

**Chemistry of *o*-Xylidene–Metal Complexes. Part 1. *o*-Xylidene-magnesium Reagents as Metallocyclic Precursors and Synthesis of  $[\text{Pt}(\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{-}o)(\text{cod})]$  (cod = cyclo-octa-1,5-diene); the X-Ray Crystal Structure of the Macrometallocycle  $[\{\text{Mg}(\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{-}o)(\text{C}_4\text{H}_8\text{O})_2\}_3]^\dagger$**

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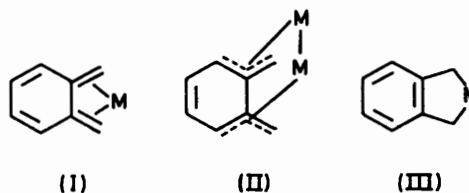
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A high-yield synthesis of a tetrahydrofuran (thf) solution of the di-Grignard reagent (A) derived from *o*-bis(chloromethyl)benzene is described, as well as that of an analogue obtained from 1,2-bis(chloromethyl)-4,5-dimethylbenzene. Cooling (A) to *ca.*  $-40^\circ\text{C}$  yields the colourless chloride-free  $\text{Mg}(\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{-}o)(\text{thf})$  of unknown structure, whereas at ambient temperature a concentrated solution ( $> ca. 0.1 \text{ mol dm}^{-3}$ ) slowly (days) deposits colourless needles of  $[\{\text{Mg}(\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{-}o)(\text{thf})_2\}_3]$ . A single-crystal X-ray structure determination of the latter ( $R = 0.054$  for 1117 'observed' reflections at 295 K) shows it to be a trimer. Crystals are orthorhombic, space group  $F2dd$ , with  $a = 24.706(8)$ ,  $b = 8.948(3)$ ,  $c = 44.315(9)$  Å, and  $Z = 8$ ; the trimeric unit lies on a crystallographic two-fold axis. Each of the three magnesiums is bridged to the other two by a  $\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{-}o$  ligand, the pseudo-tetrahedral co-ordination about each magnesium atom being completed by a pair of thf molecules. The utility of the di-Grignard reagent as a general metallocycle

precursor is illustrated by the synthesis of  $[\text{Pt}(\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{-}o)(\text{cod})]$  (cod = cyclo-octa-1,5-diene) from  $[\text{Pt}_2(\text{cod})]$ . In contrast  $[\text{PtCl}_2(\text{dppe})]$  with  $[\{o\text{-C}_6\text{H}_4(\text{CHSiMe}_3)_2\}\{\text{Li}(\text{tmen})\}_2]$  (dppe =  $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ , tmen =  $\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2$ ) affords  $[\text{Pt}(\text{dppe})_2]$ .

Realisation of the significance of the  $\beta$ -hydrogen elimination decomposition pathway in metal alkyl complexes has led to the successful synthesis of stable transition-metal alkyls with  $\beta$ -hydrogen free ligands such as the benzyl group. The *o*-xylidene analogue,  $\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{-}o$ , isoelectronic with the catecholate species, has been found to interact with metal centres in a variety of ways. In  $[\text{Fe}(\text{CO})_3(\eta^4\text{-C}_8\text{H}_8)]^1$  it behaves as an  $\eta^4$ -*o*-quinodimethide ligand, (I), while in  $[\text{Fe}_2(\text{CO})_6(\text{C}_8\text{H}_8)]^2$  it appears as a six-electron ligand, (II). Chelate derivatives, (III), metallobenzocyclopentenes, have recently been reported in preliminary publications for the Group 4,<sup>3,4</sup> 5,<sup>4</sup> 6,<sup>5,6</sup> and 8<sup>3,7,8</sup> transition metals. Intermediate metallocyclopentene (III) and  $\eta^4$ -metallocycle (I) character has been observed in  $[\text{W}(\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{-}o)_3]$  (X-ray data)<sup>6</sup> and  $[\text{Ru}(\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{-}o)(\text{PRR}'_2)_3]$  (R = Me, R' = Ph; or R = Ph, R' = Me) (n.m.r. evidence).<sup>8</sup>

In the present series of papers we examine the synthesis, properties, and structures of a variety of *o*-xylidenemetal complexes (metallobenzocyclopentenes). A synthesis for metallocyclopentenes involving oxidative addition of a 1,3-diene to form a low-valent metal complex {for example,<sup>9</sup>  $[\text{Zr}(\text{CH}_2\text{CHCHCH}_2)(\eta\text{-C}_3\text{H}_5)_2]$  from 'zirconocene' and buta-1,3-diene} is not appropriate for metallobenzocyclopentenes. Instead, in the early papers of the series, we show how synthesis may generally be achieved by an *o*-xylidene ligand-transfer reaction between an appropriate metal chloride and a



di-Grignard reagent, while in later papers the consequences of using an organo-dilithium reagent,  $[\{o\text{-C}_6\text{H}_4(\text{CHSiMe}_3)_2\}\{\text{Li}(\text{tmen})\}_2]$  (tmen = *NNN'*-tetramethylethylenediamine), will be explored. The use in metallocycle synthesis of a di-Grignard<sup>10</sup> or a dilithium<sup>11</sup> reagent has precedents.

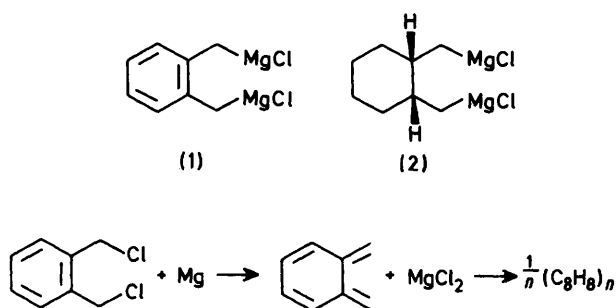
We now describe: (i) the synthesis of the di-Grignard reagent derived from *o*-bis(chloromethyl)benzene; (ii) the isolation of two crystalline chloride-free magnesium complexes therefrom; and (iii) the X-ray structure determination of one of these, a trinuclear magnesium *o*-xylidene complex. In addition, (iv), reactions of the di-Grignard reagent are exemplified by the synthesis of the complex  $[\text{Pt}(\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{-}o)(\text{cod})]$  (6) (cod = cyclo-octa-1,5-diene), whereas (v) the dilithium reagent causes  $\text{Pt}^{II} \rightarrow \text{Pt}^0$  reduction. Some of these results [(i) and (iv) and, in part, (ii)] have appeared in a preliminary form.<sup>3</sup>

### Results and Discussion

By careful optimisation of reaction conditions a successful high-yield synthesis of the di-Grignard reagent, (A), from *o*-bis(chloromethyl)benzene has been achieved, which effectively behaves as the complex (1). Although the di-Grignard reagent of the saturated analogue, *cis*-1,2-bis(chloromethyl)-cyclohexane, (2), is readily accessible,<sup>12</sup> our result is surprising

<sup>†</sup> *cyclo*-Tris[ $\mu$ -(*o*-phenylenedimethylene- $C^\alpha C^\alpha$ )-bis(tetrahydrofuran)magnesium].

Supplementary data available (No. SUP 23335, 11 pp.): structure factor amplitudes, thermal and H-atom parameters, least-squares planes. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.



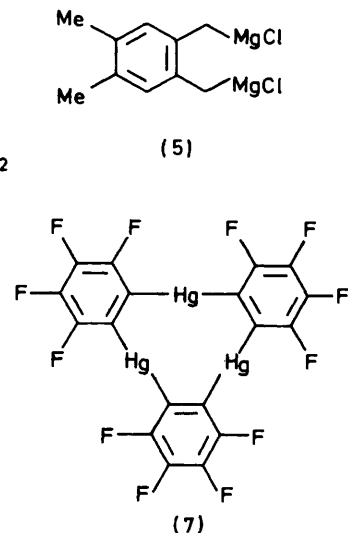
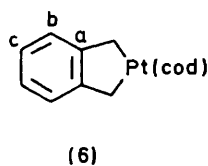
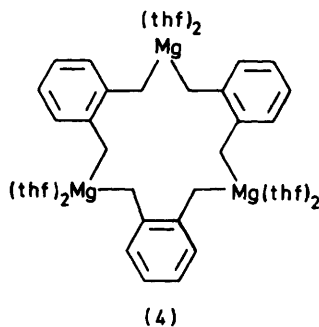
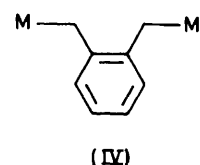
in view of an earlier failure,<sup>13</sup> in the reaction between the dichloride and magnesium leading to elimination of  $\text{MgCl}_2$  and polymerisation of the generated *o*-quinodimethide molecule.

We found that a viable synthesis of the reagent (A) is critically dependent on a number of constraints. First, it is necessary to use  $o\text{-C}_6\text{H}_4(\text{CH}_2\text{Cl})_2$  rather than the dibromide, since the latter results in elimination of  $\text{MgBr}_2$ , irrespective of whether low-temperature or reflux conditions are employed. Secondly, the use of tetrahydrofuran (thf), rather than the more common Grignard solvent diethyl ether, is essential for high yields (typically 90–96%). Finally, high dilution is necessary; the best results were obtained when concentrations were *ca.*  $0.075 \text{ mol dm}^{-3}$ . Although such a solution of (A) is not saturated, attempts directly to prepare solutions of higher concentrations resulted in significantly lower yields. It was essential to distil  $o\text{-C}_6\text{H}_4(\text{CH}_2\text{Cl})_2$  immediately prior to use and the source of the magnesium was crucial.

Efforts to obtain a dilithium reagent from either  $\alpha, \alpha'$ -dibromo- or -dichloro-*o*-xylene, in satisfactory yields, were unsuccessful. This contrasts with the readily synthesised dilithio-analogue of (2).<sup>11</sup> Direct dilithiation of *o*-xylene using *n*-butyl-lithium–tmen was considered but rejected, because of the excess of  $\text{LiBu}^n$  required<sup>14</sup> for a substantial amount of dilithiation.

The principal requirement for a viable synthesis of the di-Grignard reagent  $o\text{-C}_6\text{H}_4(\text{CH}_2\text{MgCl})_2$ , (1), compared with the saturated analogue  $o\text{-C}_6\text{H}_{10}(\text{CH}_2\text{MgCl})_2$ , (2), is the much greater dilution demanded for the former. This precludes the possibility that the coupling decomposition pathway of complex (1) involves an intramolecular elimination of  $\text{MgCl}_2$ . The formation of Grignard reagents is now widely held to implicate free-radical intermediates.<sup>15</sup> It may well be that the difference between the two systems is related to the enhanced stability of benzylic type radicals such as  $o\text{-}\dot{\text{C}}\text{H}_2\text{C}_6\text{H}_4(\text{CH}_2\text{MgCl})$  or  $o\text{-}\dot{\text{C}}\text{H}_2\text{C}_6\text{H}_4\text{CH}_2\text{Cl}$  compared with their saturated counterparts, and hence a greater probability of an intermolecular encounter with the 1,2-bis(chloromethyl)organocycle to yield a coupled aromatic product. In support of this analysis, we note (i) the difficulty in obtaining a simple benzyl-Grignard reagent such as  $\text{Mg}(\text{CH}_2\text{Ph})\text{Cl}$  without a substantial bibenzyl by-product, and (ii) the radical nature of many Grignard coupling reactions, *e.g.*  $\text{Mg}(\text{Me})\text{Br}$  with  $\text{PhCH}_2\text{Cl}$  yields *ca.* 30% of  $(\text{CH}_2\text{Ph})_2$ . The use of chlorides rather than bromides is well known, even for simple Grignard reagents  $\text{Mg}(\text{R})\text{X}$ , to reduce the extent of the coupling reaction ( $\xrightarrow{\text{RX}} \text{R}_2 + \text{MgX}_2$ ),<sup>16</sup> which is favoured both kinetically ( $\text{Br}^-$  or  $\dot{\text{B}}\text{r}$  are better leaving groups than  $\text{Cl}^-$  or  $\dot{\text{C}}\text{l}$ ) and thermodynamically (based on  $\text{CCl}$ ,  $\text{CBr}$ ,  $\text{MgCl}$ , and  $\text{MgBr}$  bond strengths).

An unusual feature of reagent (A) is that on cooling to *ca.*  $-40^\circ\text{C}$  a colourless, crystalline, extremely air-sensitive complex, analysing as  $\text{Mg}(\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{-}o)(\text{thf})$ , (3), is obtained in moderate yields (50%). Its i.r. spectrum is indicative of a thf molecule strongly bound to magnesium; thus, the strong



$\nu_{\text{asym}}(\text{C-O-C})$  band of free thf moves from  $1069 \text{ cm}^{-1}$  to lower wavenumber on co-ordination<sup>17</sup> (in the present case to  $1020 \text{ cm}^{-1}$ ). Unfortunately the sparing solubility of complex (3) precluded a cryoscopic molecular weight determination or the use of spectroscopic techniques other than  $^1\text{H}$  n.m.r. to shed light on its constitution. The latter simply indicates a symmetrically bound *o*-xylidene, there being a singlet corresponding to equivalent methylene groups and equivalent protons within each methylene while the aromatic resonances constitute an AA'BB' spectrum. In contrast,  $\eta^4$ -bonding in  $[\text{Fe}(\text{CO})_3(\eta^4\text{-CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{-}o)]$  results in *endo*- and *exo*-methylene hydrogens displaying two doublets,  $^2J(^1\text{H}^1\text{H}) = 3.2 \text{ Hz}$ .<sup>1</sup> However, the symmetry of the ligand in (3) does not discriminate between a metallocycle (III) and an oligomeric structure with *o*-xylidenes bridging successive magnesium atoms, (IV). In resorting to a single-crystal *X*-ray structure determination, crystals of complex (3) were found unsatisfactory. However, it was noted that solutions of (A) greater than *ca.*  $0.10 \text{ mol dm}^{-3}$  after several days at room temperature deposited substantial quantities of good quality crystals (4). These were massive, colourless needles, which readily lost solvent when isolated. Consequently a crystal was sealed in a capillary with mother-liquor present for the *X*-ray data collection.

The structure determination of complex (4) (see Figure and Tables 1–3) establishes the empirical formula as  $\text{Mg}(\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{-}o)(\text{thf})_2$ . The molecular formula is that of the trimer, one half of which comprises the asymmetric unit, with the other half of the molecule generated by a crystallographic two-fold axis which passes through one of the two independent magnesium atoms. In the molecule of  $[\{\text{Mg}(\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{-}o)(\text{thf})_2\}_3]$ , the three magnesium atoms are chemically equivalent as are each of the *o*-xylidene ligands and the tetrahydrofuran molecules. Each magnesium atom is bridged to the other two magnesium atoms by way of an *o*-xylidene ligand, so that the system of three magnesium atoms and three *o*-xylidene ligand moieties comprises a macro-metallocycle, somewhat reminiscent of the system  $[\{\text{Hg}(\text{C}_6\text{F}_4)\}_3]$ , (7).<sup>18</sup>

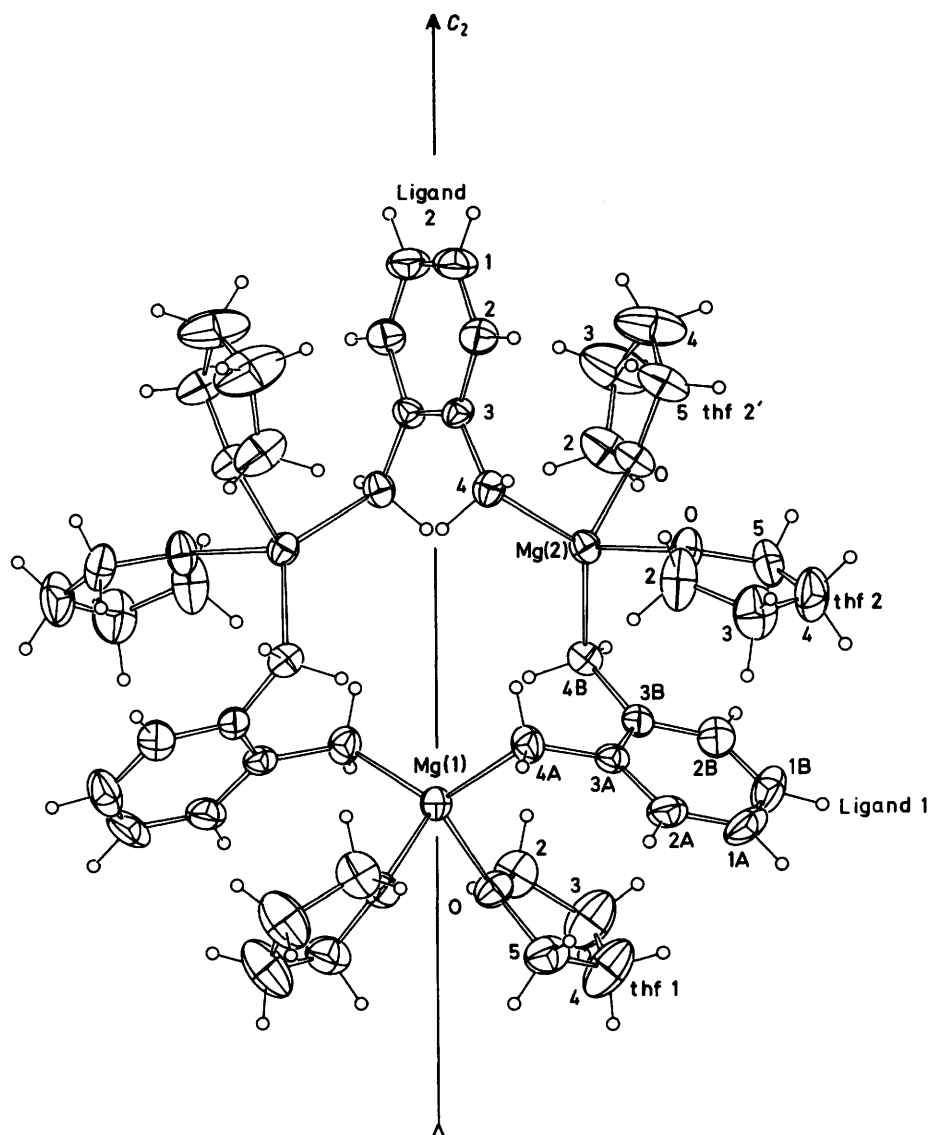


Figure. A single 'molecule' of (4), projected normal to the plane of the magnesium atoms. 20% Thermal ellipsoids are shown for the non-hydrogen atoms; the hydrogen atoms are depicted as circles of arbitrary radius 0.1 Å. Non-hydrogen-atom labelling is given

Each of the magnesium atoms is four-co-ordinated, two of the co-ordination sites being occupied by carbon atoms from a pair of non-identical *o*-xylidene ligands, and the other two being occupied by the oxygen atoms of a pair of tetrahydrofuran molecules. Although the only crystallographically imposed symmetry element is a two-fold axis through Mg(1) (see Figure), the overall point group symmetry of the trimer approximates to  $D_3$ . The Mg-C and the Mg-OC<sub>4</sub>H<sub>8</sub> distances are in the range 2.154(8)–2.170(8) and 2.063(5)–2.081(6) Å respectively; both are fairly typical values for 'tetrahedral' magnesium. Of more interest is the angular geometry about the magnesium. The angles between the carbon atoms in each case lie well above the tetrahedral values, being 126.8(3) and 130.5(3)°, while the angle between the oxygen atoms is correspondingly reduced, 94.1(2) and 94.0(2)°. This indicates that the proximity of the electron density to the magnesium atom is more pronounced in the Mg-C rather than the Mg-O bond, despite the fact that the former bonds are the longer, but in agreement with simple electronegativity considerations.

These results are consistent with electron-pair repulsion theory, predicting a 'bond-length ratio' of Mg-C to Mg-O of 0.7 for the observed tetrahedral distortion.<sup>19</sup> [Such a distortion may account for the observed 'trimeric' structure in preference to a metallocyclic alternative, based on (III), because in the latter the C-Mg-C angle (the bite angle) would inevitably be low.] Our findings on the structure of complex (4) may be compared with those for 1,7-dimagnesacyclododecane,<sup>20</sup> in which the two four-co-ordinate magnesium atoms are incorporated in a twelve-membered ring; in that case the angles C-Mg-C and O(thf)-C-O(thf) are 141.5 and 90.8°, respectively, correlating with the slightly greater observed Mg-O distances, 2.089(9) and 2.110(7) Å. The rather large difference between the C-Mg-C angles in these two compounds may also be due to steric considerations, since the twelve-membered ring 1,7-dimagnesacyclododecane is likely to be more flexible than the 15-membered ring of complex (4), because the *o*-xylidene units constitute relatively rigid linking groups between the magnesium atoms. In this context we note that in

**Table 1.** Non-hydrogen atom co-ordinates (for atom numbering, see Figure)

Atom	x	y	z	x	y	z
<b>(a) Magnesiums 1,2</b>						
	0.000 0(—)	0.000 0(—)	0.000 0(—)	0.170 0(1)	0.153 8(3)	0.045 92(5)
<b>(b) Tetrahydrofuran 1</b>						
O(1)	−0.057 2(2)	0.053 9(6)	−0.032 5(1)			
C(2)	−0.047 3(4)	0.157 1(11)	−0.056 2(2)			
C(3)	−0.077 6(7)	0.105 2(19)	−0.082 2(3)			
C(4)	−0.110 1(7)	−0.014 3(17)	−0.073 8(3)			
C(5)	−0.101 0(4)	−0.044 2(11)	−0.042 5(3)			
<b>(c) Tetrahydrofurans 2 and 2'</b>						
O(1)	0.167 6(3)	0.371 6(5)	0.061 2(1)	0.228 0(2)	0.087 7(6)	0.077 2(1)
C(2)	0.158 5(4)	0.418 2(11)	0.091 3(2)	0.279 1(4)	0.157 9(12)	0.080 7(2)
C(3)	0.137 4(6)	0.566 5(14)	0.090 3(3)	0.316 7(5)	0.048 2(18)	0.090 2(4)
C(4)	0.125 6(6)	0.603 7(13)	0.059 8(3)	0.288 5(8)	−0.087 3(17)	0.093 1(4)
C(5)	0.147 8(6)	0.488 9(11)	0.041 6(2)	0.234 0(5)	−0.063 5(13)	0.085 3(3)
<b>(d) <i>o</i>-Xylidene ligand 1, parts A,B</b>						
C(1)	−0.016 4(5)	0.394 6(14)	0.083 2(5)	0.007 7(6)	0.310 8(17)	0.104 9(3)
C(2)	−0.006 3(4)	0.359 8(10)	0.053 1(3)	0.042 7(4)	0.199 7(11)	0.096 9(2)
C(3)	0.029 2(3)	0.246 5(9)	0.044 3(2)	0.054 0(3)	0.163 7(9)	0.067 3(2)
C(4)	0.039 0(3)	0.206 4(9)	0.012 4(17)	0.095 6(3)	0.047 9(8)	0.059 8(2)
<b>(e) <i>o</i>-Xylidene ligand 2</b>						
C(1)	0.359 2(3)	0.076 8(10)	−0.000 1(3)			
C(2)	0.310 4(4)	0.149 9(9)	0.000 1(2)			
C(3)	0.259 7(3)	0.078 7(7)	0.000 2(2)			
C(4)	0.208 9(3)	0.163 1(8)	0.002 1(2)			

**Table 2.** Geometries of the magnesium environments (for atom numbering, see Figure).  $r(\text{Mg-L})$  (Å) is the metal–ligand distance; other entries are the angles (°) subtended at the magnesium by the two relevant ligand atoms

<b>(a) Mg(1): italicised atoms are generated by the two-fold rotor (<math>x, \bar{y}, \bar{z}</math>)</b>				
	$r(\text{Mg-L})$	O(1)	C(4)	O(1)
C(4)	2.154(8)	106.4(3)	126.8(3)	109.1(3)
O(1)	2.073(5)		109.1(3)	94.1(2)
C(4)				106.4(3)
O(1)				
<b>(b) Mg(2): C(4B) and C(4) belong to ligands 1,2 respectively while O(1), O(1') belong to tetrahydrofurans 2,2'</b>				
	$r(\text{Mg-L})$	O(1)	C(4)	O(1')
C(4B)	2.158(8)	107.3(3)	130.5(3)	105.8(3)
O(1)	2.063(5)		105.7(3)	94.0(2)
C(4)	2.170(8)			107.7(3)
O(1')	2.081(6)			

1,6-dimagnesacyclododecane C–Mg–C is 128°, and this ring is presumably more strained than the twelve-membered analogue.<sup>21</sup>

An indication that the magnesium–oxygen bonds in these compounds are rather weak comes from a comparison with compounds in which the magnesium has a higher co-ordination number; e.g. in octahedral six-co-ordinate complexes Mg–O is typically *ca.* 2.08 Å, as in  $[\text{NH}_4]_2[\text{Mg}(\text{OH}_2)_6][\text{SO}_4]_2$ .<sup>22</sup>

Tetrahydrofuran geometries in compound (4) are imprecise as a consequence of the presence of very high thermal motion; alternatively, the large ellipsoids (see Figure) may arise from disorder among the peripheral atoms of the solvent molecules, the skeletons of which are not significantly non-coplanar. In the *o*-xylidene moieties, the geometrical parameters suggest that the bonding to the magnesium atom is purely  $\sigma$  in nature.

**Table 3.** *o*-Xylidene geometries. Where two values occur in each entry these correspond to parts A, B of the ligand respectively (for atom numbering, see Figure)

Ligand	1	2
<b>Distances/Å</b>		
C(1)–C(1)	1.36(2)	1.37(1)
C(1)–C(2)	1.39(2), 1.37(2)	1.37(1)
C(2)–C(3)	1.39(1), 1.38(1)	1.40(1)
C(3)–C(3)	1.40(1)	1.41(1)
C(3)–C(4)	1.48(1), 1.50(1)	1.47(1)
<b>Angles/°</b>		
C(1)–C(1)–C(2)	118.4(12), 119.7(13)	118.5(8)
C(1)–C(2)–C(3)	123.0(10), 123.0(10)	124.5(8)
C(2)–C(3)–C(3)	117.2(8), 118.6(8)	117.0(7)
C(2)–C(3)–C(4)	123.2(8), 120.7(8)	121.9(6)
C(3)–C(3)–C(4)	119.5(7), 120.5(7)	121.0(7)
C(3)–C(4)–Mg	112.2(5), 110.1(5)	114.2(5)

This conclusion is supported by the observation that the magnesium atoms lie well out of the ligand aromatic planes (by 1.99–2.12 Å) on either side, and are attached to C(4) (see Figure) in each case at an angle which lies close to the tetrahedral value. The molecular parameters of the *o*-xylidene moieties provide no indication of the loss of any degree of aromaticity.

The precise nature of the solution (A) from which the complexes (3) and (4) were isolated remains to be determined. It is likely, however, that the solvated di-Grignard reagent (1) is in equilibrium with solvated magnesium chloride and  $[\text{Mg}(\text{CH}_2\text{-C}_6\text{H}_4\text{CH}_2\text{-}o(\text{thf})_x)]$ , and the latter in turn is equilibrated with one or more macro-metallo-cycles such as (4). In a thf solution of 1,7-dimagnesacyclododecane, this dimer is in equilibrium with magnesacyclohexane (the monomer), while for the smaller C<sub>3</sub> chain the solid and solution structures are exclusively

**Table 4.** Tetrahydrofuran geometries (for atom numbering, see Figure)

Tetrahydrofuran	1	2	2'
Distances/Å			
O(1)-C(2)	1.42(1)	1.42(1)	1.42(1)
O(1)-C(5)	1.46(1)	1.45(1)	1.41(1)
C(2)-C(3)	1.45(2)	1.43(2)	1.42(2)
C(3)-C(4)	1.39(2)	1.42(2)	1.40(2)
C(4)-C(5)	1.43(2)	1.42(2)	1.41(2)
Angles/°			
Mg-O(1)-C(2)	123.2(5)	126.3(5)	124.0(5)
Mg-O(1)-C(5)	125.1(5)	120.0(5)	121.0(6)
C(2)-O(1)-C(5)	107.1(7)	107.2(7)	107.7(8)
O(1)-C(2)-C(3)	106.9(9)	107.6(8)	108.0(9)
O(1)-C(5)-C(4)	107.4(10)	108.5(8)	108.0(10)
C(2)-C(3)-C(4)	109.6(12)	108.9(10)	107.5(12)
C(5)-C(4)-C(3)	108.1(13)	106.8(10)	108.8(13)

dimeric.<sup>20</sup> A monomer for the latter would require a significantly reduced C-Mg-C angle and suggests that dimerisation in that case is predetermined by the larger steric requirements of the Mg-C *vs.* Mg-O bonds. It is therefore likely that in the present case any equilibrium involving chloride-free species would be in favour of dimers or higher oligomers; for a magnesabenzocyclopentene, (III), the calculated C-Mg-C angle, based on *o*-xylidene geometry as in complex (4), is 87°.

The value of reagent (A) for generation of metallocycles is exemplified by the synthesis of  $[\text{Pt}(\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{-}o)(\text{cod})]$  (cod = cyclo-octa-1,5-diene), (6), an air-stable complex derived from (A) and  $[\text{PtI}_2(\text{cod})]$ . Alkylation with  $\text{Mg}(\text{CH}_2\text{-C}_6\text{H}_4\text{CH}_2\text{-}o)(\text{thf})$ , (3), has been noted briefly by us in the synthesis of  $[\{\text{W}(\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{-}o)_2\text{O}\}_2\text{Mg}(\text{thf})_4]$  from  $\text{W}(\text{O})\text{Cl}_4$ .<sup>5</sup>

Formulation of (6) as a metallocycle (III), as opposed to (i) an oligomeric structure with  $\sigma$  bonding, (IV), or (ii) an  $\eta^4$ - or quasi- $\eta^4$ -metallocycle (I), is based on n.m.r. data. Thus, as in (3), the two  $\text{CH}_2$  groups and the protons of each  $\text{CH}_2$  of complex (6) are equivalent and  $^2J(^{195}\text{Pt}^1\text{H})$  92 Hz for these  $\alpha$ -hydrogens is identical to that found in the platinacyclopentene  $[\text{Pt}\{\text{CH}_2\text{C}(\text{Me})=\text{C}(\text{Me})\text{CH}_2\}(\text{cod})]$ , (8), and similar to that (86 Hz) of  $[\text{Pt}\{\text{CH}_2\text{C}(\text{Ph})=\text{C}(\text{Ph})\text{CH}_2\}(\text{cod})]$ , (9), and  $[\text{Pt}\{\text{CH}_2\text{C}(\text{=CH}_2)\text{C}(\text{=CH}_2)\text{CH}_2\}(\text{cod})]$  (103 Hz) (10).<sup>23</sup> The closely similar  $\text{CH}_2$  resonances in complexes (6) ( $\tau$  6.72) and  $[\text{Pt}(\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{-}o)(\text{PEt}_3)_2]$ , (11) ( $\tau$  6.45),<sup>7</sup> also lend credence to the metallocyclic structure. As for  $^{13}\text{C}$  n.m.r., the Pt- $^{13}\text{CH}_2$  signal is readily assigned both by its intensity and position by comparison with the similar compounds (8)–(10) cited in ref. 23. The coupling constant  $^1J(^{195}\text{Pt}^{13}\text{CH}_2)$ , 795 Hz, is characteristic of a platinum(II) alkyl and is larger than expected for a platinum atom coupled to olefinic carbons<sup>24</sup> [as would be the case for the isomeric structure, (I)]. Assignment of the aromatic resonances is consistent with those observed in (11),<sup>7</sup> and the  $\text{C}_a, \text{C}_b$  resonances [see (6)] are very similar to those found in complexes (8) and (10);<sup>23</sup>  $^3J(^{195}\text{Pt}^{13}\text{C}_b)$  is 107, 110, and 82 Hz for (6), (8), and (10) respectively.

Use of the same conditions as for the synthesis of reagent (A) in the case of the durene derivative, which behaves as (5), resulted in a slightly diminished yield (79%) of the new di-Grignard reagent (B) compared with that for (A). Unlike (A), no complex was obtained on cooling (B), and subsequent concentration and cooling gave only  $\text{MgCl}_2(\text{thf})_2$ . Preliminary

investigations suggest that transition-metal derivatives obtained from (5) are more soluble than analogous products from (1).

In a previous communication we reported the syntheses

of metallocycles *meso*- $[\text{M}\{\text{CH}(\text{SiMe}_3)\text{C}_6\text{H}_4\text{CH}(\text{SiMe}_3)\text{-}o\}(\eta\text{-C}_5\text{H}_5)_2]$  (M = Ti, Zr, or Hf) derived from an organo-dilithium complex  $[\{o\text{-C}_6\text{H}_4(\text{CHSiMe}_3)_2\}\{\text{Li}(\text{tmen})\}_2]$  and a metallocene dichloride.<sup>5</sup> We now used this lithium reagent with the *d*<sup>8</sup> substrate<sup>25</sup>  $[\text{PtCl}_2(\text{dppe})]$  [dppe =  $\text{Ph}_2\text{P}(\text{CH}_2)_2\text{-PPh}_2$ ], in anticipation of generating a bis-trimethylsilylated-platinabenzocyclopentene; however, reduction resulted, with isolation of  $[\text{Pt}(\text{dppe})_2]$ . A possible source of reduction is generation of a substituted *o*-quinodimethide species, proposed in the reduction of  $\text{W}^{\text{VI}}$  to  $\text{W}^{\text{V}}$  during the alkylation of  $\text{W}(\text{O})\text{Cl}_4$  with (1) or (3).<sup>5</sup>

## Experimental

**General Procedures.**—Owing to the air-sensitivity of all complexes except the platinabenzocyclopentene (6), manipulations were carried out under a dry and oxygen-free argon atmosphere or *in vacuo* using standard Schlenk techniques. Solvents were dried over and distilled from Na (toluene or benzene), Na- $\text{Ph}_2\text{CO}$  (diethyl ether or thf), or  $\text{CaH}_2$  (pentane), under a dinitrogen atmosphere, prior to use.

**Physical and Analytical Measurements.**—Elemental analyses were performed by the microanalytical laboratory at the University of Sussex. I.r. spectra were obtained from Nujol mulls between KBr plates using a Perkin-Elmer 457 spectrometer. Hydrogen-1 n.m.r. spectra were recorded on Varian T60 or Perkin-Elmer R32 spectrometers, carbon-13 n.m.r. data on a JEOL PFT 100 instrument.

**Preparation of the Di-Grignard of  $\alpha, \alpha'$ -Dichloro-*o*-xylene, (A).**—To a suspension of magnesium powder (3.56 g, 146 mmol) (May and Baker Ltd.) in thf (10 cm<sup>3</sup>) was added 1,2-dibromoethane (0.24 cm<sup>3</sup>), and the mixture was warmed until evolution of ethylene was evident, whereafter the mixture was stirred for 5 min. The thf was removed and replaced by fresh thf (40 cm<sup>3</sup>) and the mixture was stirred rapidly at room temperature. To this was added dropwise a solution of  $\alpha, \alpha'$ -dichloro-*o*-xylene (6.41 g, 36.6 mmol) in thf (450 cm<sup>3</sup>) over a period of 3.5 h. The solution became pale green and, after addition was complete, stirring was continued for 15 h at room temperature. Filtration into a calibrated flask and standardising *via* quenching 1-cm<sup>3</sup> aliquots with 0.1 mol dm<sup>-3</sup> HCl and titrating with 0.1 mol dm<sup>-3</sup> NaOH indicated that the solution (480 cm<sup>3</sup>) was 0.073 mol dm<sup>-3</sup> of the di-Grignard reagent (A) (96%).

**Isolation of  $\text{Mg}(\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2\text{-}o)(\text{thf})$ , (3).**—When solution (A) was reduced in volume by half *in vacuo* and then cooled to -40 °C, colourless needles were obtained. These were collected by removal of the solvent at -40 °C, washing with cold (-20 °C) diethyl ether, and drying *in vacuo*. This afforded complex (3) (3.67 g, 50%), m.p. 165 °C (decomp.) (Found: C, 70.3; H, 7.9.  $\text{C}_{12}\text{H}_{16}\text{MgO}$  requires C, 71.9; H, 8.0%)  $[\text{Mg}(\text{CH}_2\text{-C}_6\text{H}_4\text{CH}_2\text{-}o) \cdot 1.33\text{thf}$  requires C, 71.3; H, 8.4%]. N.m.r.:  $^1\text{H}$  ( $[\text{H}_8]\text{thf}$ ),  $\tau$  8.71 (s, 4 H,  $\text{CH}_2$ ) and 3.52, 3.92 (centre of each multiplet of AA'BB', 4 H,  $\text{C}_6\text{H}_4$ );  $^{13}\text{C}$  (thf and  $[\text{H}_8]\text{thf}$ ,  $^1\text{H}$  decoupled), 115.9, 121.4 ( $\text{C}_b$  and  $\text{C}_c$ , not assigned), and 148.5 p.p.m. ( $\text{C}_a$ ) [labelled as in (6)]. I.r.: 3 085w, 1 564m, 1 540m, 1 343w, 1 304m, 1 274m, 1 204ms, 1 020ms, 910m, 870m, 832ms, 822m, 748m, 734m, 724ms, 675w, 595m, 514m, 453m, 418m, 387w, 370m, and 290ms cm<sup>-1</sup>.

**Preparation of the Di-Grignard Reagent of 1,2-Bis(chloromethyl)-4,5-dimethylbenzene, (B).**—To a stirred suspension of magnesium powder (0.96 g, 39.4 mmol), activated as for (A) using 1,2-dibromoethane (0.07 cm<sup>3</sup>) in thf (25 cm<sup>3</sup>), was added 1,2-bis(chloromethyl)-4,5-dimethylbenzene (2.0 g, 9.85 mmol) in thf (100 cm<sup>3</sup>) over 3 h. After 15 h the mixture was filtered to afford a solution (120 cm<sup>3</sup>) of the di-Grignard reagent (B) (0.065 mol dm<sup>-3</sup>, 79%). Successive concentration and cooling yielded only MgCl<sub>2</sub>(thf)<sub>2</sub>. Evaporation of the mother-liquors gave a yellow oil.

**Preparation of [Pt(CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>-o)(cod)], (6).**—To a stirred suspension of [PtI<sub>2</sub>(cod)] (2.84 g, 5.09 mmol) in thf (10 cm<sup>3</sup>) at room temperature was added the di-Grignard reagent (A) (60.7 cm<sup>3</sup>, 5.09 mmol; 0.084 mol dm<sup>-3</sup>). After 8 h the thf was removed by evaporation and replaced with benzene (30 cm<sup>3</sup>). An ammonium chloride solution was added and the benzene layer separated and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solution was taken to dryness and the oily residue crystallised from thf-OEt<sub>2</sub> (1 : 2) at -60 °C, with difficulty. Recrystallisation from OEt<sub>2</sub> gave colourless crystals of complex (6) (1.05 g, 51%) (Found: C, 47.5; H, 4.9. C<sub>16</sub>H<sub>20</sub>Pt requires C, 47.2; H, 5.0%), m.p. 165 °C. N.m.r.: <sup>1</sup>H (CDCl<sub>3</sub>) τ 6.72 [s, 4 H, CH<sub>2</sub>, <sup>2</sup>J(<sup>195</sup>Pt-<sup>1</sup>H) 92.0 Hz], 3.08 [m, 4 H, C<sub>6</sub>H<sub>4</sub>], 5.02 [s, br, 4 H, cod CH, <sup>2</sup>J(<sup>195</sup>Pt-<sup>1</sup>H) 41.0 Hz], and 7.67 [s, br, 8 H, cod CH<sub>2</sub>, <sup>4</sup>J(<sup>195</sup>Pt-<sup>1</sup>H) 16.0 Hz]; <sup>13</sup>C(CDCl<sub>3</sub>, <sup>1</sup>H decoupled), 34.1 [Pt-CH<sub>2</sub>, <sup>1</sup>J(<sup>195</sup>Pt-<sup>13</sup>C) 795.0 Hz], 152.5 (C<sub>a</sub>), 128.5 [C<sub>b</sub>, <sup>3</sup>J(<sup>195</sup>Pt-<sup>13</sup>C) 107 Hz], 124.3 (C<sub>c</sub>), 97.9 [cod CH, <sup>1</sup>J(<sup>195</sup>Pt-<sup>13</sup>C) 54.9 Hz], and 29.6 p.p.m. (cod CH<sub>2</sub>). I.r.: 3 045w, 1 576m, 1 332w, 1 312w, 1 286m, 1 230m, 1 178m, 1 115m, 1 070w, 1 027m, 974m, 930m, 858m, 820m, 748m, 752s, 656m, 570m, 545w, 456m, and 422m cm<sup>-1</sup>.

**Reaction of [PtCl<sub>2</sub>(dppe)] with [o-C<sub>6</sub>H<sub>4</sub>(CHSiMe<sub>3</sub>)<sub>2</sub>]-{Li(tmen)}<sub>2</sub>.**—The compound [PtCl<sub>2</sub>(dppe)] (1.07 g, 1.66 mmol) was added to a diethyl ether solution of the organodilithium complex (0.80 g, 1.62 mmol) in diethyl ether (75 cm<sup>3</sup>) at -78 °C. After 15 min, the yellow solution was warmed to room temperature, the solvent was removed *in vacuo*, and toluene (20 cm<sup>3</sup>) was added. Filtration followed by concentration *in vacuo* to ca. 5 cm<sup>3</sup>, addition of pentane (15 cm<sup>3</sup>), and cooling to -40 °C afforded yellow needles of [Pt(dppe)<sub>2</sub>] (0.80 g, 45%) (n.m.r. spectra of authentic sample<sup>26</sup>).

**Crystallography.**—**Crystal data.** Mg<sub>3</sub>(C<sub>8</sub>H<sub>8</sub>)<sub>3</sub>(C<sub>4</sub>H<sub>8</sub>O)<sub>6</sub> ≡ C<sub>48</sub>H<sub>72</sub>Mg<sub>3</sub>O<sub>6</sub>, *M* = 818.0, Orthorhombic, space group *F2dd* (variant of *C2<sub>v</sub>*, no. 43), *a* = 24.706(8), *b* = 8.948(3), *c* = 44.315(9) Å, *U* = 9 797(5) Å<sup>3</sup>, *Z* = 8, *D<sub>c</sub>* = 1.11 g cm<sup>-3</sup>, *F*(000) = 3 552, monochromatic Mo-*K*<sub>α</sub> radiation, λ = 0.7106 Å, μ<sub>Mo</sub> = 1.04 cm<sup>-1</sup>, 295 K.

**Structure determination.** A unique data set was measured within the limit 2θ<sub>max</sub> = 45°, using a Syntex *P2<sub>1</sub>* four-circle diffractometer in conventional 2θ-θ scan mode, yielding 1 660 independent reflections, 1 117 of which with *I* > 3σ(*I*) were considered 'observed' and used in the least-squares refinement without absorption correction after solution of the structure by direct methods. In the least-squares refinement, the parameters were blocked according to the xylene or furan moieties; anisotropic thermal parameters were employed for the non-hydrogen atoms, while for the hydrogen atoms (*x, y, z, U*) were constrained at estimated values. Residuals at convergence (*R, R'*) were 0.054, 0.055, reflection weights being [σ<sup>2</sup>(*F<sub>o</sub>*) + 0.0005(*F<sub>o</sub>*)<sup>2</sup>]<sup>-1</sup>. Neutral-atom scattering factors were

used, those for the non-hydrogen atoms being corrected for anomalous dispersion (*f', f''*).<sup>27</sup> Computation was carried out using the X-RAY 76 program system<sup>28</sup> implemented on a Perkin-Elmer 3240 computer.

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