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Decasubstituted decaphenylmetallocenes

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Abstract

Pentaphenylcyclopentadienes that are *para*-substituted at each phenyl group prove to be valuable new ligands. They are easily prepared in good yield and high purity from pentaphenylcyclopentadiene by acetylation and subsequent acetalation. Owing to the ease with which the electronic properties of these ligands can be modified and due to the solubility and the facile characterization of their complexes it is now possible to explore the whole field of decaarylmetallocenes. The first soluble decaarylmetallocenes with tin and lead as the metal atom are described.

Key words: Metallocenes; Cyclopentadienyl; Tin; Lead

1. Introduction

Cyclopentadienyl ligands with bulky substituents such as t-butyl [1] or phenyl [2] can form complexes that differ drastically from those containing the unsubstituted parent ligands. The bulky substituents can stabilize the complex kinetically by shielding the reactive metal center and the cyclopentadienyl ring. They can induce novel molecular structures, *e.g.* those with a lower coordinated metal center by shifting the balance between steric and electronic effects and they can stiffen the complex, so that, *e.g.* ring rotation is slowed and can be observed more easily [2]. Perphenylated cyclopentadienyl systems (with ligand **2** [3]) are especially well stabilized, even in the case of "unusual" oxidation states. This is due mainly to the stereorigidity of these systems and probably to a lesser extent to charge delocalization into the phenyl groups. In decaphenylstannocene, *e.g.* the rotation of the ten phenyl rings and of the two Cp-units, is severely restricted by steric crowding [4]. The two planar cyclopentadienyl rings are forced into a parallel orientation, and attack at the tin atom is obstructed. Thus the S_{10}-symmetrical decaphenylstannocene does not decompose up to 350°C and can be stored "indefinitely" in wet air [5]. In contrast, the very air- and water-sensitive unsubstituted stannocene [6], and even the decamethyl, decabenzyl, or octaphenyl derivatives, are markedly less stable.

The other decaphenylmetallocenes that have been synthesized and satisfactorily characterized, those with Ge [7], Sn [8], Pb [7], Ni [9], or Mo [10] as the metal atom, show similarly higher stability than the corresponding unsubstituted metallocenes. On the other hand, all the decaphenylmetallocenes and the free ligand itself are reported to be almost insoluble in all common organic solvents. This severe disadvantage of the pentaphenylcyclopentadiene ligand is due to the compact shape, which facilitates crystallization, and to protection of the metal center so minimizing interactions with the solvent. The decaphenylmetallocenes can be purified only by continuous extraction with hot toluene and characterized by NMR spectroscopy only in the solid state. The growth of crystals suitable for X-ray analysis was possible only for decaphenylstannocene which was recrystallized from hot 1-methylnaphthalene.

One obvious way of enhancing the solubility of the pentaphenylcyclopentadiene complexes is by introduction of substituents into the phenyl groups of the ligand. The substituents can inhibit the formation of

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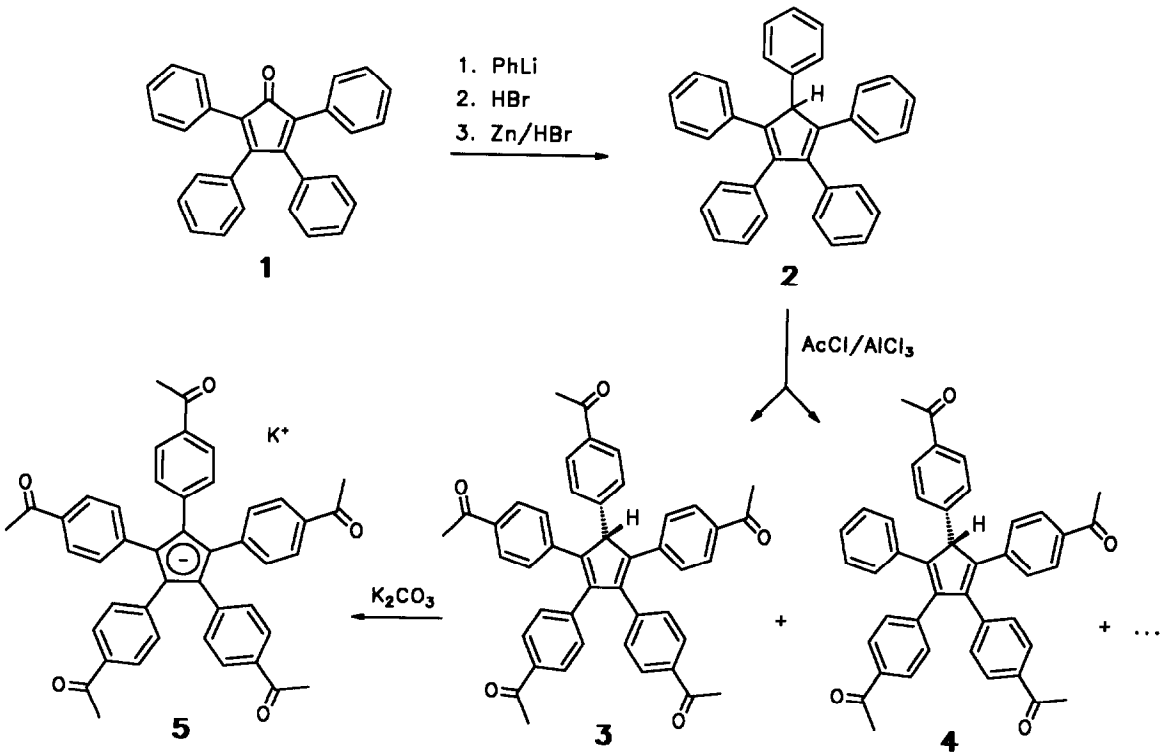
the crystal lattice or increase the interaction with the solvent. Indeed, Field *et al.* observed a significant improvement in the solubility of a (pentaphenylcyclopentadienyl) iron complex upon introduction of methyl, ethyl or t-butyl groups into the *para* position of one, two, or three of the five phenyl groups [11]. The degree of substitution did not markedly influence the spectroscopic properties of the complex. Encouraged by these observations we decided to seek the easiest route to even more highly substituted pentaphenylcyclopentadienes. Symmetrical multiple substitution by large groups was assumed to be necessary since di-t-butyl-substituted decaphenylmetallocenes are also insoluble, and the corresponding free ligands difficult to purify [12]. We obtained the Cp-ligands **6**, with the desired properties, starting by acetylation of pentaphenylcyclopentadiene **2** and subsequent acetalation of the pentaacetyl derivative **3** so formed. The synthesis of pentaacetyl derivative **3**, and its thallium(I) and sodium salts, and its haloform degradation have been described by Schumann *et al.* [13]. We describe below the preparation and properties of the hitherto unknown ketals of the pentaacetyl derivative **3** and those of the anions and the first soluble decaarylmetallocenes, **8** and **9** derived therefrom.

2. Results and discussion

2.1. Synthesis and properties of pentakis(4-acetylphenyl)cyclopentadiene(3)

Our preparation of pentaphenylcyclopentadiene (**2**) (Scheme 1) from comparatively cheap reagents (tetraphenylcyclopentadienone **1**, phenyllithium, aqueous hydrobromic acid and zinc powder) is based on the method used by Ziegler and Schnell [14]. We simplified and optimized the synthesis so that it can now be carried out in one flask, with one final work-up, on a 100 g scale in 79% overall yield. The pentaphenylcyclopentadiene was acylated with acetyl chloride in the presence of aluminum trichloride by a procedure similar to that described by Schumann *et al.* [13]. A mixture of single to five-fold acetylated diastereomers was formed (Scheme 1). The yield of the pentasubstituted derivative is > 74% if an excess of acetyl chloride is used in the synthesis.

Clean separation of the desired pentasubstituted molecule **3** from the mixture of tetra- and less-substituted isomers was brought about by a single recrystallization and is thus convenient even on a 30 g scale. The symmetry of the molecules favors their separation. There is only one pentasubstituted stereoisomer (C_s



Scheme 1. Synthesis of the pentakis(4-acetylphenyl)cyclopentadiene **3**. Ligand **4** is one of the five tetraacetylated tautomers and enantiomers formed.

symmetry), but five stereoisomers (one C_s and two pairs of C_1 enantiomers) of the tetra- or the mono-substituted ligand, respectively, and even ten stereoisomers (two C_s, eight C_1) of the di- and of the trisubstituted molecule. However, in the case of the tetrasubstituted compound, for instance, the five stereoisomers formed cannot necessarily cocrystallize. Moreover their tendency to form crystals should be poorer owing to their lower symmetry compared with the C_s symmetry of the pentasubstituted molecule. Indeed, the pure compound **3** separated out upon addition of ether or pentane to the solution in dichloromethane or acetone, whereas the mixture of the tetrasubstituted diastereomers **4** could not be made to crystallize even after purification by chromatography. Analogously, other pentasubstituted compounds, such as **6a**, can be crystallized in contrast to the by-products that accompany them. The mono- to tetra-substituted derivatives can be separated and purified by column chromatography. As expected, the complex ^{1}H-NMR spectrum of a mixture of the tetrasubstituted derivatives **4** in DMSO-d_6 was simplified upon deprotonation of the cyclopentadienyl ring with dimsyl-d_6 sodium. Only signals corresponding to only one C_{2v} symmetrical anion were detected.

The five acetyl groups in **3** markedly influence the acidity of the cyclopentadienyl core. Not only sodium amide [13] but also bases as weak as triethylamine or potassium carbonate deprotonate the yellow compound. The C_{5h}-symmetrical red anion that is formed gives rise to only one simple AA'BB' multiplet and one methyl signal in the ^{1}H-NMR spectrum. The NMR spectra of compounds **6–9** also confirm the *para*-substitution pattern. The *para*-substituents greatly simplify the ^{1}H-NMR spectra, especially in the case of product mixtures. Anions of type **7** and metallocenes **8a** and **9** show only one AA'BB' system in the aromatic region, and free ligands like **3** or **6** three such systems in the intensity ratio 2:2:1.

The charge delocalization in the anion **5** that is responsible for the acidity of the pentaacetyl derivative **3** seems to prevent the formation of stable metal complexes. If metal salts such as $SnCl_2$, $Pb(NO_3)_2$ and $FeCl_2$ or complexes such as $(C_5Ph_5)Fe(CO)_2Br$ [15], $(C_5Ph_5)Ru(CO)_2Br$ [16], $Ru_3(CO)_{12}$ and $Fe(CO)_5$ are added to a solution of the red potassium salt **5** or the ligand **3**, with or without oxidant or photolysis, no change is observed in the ^{1}H-NMR and ^{13}C-NMR spectra, the chromatograms, or the color of the solution. Furthermore, any attempt to deprotect the metallocenes **8** and **9** under acid catalysis in the presence or absence of water or acetone yielded the free ligand **3** with complete decomposition within a second. Direct coupling of cyclopentadiene **3** or plumbocene **9b** under McMurry conditions (with either $Zn/TiCl_4$ or $Li/TiCl_3$) yielded only a green polymer. No dimers of **3** or cryptate complexes could be isolated.

When solid silver triflate is added to the yellow solution of cyclopentadiene **3** in pyridine, the solution turns red and the ^{1}H-NMR spectrum shows that the spectrum of **3** is replaced by a broadened spectrum of anion **5**. This observation could be accounted for in terms of coordination of the silver cation to **3**, causing a further increase in the acidity of the cyclopentadiene and subsequent deprotonation by the solvent.

2.2. Synthesis and properties of stannocene 8a and plumbocenes 9

We protected the keto groups of the pentasubstituted Cp-anion **5** as ketals so as to increase its nucleophilicity and hence its tendency to form complexes and prevent the metal cation from coordinating the oxygen atoms. Pentakis(4-acetylphenyl)cyclopentadiene (**3**) reacted under standard conditions and acid catalysis with ethylene glycol or ethanol/triethylorthoformate to acetals **6a** or **6b** in 86% or 24% yield, respectively (Scheme 2). In contrast to the dioxolane **6a**, the bisethoxy derivative **6b** did not crystallize and had to be purified by column chromatography. The pentaacetyl derivative **3** is much more soluble than the parent compound **2**, in, for example, THF, acetone and dichloromethane. Acetalation of **3** raises the solubility further. The dioxolane derivative **6a** is soluble in ether or benzene, and the bisethoxy derivative **6b** even in hexane or a variety of more polar solvents such as ether and acetone.

The acetals **6** could be deprotonated only by strong bases such as sodium hydride in tetrahydrofuran. Yellow or reddish solutions of the cyclopentadienide salts **7** were formed, and these were used without purification for the synthesis of the lead and tin complexes or the radical **10a**. The crystalline yellow cyclopentadienide salts **7** could be precipitated by adding ether to the corresponding solution. The anions showed a basicity and chemistry similar to that of the parent compound **2**.

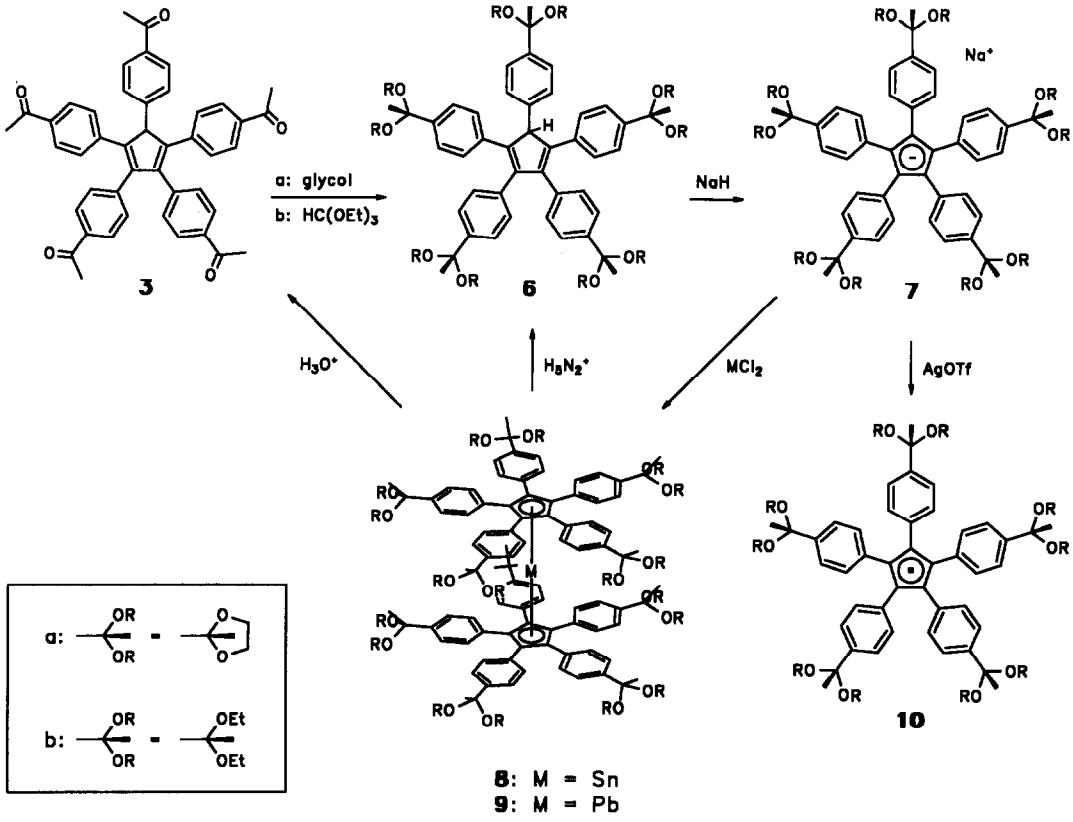
For the synthesis of stannocene (**8a**), the solution of the sodium salt **7a** was titrated slowly – (to prevent formation of mono-Cp-tin complexes) – with a solution of freshly distilled tin dichloride in THF until the color changed from red to yellow. The canary-yellow product **8a** immediately crystallized out from the reaction solution, together with sodium chloride, and was purified by recrystallization from dichloromethane/ether. For the preparation of the deep-red plumbocenes **9a** and **9b** the solution of the corresponding cyclopentadienyl anion was added to solid lead dichloride. A momentary surplus of metal ions in the reaction solution was

unlikely in this case, since lead dichloride is much less soluble in THF than tin dichloride. The stannocene **8a** and plumbocenes **9a** and **9b** were isolated in 90%, 51% and 31% yields, respectively.

The metallocenes proved to be much more soluble than the unsubstituted decaphenylmetallocenes but less soluble than the free ligands. The metallocenes derived from dioxolane **6a** are very soluble in dichloromethane, and plumbocene **9b** is soluble even in benzene or tetrahydrofurane. As mentioned above, we were unable to crystallize the purified bisethoxy cyclopentadiene **6**, only a glass or an oil being formed when the solvent was removed or non-polar solvents were added. However, the corresponding plumbocene **9b** separated as a crystalline powder upon addition of pentane to the solution in THF. Owing to the solubility of metallocenes **8a** and **9** it was possible to record the first solution ^{13}C-NMR spectra of decaphenylmetallocenes. The ^{13}C-NMR chemical shifts for metallocenes **8a** and **9a** are identical within 1 ppm, whereas two of them differ by at least 3–5 ppm from the shifts for the free anionic species **7**. Protonation of anions such as **7** seems to have only a slightly larger effect on the shift of the aryl carbons than the complexation. The IR spectra (400–4000 cm^{-1}) of stannocene (**8a**) and plumbocene (**9a**) are almost identical, and differ characteristically [12] from the spectrum of the free ligand in the range between 640 cm^{-1} and 1150 cm^{-1}.

As mentioned above, **8a** and **9** are sensitive towards acids, which cleave the acetal groups. The free pentaacetyl ligand **3** is formed. If a combination of a mild acid such as hydrazinium tosylate and a nucleophile such as hydrazine is chosen, even the vulnerable bisethoxy-acetal groups of plumbocene **9b** remain intact. Instead the lead–carbon bonds are cleaved, so that only the free bisethoxy ligand **6b** can be isolated. Nevertheless, the substituted decaphenylmetallocenes are fairly water- and air-stable even in solution. Although obviously some of the unreactivity of the unsubstituted decaphenylmetallocenes is due to their insolubility, the soluble derivatives **8a** and **9** are without doubt significantly more stable than stannocene or plumbocene itself.

Silver triflate oxidizes the cyclopentadienide salt **7a** in tetrahydrofuran cleanly to the corresponding less soluble blue-violet radical **10a**. Use of this radical should provide a second route to substituted decaphenylmetallocenes, since the unsubstituted pen-



Scheme 2.

taphenylcyclopentadienyl radical reacts with, *e.g.*, nickel(0) complexes to give decaphenylnickelocene.

3. Experimental details

All manipulations involving organometallic reagents were carried out under nitrogen in a glove box or by using standard inert-atmosphere techniques. Tetracyclone (Janssen) and phenyllithium (Aldrich) were used as received. All aprotic solvents were dried and distilled under nitrogen prior to use (dichloromethane and 1,2-dichloroethane from phosphorus pentoxide, the other aprotic solvents from sodium benzophenone ketyl). Column chromatography was performed on flash silica (E. Merck Reagents silica gel 60, 230-400 mesh ASTM).

NMR spectra were recorded on UCB-250 MHz and UCB-300 MHz instruments consisting of Cryomagnet System magnets, Nicolet 293A or 293A' pulse programmers and the Nicolet Model 1180 or 1180E data collection systems. Data are reported as follows: chemical shifts in ppm relative to internal tetramethylsilane or residual solvent peaks (number of hydrogens, multiplicity, coupling constant). The multiplicities observed are indicated as s (singlet), d (doublet), t (triplet) and q (quartet). The positions of ^{1}H or ^{13}C atoms of 4-substituted phenyl rings are given as: (C_5)-(*p*-phenyl)-(*m*-phenyl)-(*o*-phenyl)-(*i*-phenyl)-(CO), with (C_5) referring to the cyclopentadienyl ring and (CO) to the acetyl substituent. Infrared spectra were obtained on the Perkin-Elmer Model 1420 or the Bruker IFS 88. Only characteristic and/or strong signals are reported. Low-resolution mass spectra (MS: EI at 70 eV, CI or FAB), high resolution mass spectra (HRMS) and elemental analyses were provided by the Mass Spectral Service and Microanalytical Laboratory, respectively, at the University of California, Berkeley. Melting points were determined in open Pyrex capillary tubes with a Thomas-Hoover Unimelt apparatus and are uncorrected.

3.1. Pentaphenylcyclopentadiene 2

Phenyllithium (180 ml of a 1.8 M solution in hexane, 0.32 mol) was added from a syringe to a suspension of powdered tetraphenylcyclopentadienone (**1**) (100.1 g, 0.260 mol) in 500 ml of ether at −78°C. After 2 h stirring at −78°C the almost white suspension was heated to reflux for 30 min until the violet shade had vanished. The solvent was removed *in vacuo*. Acetic acid (300 ml) and then hydrobromic acid (90 ml, 48% in water) were carefully added to the white residue. After that an inert atmosphere was no longer necessary. When heated under reflux for 30 min the suspension turned orange. During 5 h additional aqueous HBr (70 ml) and then zinc dust (70 g, 1.1 mol) were added in small portions to the boiling suspension. After another 5 h of refluxing the solution was cooled to room temperature and the precipitate filtered off. The product **2** was recrystallized from dichloromethane/ether: 92.1 g, 79%; slightly yellow powder; m.p. 253°C; the spectroscopic data agree with those in ref. 17.

3.2. Pentakis(4-acetylphenyl)cyclopentadiene (3)

A solution of aluminum trichloride (75.3 g, 565 mmol) and acetylchloride (38.19 ml, 538 mmol) in 1,2-dichloroethane (200 ml) was made up at −78°C and then added to pentaphenylcyclopentadiene (**2**) (30.0 g, 67.2 mmol) in the same solvent (300 ml) at −78°C. The red suspension was allowed to warm to room temperature. After 3 days the mixture was added to ice and acidified with concentrated hydrochloric acid. The aqueous layer was extracted twice with dichloromethane. The combined organic layers were washed twice with water and dried with sodium sulfate. Partial evaporation of the solvent and addition of ether precipitated the product **3**, which was purified by recrystallization from dichloromethane/ether: 32.9 g, 74%; yellow crystals; m.p. > 260°C (dec.); the spectroscopical data are in accord with the data given in ref. [13]; IR (KBr, cm^{-1}) 1689vs, 1677vs, 1673vs, 1601vs, 1421s, 1402s, 1355s, 1265vs, 1256s, 1191s, 1180s, 1012m, 955s, 843vs, 833s, 647s; UV (CH_2Cl_2) 371, 289 nm; Anal. Found: C, 82.26; H, 5.57. $C_{45}H_{36}O_5$ (656.77) calcd.: C, 82.29; H 5.53%.

Chromatography of the supernatant liquor yielded the tetra- and lower substituted products as a mixture of diastereomers. The tetrasubstituted isomers (*e.g.* **4**) were be obtained only as a yellow glass: IR (KBr, cm^{-1}): 1684vs, 1603s, 1404w, 1358m, 1267vs, 1182w, 958w, 847m, 835m, 649w; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.450 (*ca.* 4H, s), 2.457 (*ca.*6H, s), 2.500 (*ca.* 4H, s), 2.502 (*ca.* 2H, s), 2.533 (*ca.* 2H, s), 2.537 (*ca.* 4H, s), 2.545 (*ca.* 2H, s), 2.550 (*ca.* 2H, s), 5.25 (*ca.* 1H, s), 5.27 (*ca.* 3H, s), 5.30 (*ca.* 2H, s), 6.9–7.9 (*ca.* 100H, m); MS *m/z* (rel. intensity) 615 ($M^+ + H$, 47%), 614 (M^+, 100), 599 (12), 572 (19), 498 (33), 483 (11), 292 (17), 202 (18), 147 (24). A single red anion was formed by deprotonation of the mixture of tetrasubstituted isomers in DMSO-d_6 with dimsyl-d_5 sodium: ^{1}H NMR (300 MHz, DMSO-d_6): δ 3.13 (CHD_2, quintet, J = 1.6 Hz), 6.65 (4H, d, J = 8.4 Hz), 6.69 (m), 6.73 (4H, d, J = 8.4 Hz), 6.91 (m), 7.41 (4H, d, J = 8.4 Hz), 7.48 (4H, d, J = 8.4 Hz), 8.32 (s). Bromo(pentaphenyl)cyclopentadiene reacts with strong Lewis acids, and so attempts to carry out Friedel-Crafts acetylation failed. Acetylation of decaphenylstannocene destroyed the complex, although Schumann *et al.* were able to acy-

late octaphenylferrocene to give its octaacylated derivative [18].

3.3. Potassium pentakis(4-acetylphenyl)cyclopentadienide (5)

A slurry of pentakis(4-acetylphenyl)cyclopentadiene (**3**) (1.28 g, 1.96 mmol) and potassium carbonate (2.70 g, 19.5 mmol) in acetonitrile (20 ml) was ground in a mortar under nitrogen for 20 min. The red solution was filtered and the filtrate was treated with ether, upon which the product **5** crystallized out: 1.14 g, 84%; red crystals; m.p. 240°C (dec.); IR (KBr, cm^{-1}): 1682s, 1584s, 1547w, 1437w, 1404w, 1358m, 1269vs, 1181w, 1145w, 958w, 845w; ^{1}H NMR (300 MHz, CD_3OD): δ 2.49 (CHD_2, quintet, J = 1.9 Hz), 6.74 (10H, *m*-phenyl, d, J = 8.3 Hz), 7.51 (10H, *o*-phenyl, d, J = 8.2 Hz); ^{13}C NMR (75 MHz, CD_3OD): δ 47.7 (CD_3, quintet, J = 21 Hz), 122.5 (C_5), 127.1 (*o*-phenyl), 130.8 (*m*-phenyl), 131.1 (*p*-phenyl), 146.4 (*i*-phenyl), 197.2 (CO); UV (CH_2Cl_2) 465 sh, 416, 290 nm; Anal. Found: C, 76.77; H, 6.03. $C_{45}H_{35}O_5K$ (694.88) calcd.: C, 77.78; H, 5.08%.

3.4. Pentakis[4-(2-methyl-1,3-dioxa-2-cyclopentyl)phenyl]cyclopentadiene (6a)

A mixture of pentakis(4-acetylphenyl)cyclopentadiene (**3**) (12.0 g, 18.3 mmol), ethylene glycol (20.0 ml, 357 mmol), toluenesulfonic acid (10 mg, 0.06 mmol) and toluene (60 ml) was heated under reflux for 9 h in a Dean-Stark apparatus. The brown mixture was washed with a solution of KOH (2 g) in 100 ml of water and then three times with water. The solvent was removed *in vacuo*. The residual **6a** was recrystallized from ether/pentane: 13.7 g, 86%; pale yellow crystals; m.p. 222–226°C; IR (KBr, cm^{-1}): 2986m, 2892m, 1690w, 1404w, 1375m, 1255s, 1199s, 1095m, 1083m, 1042vs, 1017s, 948m, 873m, 850m, 839m; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.53 (6H, s), 1.56 (3H, s), 1.60 (6H, s), 3.67 (10H, m), 3.92 (10H, m), 6.97 (4H, d, J = 8.3 Hz), 6.98 (4H, d, J = 8.5 Hz), 7.11 (4H, d, J = 8.5 Hz), 7.12 (2H, d, J = 8.3 Hz), 7.23 (4H, d, J = 8.4 Hz), 7.27 (2H, d, J = 8.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.96, 26.98, 27.18, 64.14, 64.19, 108.46, 108.52, 108.54, 124.36, 124.54, 124.57, 128.31, 129.60, 134.76, 135.66, 140.83, 141.26, 144.03, 145.54; MS m/z (rel. intensity) 877 (M^+, 61), 876 ($M^+ - H$, 100), 861 (32), 832 ($M^+ - CH_2CH_2OH$, 73), 817 (39), 788 (32), 773 (29); Anal. Found: C, 75.58; H, 6.44. $C_{55}H_{56}O_{10}$ (877.04) calcd.: C, 75.32; H, 6.44%.

3.5. Pentakis[4-(1,1-diethoxyethyl)phenyl]cyclopentadiene (6b)

A suspension of pentakis(4-acetylphenyl)cyclopentadiene (**3**) (3.35 g, 5.09 mmol) in ethanol (3.5 ml, 60 mmol), triethylorthoformate (5.9 g, 40 mmol), concentrated hydrochloric acid (0.03 ml) and 5 ml of dichloromethane was stirred for 2 days. Pyrrolidine (0.3 ml, 3 mmol and then aqueous potassium carbonate (2 ml) were added to the black green solution. The mixture was evaporated to dryness. Chromatography of the residue (silica gel, with hexane containing 5% triethylamine) yielded the desired product **6b**, as the second band: 1.28 g, 24%; pale yellow-green fluorescent glass; IR (neat, cm^{-1}): 2973s, 2933m, 2883m, 1268m, 1172m, 1123m, 1092m, 1051vs, 1018w, 950s, 843w, 617w; ^{1}H NMR (300 MHz, C_6D_6): δ 1.05 (12H, t, J = 7.1 Hz), 1.06 (6H, t, J = 7.1 Hz), 1.09 (12H, t, J = 7.1 Hz), 1.37 (6H, s), 1.38 (3H, s), 1.46 (6H, s), 3.18 –3.34 (20H, m), 5.15 (1H, s), 7.24 (4H, d, J = 8.5 Hz), 7.31 (4H, d, J = 8.6 Hz), 7.35 (2H, d, J = 8.4 Hz), 7.43 (4H, d, J = 8.6 Hz), 7.49 (4H, d, J = 8.4 Hz), 7.55 (2H, d, J = 8.3 Hz); ^{13}C NMR (75 MHz, C_6D_6): δ 15.52, 15.55, 15.60, 26.81, 26.89, 26.95, 56.49, 56.55, 56.59, 56.61, 59.42, 101.14, 101.18, 101.21, 126.11, 126.40, 129.00, 130.13, 135.41, 136.17, 138.18, 142.49, 142.52, 142.75, 144.64, 146.75; MS m/z (rel. intensity) 1027.6 (M^+, 71), 1026.6 ($M^+ - H$, 100), 982.6 (64), 981.6 (88), 952.5 (14), 937.5 (14), 935.5 (14), 907.5 (15), 657.2 (14), 641.2 (25).

3.6. Sodium pentakis[4-(2-methyl-1,3-dioxa-2-cyclopentyl)phenyl]cyclopentadiene (7a)

A suspension of sodium (or potassium) hydride (43 mg, 1.8 mmol) in a solution of pentakis[4-(2-methyl-1,3-dioxa-2-cyclopentyl)phenyl]cyclopentadiene (**6a**) (353 mg, 0.402 mmol) in tetrahydrofuran (10 ml) was stirred for 2 days. The excess of sodium hydride was filtered off. This freshly prepared solution of the cyclopentadienide salt was red, probably due to impurities, and turned yellow upon standing under nitrogen for one week without noticeable change in the spectra. The solution was used without purification for the synthesis of the lead and the tin complexes. The beige sodium salt **7a** crystallized upon addition of ether to the red solution: 178 mg, 49%; beige crystalline powder; ^{1}H NMR (300 MHz, THF-d_8): δ 1.51 (15H, s), 3.68 (10H, m, J = 6.8 Hz), 3.87 (10H, m, J = 6.9 Hz), 6.57 (10H, d, J = 8.3 Hz), 6.82 (10H, d, J = 8.3 Hz); ^{13}C NMR (75 MHz, THF-d_8): δ 28.25 (CH_3, q), 64.91 (CH_2, t), 109.77 (C[OR]$_2$, s), 120.99 (s), 124.34 (d), 131.80 (d), 137.97 (s), 141.28 (s).

An analogous procedure gives sodium pentakis[4-(1,1-diethoxyethyl)phenyl]cyclopentadienide (**7b**): yellow solution, pale yellow crystals: ^{1}H NMR (300 MHz, THF-d_8): δ 1.08 (30H, t, J = 7.6 Hz), 1.42 (15H, s), 3.31 (20H, q, J = 7.5 Hz), 6.69 (10H, d, broad) 6.89 (10H, d, broad); ^{13}C NMR (75 MHz, THF-d_8): δ 15.88, 26.34, 56.71, 102.14, 124.68, 131.94, 132.10, 136.60, 142.94.

3.7. Decakis[4-(2-methyl-1,3-dioxa-2-cyclopentyl)phenyl]stannocene (8a)

A solution of sodium pentakis[4-(2-methyl-1,3-dioxa-2-cyclopentyl)phenyl]cyclopentadienide (**7a**) (1.17 mmol) in 15 ml of THF was titrated slowly with a solution of freshly distilled tin dichloride (0.19 g, 1.0 mmol) in THF (3 ml) until the color changed from red to yellow. The yellow precipitate **8a** was filtered off and extracted with dichloromethane (10, 3, 3 ml). Addition of ether to the extract furnished red crystals of **8a**: 0.99 mg, 90%; yellow crystals; m.p. > 300°C; IR (KBr, cm^{-1}): 2992m, 2890m, 1610w, 1513w, 1374m, 1254s, 1199s, 1182s, 1141m, 1096m, 1076w, 1040vs, 1015s, 948w, 870m, 857m, 839m; ^1H NMR (300 MHz, $CDCl_3$): δ 1.53 (15H, s), 3.66 (10H, m, $J = 6.5$ Hz), 3.92 (10H, m, $J = 6.6$ Hz), 6.57 (10H, d, $J = 8.4$ Hz), 6.75 (10H, d, $J = 8.2$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 27.66, 64.36, 108.69, 123.97, 125.80, 131.99, 132.98, 141.07; MS m/z (rel. intensity) 1872 (M^+, 4.6), 1871 ($M^+ = Cp^{\phi}_2Sn^+$, 5.0), 1870 (M^+, 4.6), 1828 ($M^+ - CH_2CH_2O$, 4.8), 1827 ($M^+ - CH_2CH_2O$, 4.6), 1826 ($M^+ - CH_2CH_2O$, 4.3), 998 ($Cp^{\phi}Sn^+$, 73), 997 ($Cp^{\phi}Sn^+$, 86), 996 ($Cp^{\phi}Sn^+$, 100), 995 ($Cp^{\phi}Sn^+$, 91), 994 ($Cp^{\phi}Sn^+$, 97), 993 ($Cp^{\phi}Sn^+$, 80), 992 ($Cp^{\phi}Sn^+$, 78), 966 (18), 952 (77), 907 (40), 877 (66), 460 (38); Anal. Found: C, 70.54; H, 5.90. $C_{110}H_{110}O_{20}Sn$ (1870.76) calcd.: C, 70.62; H, 5.93%.

We had been able to prepare the zwitterionic isomer $[Fe(\eta^5\text{-}C_5Ph_5)\{(\eta^6\text{-}C_6H_5)C_5Ph_4\}]$ of decaphenylferrocene [19] in 25% yield by heating lithium pentaphenylcyclopentadienide and $FeCl_2 \cdot 2THF$ in toluene (95°C, 5 h) followed by an aqueous workup and chromatography (spectra in accord with ref. 19 and an authentic sample). However, attempts to synthesize an analogous zwitterionic ferrocene with ten 4-(2-methyl-1,3-dioxa-2-cyclopentyl) substituents from **7a** and $FeCl_2 \cdot 2THF$ were unsuccessful.

3.8. Decakis[4-(2-methyl-1,3-dioxa-2-cyclopentyl)phenyl]plumbocene (9a)

A suspension of lead dichloride (1.02 g, 3.74 mmol) in a solution of sodium pentakis[4-(2-methyl-1,3-dioxa-2-cyclopentyl)phenyl]cyclopentadienide (**7a**) (3.17 mmol, see above) in 10 ml of THF was stirred for five days. Ether (5 ml) was then added and the red precipitate was filtered off and extracted with dichloromethane (10 ml, 3 ml, 3 ml). Addition of ether to the extract furnished red crystals of **9a**: 1.57 g, 51%; red crystals; m.p. > 300°C; IR (KBr, cm^{-1}): 2992m, 2890m, 1610w, 1513w, 1374m, 1250s, 1199s, 1182s, 1141m, 1096m, 1076w, 1039vs, 1015s, 948w, 870m, 857m, 839m; ^1H NMR (300 MHz, $CDCl_3$): δ 1.60 (15H, s), 3.73 (10H, m, $J = 6.4$ Hz), 4.00 (10H, m, $J = 6.5$ Hz), 6.62 (10H, d, $J = 8.4$ Hz), 6.86 (10H, d, $J = 8.3$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 27.63, 64.31, 108.62, 124.00, 126.83, 132.09, 132.69, 140.95; MS m/z (rel. intensity) 1960.9 (M^+, 1.9), 1959.9 (M^+, 2.0), 1958.9 ($M^+ = Cp^{\phi}_2Pb^+$, 2.5), 1957.9 (M^+, 2.1), 1915.4 (2.0), 1869.2 (1.3), 1084.4 ($Cp^{\phi}Pb^+$, 53), 1083.4 ($Cp^{\phi}Pb^+$, 100), 1082.4 ($Cp^{\phi}Pb^+$, 55), 1039.4 (46), 995.4 (17), 876.4 (74), 833.4 (48), 460.2 (96); HRMS calcd. for $C_{55}H_{55}O_{10}{}^{208}Pb$: 1082.3554, found: 1082.3532; Anal. Found: C, 67.57; H, 5.70; Pb, 11.1. $C_{110}H_{110}O_{20}Pb$ (1959.3) calcd.: C, 67.43; H, 5.66; Pb 10.6%. A red powder that precipitated from a solution of plumbocene **9a** and a trace of toluenesulfonic acid in acetone turned out to be rather unstable and decomposed upon attempted dissolution in dichloromethane.

3.9. Decakis[4-(1,1-diethoxyethyl)phenyl]plumbocene (9b)

A suspension of lead dichloride (149 mg, 0.53 mmol) in a solution of sodium pentakis[4-(1,1-diethoxyethyl)phenyl]cyclopentadienide (**7b**) (1.068 mmol) in 10 ml of THF was stirred for 4 days. The red solution was then filtered through Celite, concentrated, and treated with pentane. Red crystals of the product **9b** separated: 385 mg, 31%; red powder; m.p. 280°C (dec.); IR (KBr, cm^{-1}): 2976s, 2937w, 2894m, 1283m, 1268s, 1172s, 1143m, 1125s, 1092s, 1051vs, 1017w, 950s, 859m, 841w; ^1H NMR (300 MHz, C_6D_6): δ 0.89 (30H, t, $J = 7.0$ Hz), 1.31 (15H, s), 3.14 (20H, q, $J = 7.0$ Hz), 6.85 (10H, d, $J = 8.3$ Hz), 7.01 (10H, d, $J = 8.4$ Hz); ^{13}C NMR (75 MHz, C_6D_6): δ 15.64, 27.62, 56.75, 101.39, 125.83, 127.92, 132.64, 133.50, 142.30; MS m/z (rel. intensity) 2262.3 (M^+, 0.69), 2261.4 (M^+, 1.39), 2260.3 ($M^+ = Cp^{\phi}_2Pb^+$, 1.55), 2259.3 (M^+, 1.45), 2258.2 (M^+, 0.94), 2217.2 ($M^+ - EtOH$, 1.0), 2216.2 ($M^+ - EtOH$, 2.2), 2215.2 ($M^+ - EtOH$, 2.7), 2214.2 ($M^+ - EtOH$, 3.2), 2213.1 ($M^+ - EtOH$, 2.6), 2212.1 ($M^+ - EtOH$, 1.6), 2168.0 ($M^+ - 2EtOH$, 1.7), 1235.6 ($Cp^{\phi}Pb^+$, 25), 1234.6 ($Cp^{\phi}Pb^+$, 60), 1233.6 ($Cp^{\phi}Pb^+$, 100), 1232.6 ($Cp^{\phi}Pb^+$, 55), 1231.6 ($Cp^{\phi}Pb^+$, 39), 1187.5 (27), 1159.5 (28), 1026.6 (51), 981.5 (65), 935.5 (37); Anal. Found: C, 68.27; H, 7.55. $C_{130}H_{170}O_{20}Pb$ (2260.0) calcd.: C, 69.09; H, 7.58%.

3.10. Pentakis[4-(2-methyl-1,3-dioxa-2-cyclopentyl)phenyl]cyclopentadienyl (10a)

The red solution of sodium pentakis[4-(2-methyl-1,3-dioxa-2-cyclopentyl)phenyl]cyclopentadienide (**7a**) (1.199 mmol) in 15 ml of THF was added to a solution of silver triflate in 7 ml THF at −90°C. A pale yellow suspension was immediately formed. When warmed above −60°C the mixture turned blue-violet, and almost black crystals separated. The mixture was allowed to warm to room temperature and THF was added to dissolve the crystals. The solution was filtered through

celite. The radical **10a** that separated upon addition of pentane was extremely air sensitive, and decomposed within a few weeks even under nitrogen: 0.44 g, 42%. Apparently because of their sensitivity, the dark blue crystals did not give satisfactory analytical data.

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