Metal Complexes derived from the *o*-Xylylidene Ligand, *o*-$C_6H_4(CH_2^-)_2$, and the *X*-Ray Crystal and Molecular Structure of the Metallocycle $[Zr(\eta\text{-}C_5H_5)_2\{(CH_2)_2C_6H_4\text{-}o\}]$

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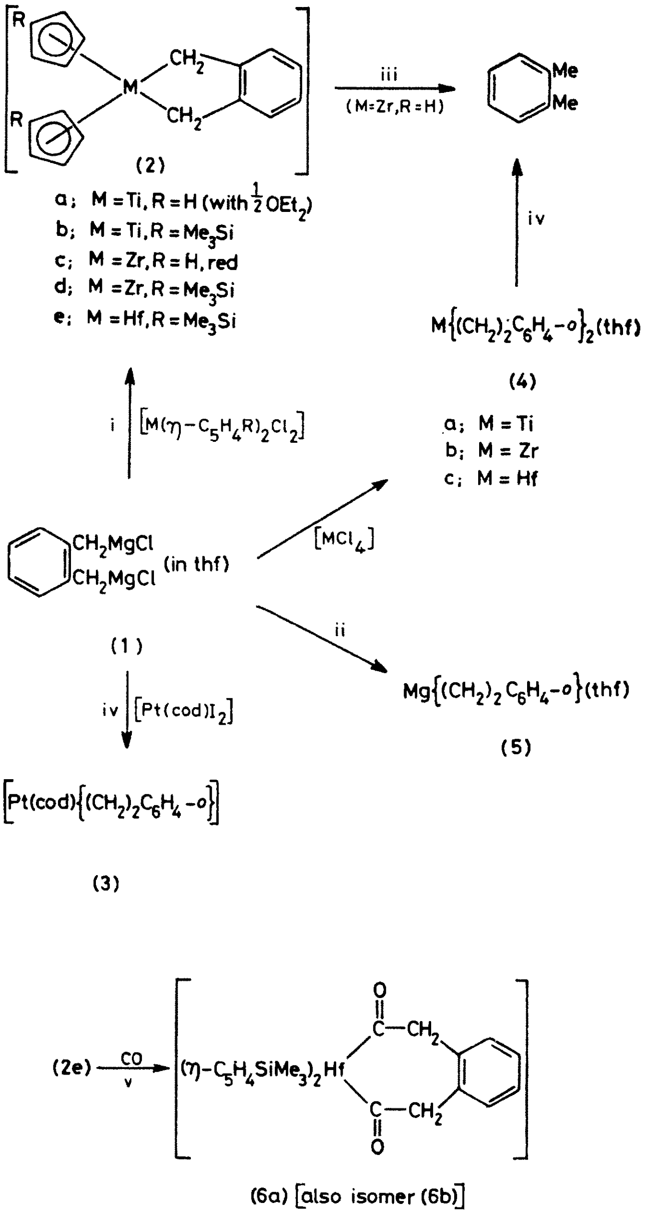
Summary From the new di-Grignard reagent *o*-$C_6H_4(CH_2MgCl)_2$ [abbreviated as $L(MgCl)_2$] (i) the thermally stable metallobenzocyclopentenes $[M(\eta\text{-}C_5H_4R)_2L]$ (R = Me_3Si and M = Ti, Zr, or Hf; or R = H and M = Ti or Zr) and [Pt(cod)L], (ii) the η^1-diacyl $[Hf(\eta\text{-}C_5H_4SiMe_3)_2\{C(:O)LC(:O)\}]$ *via* $[Hf(\eta\text{-}C_5H_4SiMe_3)_2L]$ and CO, and (iii) the pyrophoric ML_2(thf) (M = Ti, Zr, or Hf) and MgL(thf) have been obtained; *X*-ray analysis of the title compound to $R = 0{\cdot}021$ shows an average Zr–CH_2 distance of 2·300(2) Å, $\angle CH_2ZrCH_2 = 77{\cdot}4(2)°$, with the methylene carbons 0·11 and 0·12 Å out of the plane of the C_6 ring.

WE draw attention to the new bidentate alkyl ligand *o*-$C_6H_4(CH_2^-)_2$ which promises to have an extensive organometallic chemistry. Like the isoelectronic catecholate dianion, *o*-$C_6H_4(O^-)_2$, it may, in principle, bridge two metals, act as a chelate (in metallobenzocyclopentenes), or bind to a metal as a substituted mono- or di-η^3-allyl ligand;[1] by intramolecular electron transfer it may alternatively behave as the neutral *o*-quinodimethide.[2] {From a buta-1,3-diene and either (a) Mg with $[Hf(cot)Cl_2]$ or (b) $[Pt(cod)_2]$ (cot = cyclo-octatetraene, cod = cyclo-octa-1,5-diene), the metallocyclopentene $[Hf(cot)(CH_2CH:CHCH_2]$[3] or $[Pt(cod)\{CH_2C(Me):C(MeO)CH_2\}]$[4] have been obtained.}

The key feature, (a), is the unexpected[5] high yield (96%) synthesis of the di-Grignard reagent (**1**), obtained as a dilute solution (*ca.* 0·075 M) in tetrahydrofuran (thf) from *o*-$C_6H_4(CH_2Cl)_2$. The choice of dihalide, solvent, and dilution is critical; $(CH_2Br)_2$ was used as activator. Further noteworthy aspects of this work are: (b) the preparation of metallobenzocyclopentenes, ranging from the d^0 Ti^{IV}, Zr^{IV}, and Hf^{IV} compounds (**2**) to the d^8 Pt^{II} cyclo-octa-1,5-diene complex (**3**) (see Scheme);† (c) crystallographic data on one of these, (**2c**), which confirm the formulation (see Figure); (d) the isolation of complexes free from π^*-acceptor ligands: the pyrophoric, insoluble Ti^{IV}, Zr^{IV}, and $Hf^{IV}ML_2$(thf), (**4**), and the crystalline thf-soluble MgL(thf), (**5**), [L = $(CH_2)_2C_6H_4$-*o*]; and (e) the easy carbonylation of $[Hf(\eta\text{-}C_5H_4SiMe_3)_2L]$, (**2e**), to give the 1:2 CO adduct (**6a**), a novel metallobenzocyclohepta-2,7-dione.

The relatively high thermal stability of the d^0 complexes (**2**), (*cf.* the m.p.'s, and the formation of *o*-xylene on pyrolysis) contrasts with the lability of saturated analogues: *e.g.*, $[Ti(\eta\text{-}C_5H_5)_2(CH_2)_4]$ decomposes by β-elimination below −20 °C.[6] Heating ZrL_2(thf) (**4b**), at 190 °C gave thf, *o*-xylene, and a brown highly pyrophoric residue.



SCHEME. *Reagents and conditions*: i, thf, −78 °C and warming to *ca.* 20 °C. ii, Removal of bulk of thf *in vacuo* and cooling. iii, In low yield by prolonged heating at 150 °C or photolysis. iv, Heat to 190 °C *in vacuo*. v, n-pentane 1 atm CO, *ca.* 20 °C.

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† The new compounds (**2**)—(**6**) have been characterised by analytical and spectral data. (**2a**), violet, m.p. 132 °C; (**2b**), blue, m.p. 130 °C; (**2c**), red, m.p. 177 °C; (**2d**), red, m.p. 133 °C; (**2e**), yellow, m.p. 128 °C; (**3**), white, m.p. 165 °C; (**4a**), black, m.p. 130 °C (decomp.); (**4b**), yellow, m.p. 120 °C (decomp.); (**4c**), pale yellow, m.p. 130 °C (decomp.); (**5**), white, m.p. 165 °C; (**6a**), white, m.p. 224 °C.

The insolubility of compounds (**4**) and of MgL(thf) (except in thf), (**5**), suggests that these may be polymers, with the *o*-xylylidene ligand L bridging successive metal atoms. The metallobenzocyclopentene formulations for complexes (**2**) and (**3**) rest not only on the *X*-ray data for (**2c**) but also on n.m.r. observations. For example, in [Pt(cod)L] (**3**), the two CH_2's of L are equivalent and $^2J(^{195}Pt-^1H)$ (92 Hz) is identical to that found in $[Pt(cod)CH_2C(Me):C(Me)CH_2]$, and the high $^1J(^{195}Pt-^{13}CH_2)$ (795 Hz) is characteristic of a Pt^{II} alkyl. The average $Zr-CH_2$ bond length in (**2c**), 2·300(2) Å, is appropriate for a Zr^{IV} alkyl.[7] The 'angle of fold' [defined as that made by the plane of Zr, C(1), and C(8) with the extension of that of C(1), C(2), C(3), and C(8)] is 53·1°, and C(1) and C(8) are 0·11 and 0·12 Å out of the plane of the C_6 group (see Figure). The crystal structure was solved from 970 observed reflections and refined to R = 0·021, with anisoptropic thermal parameters for all non-hydrogen atoms.

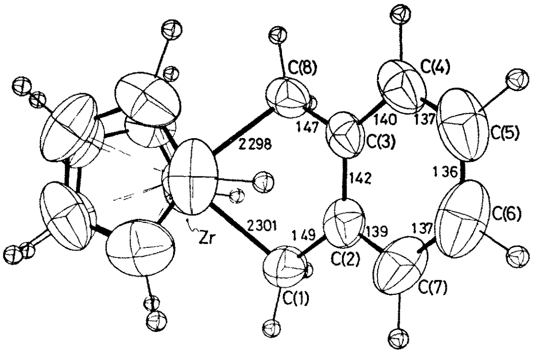

FIGURE. Molecular structure of $[Zr(\eta-C_5H_5)_2\{(CH_2)_2C_6H_4-o\}]$, showing important bond lengths and the $\angle CH_2ZrCH_2$ angle. The $Zr-C(\eta)$ bond lengths range from 2·496(7) to 2·546(7) Å, and average 2·521 Å. E.s.d.'s are Zr–C 0·005, C–C 0·02.

Crystal data: $C_{18}H_{18}Zr$, M = 325·6, orthorhombic, a = 8·276(6), b = 11·075(7), c = 15·721(7) Å, U = 1440·9 Å^3, Z = 4, D_c = 1·50 g cm^{-3}, μ(Mo-K_α) = 7·35 cm^{-1}, $F(000)$ = 664, λ(Mo-K_α) = 0·71069 Å, space group $P2_12_12_1$.‡

The formation of the chelating Hf^{IV} η^1-diacyl (**6a**) from CO and $[Hf(\eta-C_5H_4SiMe_3)_2L]$, (**2e**), contrasts with (i) the η^2-monoacyl obtained from $[Zr(\eta-C_5H_5)_2R^1R^2]$ [$R^1 = R^2$ = alkyl[8a–c] or aryl[8b,8d], or R^1 = Me[8c] and $R^2 = (Me_3Si)_2CH$] or $[Hf(\eta-C_5H_5)_2R_2]$ (R = Me,$PhCH_2$, or Ph),[8b] (ii) the rearrangement or C–C coupling observed for the reaction of CO with $[Zr(\eta-C_5Me_5)_2Me_2]$ or $[Zr(\eta-C_5H_5)_2(CH_2)_4]$,[9] and (iii) the formation of $[Ti(\eta-C_5H_4R)_2(CO)_2]$ from complexes (**2a**) or (**2b**).

The assignment of structure for the metallobenzocyclohepta-2,7-dione (**6a**) was aided by repeating the carbonylation with ^{13}CO, whence $\nu(^{12}CO)$ = 1668 cm^{-1}, *cf.*,[6] 1720 cm^{-1} in $[Ti(\eta-C_5H_5)_2\{\eta^1-C(:O)(CH_2)_4\}]$, $\nu(^{13}CO)$ = 1613 cm^{-1}, $\tau(CH_2)$ = 6·45, $^2J(^{13}COC^1H_2)$ = 4 Hz, $\delta(^{13}CH_2)$ = 36·3 p.p.m., $^1J(^{13}CO^{13}CH_2)$ = 61 Hz, and $\delta(CO)$ = 135·0 p.p.m. (i.r. data in Nujol, ^1H n.m.r. in CD_2Cl_2, and ^{13}C n.m.r. in $CDCl_3$). Complex (**6a**) rearranges to an isomer (**6b**) (believed to be a conformer) in $CDCl_3$ at *ca.* 35 °C in *ca.* 3 h, and (**6b**) reverts to (**6a**) at *ca.* 0 °C. Spectroscopic data for complex (**6b**) again shows identity of the CO, CH_2, Me_3Si, and C_5H_4 pairs, with $\nu(^{12}CO)$ = 1620 cm^{-1}, $\tau(CH_2)$ = 6·52, $\delta(^{13}CH_2)$ = 33·8 p.p.m., and $\delta(CO)$ = 130·8 p.p.m.

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‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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