{37}H_{30}O.C_3H_8O$ requires C, 87·2; H, 7·0%). ^{1}H n.m.r. (400 MHz, $CDCl_3$): δ 2·24, 6H, s, CH_3; 2·54, 1H, s, OH; 6·6–7·6, 23H, m, ArH. ^{13}C n.m.r. (100 MHz, $CDCl_3$): δ 21·22 (2×CH_3), 90·16 (C_{quat}), 125·15 (CH), 126·78 (CH), 127·85 (CH), 128·34 (CH), 128·57 (CH), 129·57 (CH), 129·84 (CH), 132·18 (C_{quat}), 134·24 (C_{quat}), 136·58 (C_{quat}), 140·48 (C_{quat}), 142·58 (C_{quat}), 147·88 (C_{quat}). M.s.: *m/z* 491 (40%), 490 (M, 100), 475 (10), 474 (24), 398 (10), 370 (10), 192 (18), 105 (11).

*2,5-Diphenyl-1,3,4-tri(*p*-tolyl)cyclopenta-2,4-dien-1-ol (5b)*

A Grignard reagent, prepared from *p*-bromotoluene (3·42 g, 20 mmol) in diethyl ether (80 ml), was added slowly over 90 min to a well stirred solution of 2,5-diphenyl-3,4-di(*p*-tolyl)cyclopenta-2,4-dien-1-one (4·50 g, 11 mmol) in dry, degassed benzene (80 ml). The colour of the solution changed from an intense red/purple to yellow/gold when the addition was complete, and a white solid precipitated. The solution was stirred for 16 h at room temperature, then washed with saturated aqueous ammonium chloride solution and water (3×200 ml). The solvent was removed on a rotary evaporator, and the residue was dried in vacuum, then recrystallized from propan-1-ol/dichloromethane/n-heptane (150 : 30 : 100 v/v/v). The product was collected, washed with n-heptane and dried in vacuum. *2,5-Diphenyl-1,3,4-tri(*p*-tolyl)cyclopenta-2,4-dien-1-ol* was obtained as a pale yellow crystalline solid (5·08 g) as a propan-1-ol solvate, m.p. 110–115°. The propan-1-ol could not be removed in vacuum (Found: C, 87·2; H, 7·0. $C_{38}H_{32}O.C_3H_8O$ requires C, 87·2; H, 7·1%). ^{1}H n.m.r. (400 MHz, $CDCl_3$): δ 2·25, 6H, s, CH_3; 2·26, 3H, s, CH_3; 2·51, 1H, s, OH; 6·7–6·9, 8H, AA′XX′, 2×tolyl ArH); 7·0, 10H, m, 2×C_6H_5; 7·1–7·4, 4H, AA′XX′, tolyl ArH. ^{13}C n.m.r. (100 MHz, $CDCl_3$): δ 21·04 (CH_3), 21·21 (2×CH_3), 90·13 (C_{quat}), 125·08 (CH), 128·72 (CH), 127·61 (CH), 128·54 (CH), 129·09 (CH), 129·59 (CH), 129·84 (CH), 132·27 (C_{quat}), 134·32 (C_{quat}), 138·17 (C_{quat}), 138·51 (C_{quat}), 137·29 (C_{quat}), 142·39 (C_{quat}), 147·64 (C_{quat}). M.s.: *m/z* 505 (40%), 504 (M, 100), 489 (18), 412 (10), 192 (11), 119 (10).

*1-Bromotriphenyldi(*p*-tolyl)cyclopenta-2,4-diene (6a) (Mixture of Isomers)*

1,2,5-Triphenyl-3,4-di(*p*-tolyl)cyclopenta-2,4-dien-1-ol (5a) (4·86 g, 9·9 mmol) was dissolved in a mixture of glacial acetic acid (60 ml) and acetic anhydride (20 ml) at *c.* 80°. A solution of HBr (5 ml, 48%) in glacial acetic acid (10 ml) was added slowly over 30 min. The solution was stirred at 80° for 5 h and then at room temperature for 16 h. The solution was cooled in ice; the resultant solid was collected and washed with ethanol, and recrystallized from dichloromethane (60 ml)/hexane (50 ml) to yield a solid which was collected by filtration, washed with a small quantity of cold hexane, and dried over potassium hydroxide in vacuum. *1-Bromotriphenyldi(*p*-tolyl)cyclopenta-2,4-diene* (mixture of isomers) was obtained as a bright yellow crystalline solid (4·5 g, 82%), m.p. 185–190° (Found: C, 80·4; H, 5·3. $C_{37}H_{29}Br$ requires C, 80·3; H, 5·3%). ^{1}H n.m.r. ($CDCl_3$): δ 2·19, 2·24, 2·25, 2·28, 4×s, 6H, CH_3; 6·8–7·6, m, 23H, ArH. ^{13}C n.m.r. ($CDCl_3$): δ 21·02, 21·13, 21·23 (3×CH_3), 125·16, 126·81, 126·93, 126·97, 127·03, 127·31, 127·51, 127·58, 127·65, 127·72, 128·16, 128·28, 128·44, 128·49, 128·58, 129·00, 129·57, 129·85, 129·94, 129·97, 130·07, 130·25, 130·28, 130·52, 130·56, 130·59, 131·25, 131·37, 131·82, 131·94, 132·93, 134·36, 134·50, 134·94, 134·98, 135·15, 136·19, 136·60, 136·64, 136·74, 137·38, 141·31, 141·44, 141·78, 141·99, 147·87, 148·24 (Ar C and Cp C). M.s.: *m/z* 555 (<1%), 554 (<1), 553 (<1), 552 (<1), 476 (13), 475 (43), 474 (100), 473 (25), 472 (10), 165 (8), 119 (12), 105 (19), 91 (12), 77 (10), 57 (27).

*1-Bromodiphenyltri(*p*-tolyl)cyclopenta-2,4-diene (6b) (Mixture of Isomers)*

2,5-Diphenyl-1,3,4-tri(*p*-tolyl)cyclopenta-2,4-dien-1-ol (5b) (4·57 g, 9·1 mmol) was dissolved in glacial acetic acid (80 ml), and a solution of 48% HBr (5 ml) in glacial acetic acid (20 ml) was added slowly. The solution was stirred at 80° for 1 h and then at room temperature for 16 h. Water (300 ml) was added to the solution, and the yellow precipitate was collected by filtration, washed with water and dried in vacuum. A sample of the compound was purified

by chromatography on a short silica column (CH_2Cl_2/hexane) to yield *1-bromodiphenyltri(p-tolyl)cyclopenta-2,4-diene* (mixture of isomers) as a yellow crystalline solid, m.p. 58–65° (Found: C, 80·8; H, 5·8. $C_{38}H_{31}Br$ requires C, 80·4; H, 5·5%). ^1H n.m.r. ($CDCl_3$): δ 2·17, 2·18, 2·20, 2·22, 2·29, 5×s, 9H, CH_3; 6·8–7·4, m, 22H, ArH. ^{13}C n.m.r. ($CDCl_3$): δ 14·06, 21·0, 21·11, 21·21, 22·62, 31·56 (CH_3), 125·04, 126·74, 126·86, 126·98, 127·13, 127·29, 127·50, 127·57, 127·62, 127·67, 127·70, 127·82, 128·13, 128·25, 128·39, 128·43, 128·55, 128·65, 128·96, 129·12, 129·23, 129·39, 129·58, 129·81, 129·84, 129·93, 129·96, 130·08, 130·28, 130·54, 130·58, 130·83, 131·28, 131·41, 131·60, 131·88, 131·95, 133·03, 134·57, 135·21, 135·26, 136·32, 136·51, 136·56, 136·56, 136·66, 137·30, 141·43, 141·47, 141·66 (Ar C and Cp C). M.s.: *m/z* 569 (<1%), 568 (<1), 567 (<1), 566 (<1), 525 (<1), 524 (<1), 523 (2), 522 (4), 492 (4), 490 (12), 489 (49), 488 (100), 487 (22), 486 (4).

Iron Complexes

Bromodicarbonyl(pentaphenylcyclopentadienyl)iron(II) derivatives were prepared in an analogous procedure to that reported[5,9] for (η^5-C_5Ph_5)$Fe(CO)_2Br$.

Bromodicarbonyl(pentaphenylcyclopentadienyl)iron(II) (7a) was prepared as described previously[9] and was characterized as follows. M.p. 245–250° (dec.) [lit.[7] >230° (dec.)]. I.r.: ν_{max} (KBr, cm^{-1}) 2031·0s, 1987·6s (CO); ν_{max} (CH_2Cl_2, cm^{-1}) 2037·6s, 1996·3s (CO) [lit.[5] ν_{max} 2040, 2000 cm^{-1} (CO)]. ^1H n.m.r. (400 MHz, $CDCl_3$): δ 6·07–8·00, m. ^{13}C n.m.r. (15 MHz, $CDCl_3$): δ 101·0 (Cp C), 127·6, 128·3, 129·7, 132·2 (Ar C), 213·4 (CO). M.s.: *m/z* 636 (M, <1%), 583 (14), 582 (32), 581 (14), 580 (32), 447 (36), 446 (100), 445 (71), 367 (18), 366 (11), 365 (16), 364 (10), 363 (15), 289 (27), 291 (11), 290 (11), 267 (14), 265 (18), 176 (13), 175 (12), 167 (16), 165 (16).

Bromodicarbonyl[2,3,4,5-tetraphenyl-1-(p-tolyl)cyclopenta-2,4-dienyl]iron(II) (7b) was obtained as a red powder (0·61 g, 47%), m.p. 168–172° (Found: C, 70·0; H, 4·0. $C_{38}H_{27}BrFeO_2$ requires C, 70·2; H, 4·2%). I.r.: ν_{max} (KBr, cm^{-1}) 2024·3s, 1980·9s (CO); ν_{max} (CH_2Cl_2, cm^{-1}) 2036·8s, 1994·4s (CO). ^1H n.m.r. (400 MHz, CD_2Cl_2): δ 2·24, s, 3H, CH_3; 6·93–7·25, m, 14H, ArH. ^{13}C n.m.r. (15 MHz, CD_2Cl_2): δ 20·9 (CH_3), 100·5, 101·5 (Cp C), 126·4, 127·5, 127·6, 128·2, 129·8, 130·0, 132·0, 132·2, 138·4 (Ar C), 213·8 (CO). M.s.: *m/z* 650 (M, 10%), 603 (12), 516 (22), 515 (44), 514 (13), 513 (16), 475 (16), 462 (23), 461 (67), 460 (100), 459 (81), 458 (17), 381 (17), 380 (10), 379 (10), 367 (20), 366 (16), 365 (20), 364 (10), 352 (10), 305 (13), 291 (19), 290 (13), 289 (29), 281 (13), 267 (13), 265 (20), 191 (15), 179 (15), 178 (17), 167 (17), 165 (26), 105 (36), 91 (16), 77 (15).

Bromodicarbonyl[1-(p-ethylphenyl)-2,3,4,5-tetraphenylcyclopenta-2,4-dienyl]iron(II) (7c) was obtained as an air-stable tan powder (62%) on recrystallization from benzene/light petroleum, m.p. 128–131° (Found: C, 70·2; H, 4·4. $C_{39}H_{29}BrFeO_2$ requires C, 70·5; H, 4·4%). I.r.: ν_{max} (KBr, cm^{-1}) 2028·1s, 1986·7s (CO); ν_{max} (CH_2Cl_2, cm^{-1}) 2036·8s, 1994·4s (CO). ^1H n.m.r. (400 MHz, CD_2Cl_2): δ 1·18, t, 3H, CH_2CH_3; 2·59, q, 2H, CH_2CH_3; 6·93–7·35, m, 16H, ArH. ^{13}C n.m.r. (15 MHz, CD_2Cl_2): δ 15·1 (CH_2CH_3), 28·8 (CH_2CH_3), 101·1, 102·0 (Cp C), 127·0, 127·5, 128·0, 128·7, 130·3, 130·4, 132·3, 132·7 (Ar C), 214·2 (CO). M.s.: *m/z* 665 (M, <1%), 476 (10), 475 (42), 474 (100), 473 (11), 472 (19), 105 (11), 44 (24).

Bromo[1-(p-t-butylphenyl)-2,3,4,5-tetraphenylcyclopenta-2,4-dienyl]dicarbonyliron(II) (7d) was obtained as a red air-stable solid (92%), m.p. 143–146° (Found: C, 70·9; H, 4·7. $C_{41}H_{33}BrFeO_2$ requires C, 71·0; H, 4·9%). I.r.: ν_{max} (KBr, cm^{-1}) 2033·0s, 1989·6s (CO); ν_{max} (CH_2Cl_2, cm^{-1}) 2036·8s, 1994·4s (CO). ^1H n.m.r. (400 MHz, CD_2Cl_2): δ 1·25, s, 9H, $(CH_3)_3C$; 7·00–7·35, m, 13H, ArH. ^{13}C n.m.r. (15 MHz, CD_2Cl_2): δ 31·3 (CH_3), 34·9 [$(CH_3)\mathbf{C}$], 101·5, 102·1, 102·3 (Cp C), 125·0, 127·1, 128·1, 128·8, 130·5, 130·8, 132·4, 132·8 (Ar C), 214·5 (CO). M.s.: *m/z* 693 (M, <1%), 557 (12), 503 (41), 502 (100), 501 (23), 500 (12), 487 (17), 444 (12), 429 (10), 428 (22), 367 (15), 291 (12), 289 (12), 265 (10), 167 (10), 105 (29), 91 (12), 77 (12), 57 (45), 41 (12).

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