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Phenyl derivatives of mercury functionalised in the 2-position with either a formyl or a vinyl group. Crystal structures of $Hg[C_6H_4(CHO)\text{-}2]Cl$ and $Hg[C_6H_4(CH{=}CH_2)\text{-}2]_2$

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Abstract

A convenient preparation of $Hg[C_6H_4(CH_2OH)\text{-}2]Cl$ (**1**) involves treatment of dilithiated benzyl alcohol with $HgCl_2$. **1** is smoothly oxidised to $Hg[C_6H_4(CHO)\text{-}2]Cl$ (**2**) by reaction with pyridinium chlorochromate (PCC). The crystal structure of **2** reveals a two coordinate linear arrangement at mercury supplemented by weaker interactions with the aldehyde oxygen atoms both intramolecularly and intermolecularly. Treatment of **2** with NaI effects symmetrisation with the formation of $Hg[C_6H_4(CHO)\text{-}2]_2$ (**3**). Reaction between **3** and the Wittig reagent $Ph_3P{=}CH_2$ results in the formation of $Hg[C_6H_4(CH{=}CH_2)\text{-}2]_2$ (**4**). The crystal structure of **4** has been determined. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Organometallic complexes; *o*-Vinylphenyl complexes; *o*-Formylphenyl complexes; Mercury

1. Introduction

In previous work we have established that a convenient route to coordinatively unsaturated σ-aryl derivatives of ruthenium and osmium, $M(Ar)Cl(CO)(PPh_3)_2$, involves treatment of $MHCl(CO)(PPh_3)_3$ with $HgAr_2$ [1]. This transfer reaction has proved to be quite general and aryl groups bearing various functionalities have been successfully introduced to ruthenium or osmium [2]. Where the functional group is in the *ortho*-position and contains a potential donor atom there may be a chelating interaction with the metal centre, as observed for example in the *o*-nitrophenyl derivatives [3] and in the *o*-halophenyl derivatives [4]. In connection with other studies we required phenyl derivatives of ruthenium and osmium bearing *o*-formyl and *o*-vinyl substituents. It was therefore necessary to have available the corresponding mercury complexes and in this paper we describe the syntheses and structures of *o*-formylphenyl and *o*-vinylphenyl derivatives of mercury.

2. Results and discussion

2.1. Selective synthesis of $Hg[C_6H_4(CH_2OH)\text{-}2]Cl$ (1)

The compound, $Hg[C_6H_4(CH_2OH)\text{-}2]Cl$, seemed to offer, by the simple chemical transformations outlined in Scheme 1, convenient routes to the required *o*-formylphenyl and *o*-vinylphenyl derivatives of mercury. $Hg[C_6H_4(CH_2OH)\text{-}2]Cl$ has been described previously, in rather low yield, as one of the products of the direct mercuration of benzyl alcohol with $Hg(OAc)_2$ followed by treatment with NaCl [5]. The mixture from this reaction contains dimercurated as well as the 2-, and 4-substituted products but these workers were able to isolate $Hg[C_6H_4(CH_2OH)\text{-}2]Cl$ by fractional crystallisation and to oxidise it readily with $KMnO_4$ to $Hg[C_6H_4(CO_2H)\text{-}2]Cl$ [5]. However, in our hands this direct mercuration and fractional crystallisation procedure did not give pure $Hg[C_6H_4(CH_2OH)\text{-}2]Cl$, the product always being contaminated (as revealed by thin layer chromatography) with $Hg[C_6H_4(CH_2OH)\text{-}4]Cl$. To avoid this difficult separation of isomers a selective synthesis of $Hg[C_6H_4(CH_2OH)\text{-}2]Cl$ was sought. Meyer and Seebach showed that double deprotonation of benzyl alcohol with butyl lithium in the presence of

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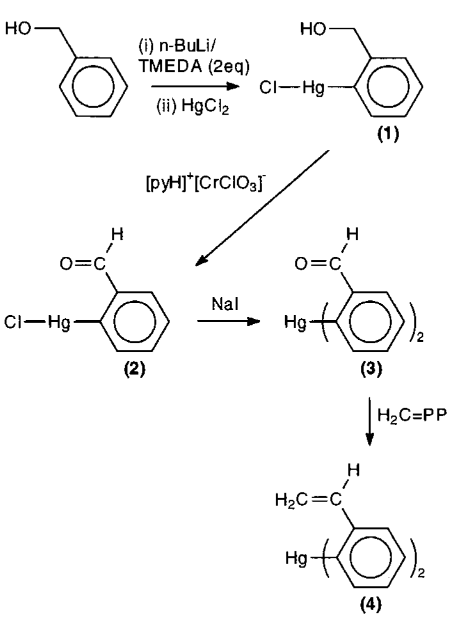

Scheme 1. Synthesis of *o*-formylphenyl and *o*-vinylphenyl derivatives of mercury.

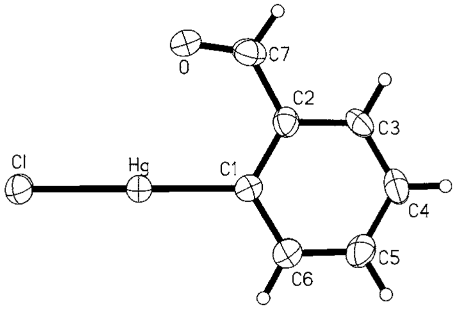

Fig. 1. Molecular geometry of Hg[C_6H_4(CHO)-2]Cl (**2**).

TMEDA, followed by addition of Me_3SnCl provided a convenient way to prepare Me_3Sn[C_6H_4(CH_2OH)-2] [6]. Accordingly, dilithiated benzyl alcohol was treated with $HgCl_2$ (see Scheme 1) to produce pure Hg[C_6H_4(CH_2-OH)-2]Cl (**1**) in 56% yield.

2.2. Synthesis of Hg[C_6H_4(CHO)-2]Cl (2) from oxidation of 1 with PCC

The oxidation of alcohols to aldehydes with pyridinium chlorochromate (PCC) is a well-known procedure in organic chemistry [7], and there is even precedent for this procedure effecting oxidation of an alcohol function in a complex alkyl ligand bound to mercury [8]. Room temperature oxidation of a dichloromethane solution of **1** with PCC (see Scheme 1) proved to be an effective way to prepare pure Hg[C_6H_4(CHO)-2]Cl (**2**) in better than 70% yield. Compound **2** is much more soluble in organic solvents than **1**. The IR spectrum of **2** shows absorptions at 1694, 1661, and 1632 cm^{-1} in the region expected for an aldehyde function. The ^{1}H-NMR spectrum of **2** shows the resonances expected for the aromatic protons as a two proton multiplet at 7.57–7.61, and as apparent doublets at 7.74 ($^3J_{HH} = 7.3$ Hz) and 7.90 ppm ($^3J_{HH} = 7.4$ Hz). A resonance at 10.14 ppm is assigned to the aldehyde proton. In the ^{13}C-NMR spectrum signals for the tertiary aromatic carbons occur at 129.58, 135.75, 135.99 and 137.62 ppm, while the resonance for the aldehyde carbon appears at 193.69 ppm. A single crystal X-ray diffraction study was performed on this compound to examine whether the aldehyde oxygen interacts with the mercury.

Table 1
Data collection and processing parameters [a]

Compound	**2**	**4**
Empirical formula	C_7H_5ClHgO	$C_{16}H_{14}Hg$
Molecular weight	341.15	406.86
Temperature (K)	203	200
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/c$	*Pbcn*
Unit cell dimensions		
a (Å)	7.4413(3)	15.5833(2)
b (Å)	10.9583(3)	10.820592)
c (Å)	9.5083(3)	15.9340(3)
β (°)	102.5130(10)	
V ($Å^3$)	756.93(4)	2686.78(8)
Z	4	8
D_{calc} (g cm^{-3})	2.994	2.012
F(000)	608	1520
μ (mm^{-1})	20.61	11.43
Crystal size (mm)	0.21 × 0.16 × 0.08	0.45 × 0.21 × 0.03
θ(Min–max) (°)	2.8–26.0	2.3–27.3
Reflections collected	4728	15678
Independent reflections	1482 [$R_{int} = 0.0551$]	2960 [$R_{int} = 0.0674$]
A (min–max)	0.098–0.289	0.079–0.725
Function minimised	$w(F_o^2-F_c^2)^2$	$w(F_o^2-F_c^2)^2$
Goodness-of-fit on F^2	1.067	1.055
R (observed data)	0.0482	0.0443
R (all data)	0.1315	0.1311
Least-squares weights *a*, *b*	0.089, 0.000	0.068, 3.354
Difference map (min and max) (e $Å^{-3}$)	+3.43 and −2.97	+1.89 and −1.78

[a] $R = F_o - F_c/F_o$; $wR_2 = \{[w(F_o^2-F_c^2)^2]/[w(F_o^2)^2]\}^{1/2}$; weight = 1.0/$[{}^2(F_o^2)+a^*P^2+b^*P]$; $P = (F_o^2+2F_c^2)/3$.

2.3. Crystal structure of Hg[C_6H_4(CHO)-2]Cl (2)

Crystals of **2** suitable for X-ray analysis were grown from ethanol–benzene. The molecular geometry of this complex is depicted in Fig. 1 and selected interatomic distances and bond angles are given in Table 2. The structure reveals a linear arrangement about the mercury atom which is bonded both to a chloride and an *o*-formylphenyl group. The oxygen of the aldehyde group is pointing towards the mercury, the mercury–oxygen distance being 2.824(7) Å. A survey of 494 compounds containing mercury–oxygen bonds in the Cambridge Crystallographic Database reveals an average mercury–oxygen bond length of 2.538 Å, with a standard deviation of 0.273 Å. The mercury–oxygen distance of 2.824(7) Å in **2** is within the range of observed mercury–oxygen bond lengths. Despite this bonding interaction, the phenyl ring is not appreciably tilted since the Hg–C(1)–C(2) angle (119.8(9)°) is only slightly less than the Hg–C(1)–C(6) angle (121.3(7)°). An examination of the packing geometry of complex **2** reveals that the mercury atom is effectively four coordinate, since each mercury atom has two oxygen interactions. One is intramolecular, and the other is intermolecular, from an aldehyde oxygen of a neighbouring molecule (see Fig. 2). The Hg–O distance for the intermolecular interaction is 2.989(13) Å, slightly longer than that observed for the intramolecular interaction (2.824(7) Å). The O(A)–Hg–O(B) angle is 161.19(7)° and the C(1)–Hg–Cl angle is 173.8(2)°. A second intermolecular interaction (2.83 Å) exists between the aldehyde hydrogen and a neighbouring chloride. The consequence of these combined interactions is that a zig-zag chain is formed (see Fig. 2).

Table 2
Selected bond lengths (Å) and angles (°) for **2** [a]

Bond lengths	
Hg–C(1)	2.056(10)
Hg–Cl	2.326(3)
Hg–O	2.824(7)
Hg–O # 1	2.989(13)
O–C(7)	1.208(13)
Cl–H(7A)	2.83
Bond angles	
C(1)–Hg–Cl	173.8(2)
C(1)–Hg–O	71.9(3)
Cl–Hg–O	108.41(17)
O–Hg–O # 1	161.19(7)
Hg–C(1)–C(2)	119.8(7)
Hg–C(1)–C(6)	121.3(7)

[a] Symmetry transformations: # 1 − *X*, *Y* + 1/2, 1/2 − *Z*.

Table 3
Selected bond lengths (Å) and angles (°) for **4**

Bond lengths	
Hg–C(11)	2.092(7)
Hg–C(21)	2.096(6)
C(12)–C(17)	1.471(13)
C(17)–C(18)	1.325(12)
C(22)–C(27)	1.458(11)
C(27)–C(28)	1.337(12)
Bond angles	
C(11)–Hg–C(21)	178.2(3)
C(16)–C(11)–C(12)	118.7(7)
C(16)–C(11)–Hg	119.2(5)
C(12)–C(11)–Hg	122.1(7)
C(18)–C(17)–C(12)	128.5(9)
C(26)–C(21)–C(22)	118.8(7)
C(26)–C(21)–Hg	118.6(5)
C(22)–C(21)–Hg	122.4(6)
C(28)–C(27)–C(22)	128.7(8)

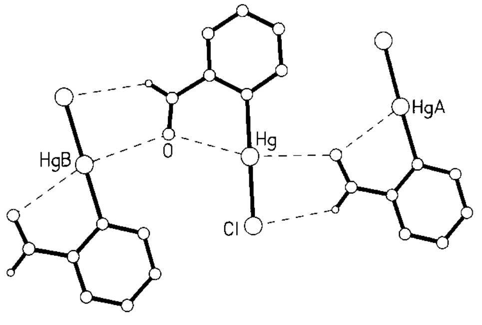

Fig. 2. Section of chain in the crystal of $Hg[C_6H_4(CHO)\text{-}2]Cl$ (**2**).

2.4. Symmetrisation of $Hg[C_6H_4(CHO)\text{-}2]Cl$ (2) to $Hg[C_6H_4(CHO)\text{-}2]_2$ (3)

Treatment of compound **2** with hydrazine hydrate in ethanol, or with basic sodium stannite, or alternatively with copper and ammonia all failed to effect the desired symmetrisation of $Hg[C_6H_4(CHO)\text{-}2]Cl$ to $Hg[C_6H_4(CHO)\text{-}2]_2$. However, $Hg[C_6H_4(CHO)\text{-}2]_2$ (**3**) was obtained in good yield by treatment of compound **2** with NaI in acetone (see Scheme 1). The IR spectrum of compound **3** includes many absorptions in the 1770–1550 cm^{-1} range appropriate for an aromatic aldehde. The ^{1}H-NMR spectrum shows resonances for the aromatic protons as apparent triplets at 7.50 ppm ($^3J_{HH}$ = 7.6 Hz) and 7.71 ($^3J_{HH}$ = 7.2 Hz), and apparent doublets at 7.81 ($^3J_{HH}$ = 7.2 Hz) and 7.93 ppm ($^3J_{HH}$ = 7.2 Hz). The aldehyde proton resonance is observed as a singlet at 10.27 ppm. The ^{13}C-NMR spectrum shows resonances for the aromatic carbons at 127.97, 134.29, 135.14, 139.10, 143.97 (C_q) and 168.47 ppm (C_q). A resonance assigned to the aldehyde carbon is observed at 195.48 ppm.

2.5. Synthesis of $Hg[C_6H_4(CH{=}CH_2)\text{-}2]_2$ (4)

Drefahl and Lorentz have reported that the *para*-substituted compound, $Hg[C_6H_4(CHO)\text{-}4]_2$ can be converted smoothly into $Hg[C_6H_4(CH{=}CH_2)\text{-}4]_2$ by treatment with $Ph_3P{=}CH_2$ [9]. Accordingly, compound **3** was treated with $Ph_3P{=}CH_2$ to produce $Hg[C_6H_4(CH{=}CH_2)\text{-}2]_2$ (**4**) in high yield (see Scheme 1). In the ^{1}H-NMR spectrum of **4** the three protons of the vinyl group are apparent from the presence of three doublet of doublet resonances with a geminal coupling constant of 1 Hz and vicinal coupling constants of 17 Hz (*trans*) and 11 Hz (*cis*), respectively. In the ^{13}C-

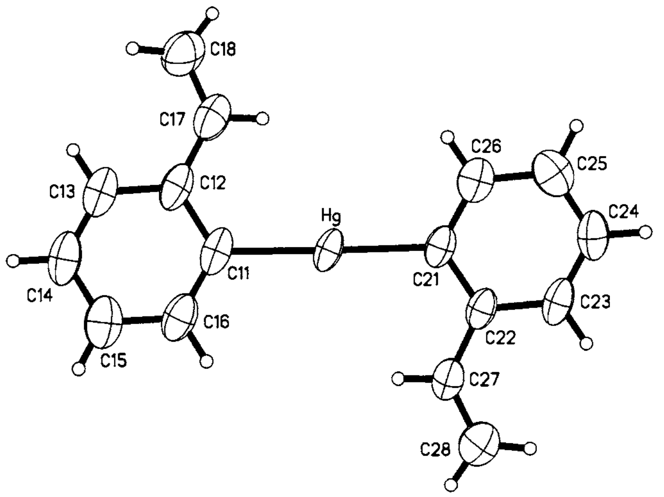

Fig. 3. Molecular geometry of $Hg[C_6H_4(CH{=}CH_2)\text{-}2]_2$ (**4**).

NMR spectrum of **4** the vinyl carbons appear at 140.72 (methine) and 114.68 (methylene), while the mercury-bound carbon appears at 170.69 ppm.

2.6. Crystal structure of $Hg[C_6H_4(CH{=}CH_2)\text{-}2]_2$ (4)

The molecular geometry of this complex is depicted in Fig. 3 and selected interatomic distances and bond angles are given in Table 3. As expected the structure reveals a linear arrangement about the mercury atom, (C(11)–Hg–C(21), 178.2(3)°), with almost identical Hg–C distances of 2.092(7) and 2.096(6) Å. The molecule is not quite planar with a twist angle between the two phenyl rings of 14.1(2)°. The vinyl groups are on opposite sides of the C–Hg–C vector and the C–C double bonds point away from the mercury. Each vinyl group is almost in the plane of the phenyl ring to which it is attached. The C–C bond distances in the vinyl groups are 1.325(12) and 1.337(12) Å. There are no significant intermolecular interactions.

3. Conclusions

A convenient and selective synthesis of $Hg[C_6H_4(CH_2OH)\text{-}2]Cl$ has been devised from reaction of dilithiated benzyl alcohol with $HgCl_2$. $Hg[C_6H_4(CH_2OH)\text{-}2]Cl$ can be smoothly oxidised to $Hg[C_6H_4(CHO)\text{-}2]Cl$ by reaction with pyridinium chlorochromate without any damage to the Hg–C bond. The crystal structure of $Hg[C_6H_4(CHO)\text{-}2]Cl$ reveals a complicated geometry where there are both intramolecular and intermolecular Hg–O interactions involving the aldehyde oxygen atoms. Symmetrisation of $Hg[C_6H_4(CHO)\text{-}2]Cl$ and subsequent reaction with the Wittig reagent, $Ph_3P{=}CH_2$, results in the formation of $Hg[C_6H_4(CH{=}CH_2)\text{-}2]_2$. Unlike the structure of $Hg[C_6H_4(CHO)\text{-}2]Cl$, the structure of $Hg[C_6H_4(CH{=}CH_2)\text{-}2]_2$ shows neither intramolecular nor intermolecular interactions.

4. Experimental

4.1. General procedures and instruments

Standard laboratory procedures were followed as have been described previously [10]. Infrared spectra (4000–400 cm^{-1}) were recorded as Nujol mulls between KBr plates on a Perkin–Elmer Paragon 1000 spectrometer. NMR spectra were obtained on a Bruker DRX 400 spectrometer at 25°C. ^1H-, and ^{13}C-NMR spectra were obtained operating at 400.1 (^1H) and 100.6 (^{13}C) MHz, respectively. Resonances are quoted in ppm, coupling constants in Hertz, and ^1H-NMR spectra referenced to either tetramethylsilane (0.00 ppm) or the proteo-impurity in the solvent (7.25 ppm for $CHCl_3$). ^{13}C-NMR spectra were referenced to $CDCl_3$ (77.00 ppm). Mass spectra were recorded using the fast atom bombardment technique with a Varian VG 70-SE mass spectrometer. Elemental analyses were obtained from the Microanalytical Laboratory, University of Otago.

4.2. Preparation of $Hg[C_6H_4(CH_2OH)\text{-}2]Cl$ (1)

Benzyl alcohol (1.406 g, 13 mmol) and TMEDA (3.02 g, 26 mmol) were dissolved in pentane (25 ml) at 0°C. To this vigorously stirred solution was added *n*-butyllithium (1.6 mol l^{-1} in hexane) (18.2 ml, 26 mmol). The first half of the addition was done slowly over 10 min. The solution was a light brown colour at the end of the addition. This light brown solution was then heated under reflux for 11 h, under nitrogen. The resulting dark brown suspension was decanted off from insoluble materials and pentane (20 ml) was added. The resulting suspension was cooled in a dry ice–acetone bath and $HgCl_2$ (2.715 g, 10 mmol) dissolved in tetrahydrofuran (5 ml) was added. The mixture was stirred as it warmed to room temperature. The mixture was then extracted with three portions of water (50 ml) and the combined extracts then neutralised by the addition of dry ice to yield pure **1** as a white microcrystalline solid (2.503 g, 56% yield), which was filtered and dried in vacuo. M.p. 128°C. m/z 343.98707: C_7H_7HgOCl requires 343.98391. Anal. Found: C, 25.31; H, 1.95. Calc. for C_7H_7HgOCl: C, 24.50; H, 2.06%. IR (cm^{-1}): 3232, 3053, 2922, 1202, 1025. ^1H-NMR ($CDCl_3$; δ): 4.75 (s, 2H, CH_2), 7.24–7.4 (m, 4H, C_6H_4). ^{13}C-NMR ($CDCl_3$; δ): 65.52 (s, CH_2), 144.98 (s, quaternary, C_6H_4), 137.01 (s, C_6H_4), 129.03 (s, C_6H_4), 128.01 (s, C_6H_4), 127.81 (s, C_6H_4).

4.3. Preparation of $Hg[C_6H_4(CHO)\text{-}2]Cl$ (**2**)

Compound **1** (0.533 g, 16 mmol) was dissolved in dichloromethane (100 ml), and added to a suspension of pyridinium chlorochromate (0.5022 g, 23 mmol) in dichloromethane (200 ml) at r.t. A dark brown coloured suspension was slowly formed. After 2 h the brown suspension was filtered through a Celite pad, and the filtrate passed down a short silica column to remove coloured impurities. The dichloromethane was removed from the eluant on a rotary evaporator and ethanol (20 ml) was added to give white needles of pure **2** (0.391 g, 74% yield). m/z 341.9720; C_7H_5ClHgO requires 341.9735. Anal. Found: C, 24.65; H, 1.47. Calc. for C_7H_5ClHgO: C, 24.71; H, 1.21%. IR (cm^{-1}): 3130, 1694, 1661, 1632, 1607, 1575, 1562, 1399, 1295, 1261, 1199, 1162, 1115, 1070, 1050, 1016, 957, 843, 826, 806, 761, 696, 662. ^1H-NMR ($CDCl_3$; δ): 7.57–7.61 (m, 2H, C_6H_4); 7.74 (t, apparent, 1H, C_6H_4, $^3J_{HH} = 7.3$); 7.90 (d, apparent, 1H, C_6H_4, $^3J_{HH} = 7.4$); 10.14 (s, 1H, CHO). ^{13}C-NMR (C_6D_6; δ): 129.58 (s, C_6H_4); 135.75 (s, C_6H_4); 135.99 (s, C_6H_4); 137.62 (s, C_6H_4); 193.69 (s, CHO).

4.4. Preparation of $Hg[C_6H_4(CHO)\text{-}2]_2$ (**3**)

Compound **2** (1.00 g, 2.90 mmol) was added to a solution of NaI (4.35 g, 29 mmol) in acetone (100 ml) previously dried over 4 Å molecular sieves. A white flocculant solid formed immediately, and the reaction mixture was stirred for a further 25 min. The solution was then filtered through a Celite pad and the volume of the filtrate reduced to ca. 1 ml. Water (10 ml) was added dropwise to give pure **3** as a white crystalline solid, which was recovered by filtration (622 mg, 52%). m/z 412.0385; $C_{14}H_{10}HgO_2$ requires 412.0387. Anal. Found: C, 40.93; H, 2.45. Calc. for $C_{14}H_{10}HgO_2$: C, 40.32; H, 1.92%. IR (cm^{-1}): 3116, 1772, 1693, 1680, 1659, 1651, 1631, 1581, 1556, 1453, 1294, 1261, 1193, 1117, 839, 790, 751, 6661, 426. ^1H-NMR ($CDCl_3$; δ): 7.50 (t, apparent, 1H, C_6H_4, $^3J_{HH} = 7.6$); 7.71 (t, apparent, 1H, C_6H_4, $^3J_{HH} = 7.2$); 7.81 (d, apparent,1H, C_6H_4, $^3J_{HH} = 7.2$); 7.93 (d, apparent, 1H, C_6H_4, $^3J_{HH} = 7.2$); 10.27 (s, 1H, CHO). ^{13}C-NMR (C_6D_6; δ): 127.97 (s, C_6H_4); 134.29 (s, C_6H_4); 135.14 (s, C_6H_4); 139.10 (s, C_6H_4); 143.97 (s, C_6H_4 quaternary); 168.47 (s, C_6H_4 quaternary); 195.48 (s, CHO).

4.5. Preparation of $Hg[C_6H_4(CH{=}CH_2)\text{-}2]_2$ (**4**)

A solution of $Ph_3P(CH_3)Br$ (4.086 g, 11 mmol) and n-butyllithium (1.6 mol l^{-1} in hexane) (7.15 ml, 11 mmol) in THF (20 ml) was stirred at room temperature for 2 h. To this solution was added dropwise, a solution of **3** (0.94 g, 2 mmol) in THF (20 ml). A precipitate formed immediately which dissolved over 4 h to leave a yellow orange solution. This solution was left to stand at room temperature for 14 h. Saturated NH_4HCO_3 (10 ml) was added and the resulting orange solution extracted three times with dichloromethane (30 ml). The combined extracts were then dried with $CaCl_2$ and the solvent removed under reduced pressure. The solid product was recrystallised from 80% ethanol and final purification was effected by chromatography on a short silica column using dichloromethane as eluent. Removal of solvent afforded pure **4** as an off-white crystalline solid (0.672 g, 72% yield). M.p. 76–78°C. m/z 408.07950, C_8H_7Hg requires 408.08018. Anal. Found: C, 47.14; H, 3.49. Calc. for C_8H_7Hg: C, 47.23; H, 3.47%. IR(cm^{-1}): 1620, 1412, 978, 907, 774, 737. ^1H-NMR ($CDCl_3$; δ): 5.38 (dd, 1H, $CH{=}CH_2$, $^3J_{HH} = 11$, $^2J_{HH} = 1$); 5.83 (dd, 1H, $CH{=}CH_2$, $^3J_{HH} = 17$, $^2J_{HH} = 1$); 7.13 (dd, 1H, $CH{=}CH_2$, $^3J_{HH} = 17$, $^3J_{HH} = 11$); 7.27–7.64 (m, 4H, C_6H_4). ^{13}C-NMR ($CDCl_3$; δ): 114.68 (s, $CH{=}CH_2$); 140.72 (s, $CH{=}CH_2$); 170.69 (s, quaternary, C_6H_4); 145.59 (s, quarternary, C_6H_4); 137.4 (s, C_6H_4); 128.05 (s, C_6H_4); 127.66 (s, C_6H_4); 126.6 (s, C_6H_4).

4.6. X-ray crystal structure determinations for complexes, **2** and **4**

X-ray data collection for **2** and **4** was on a Siemens SMART diffractometer with a CCD area detector, using graphite monochromated Mo–K_α radiation ($\lambda = 0.71073$ Å). Data were integrated and Lorentz and polarisation correction applied using SAINT [11] software. Semi-empirical absorption corrections were applied based on equivalent reflections using SADABS [12]. The structures were solved by Patterson and Fourier methods and refined by full-matrix least-squares on F^2 using programs SHELXS [13] and SHELXL [14]. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were included in calculated positions and refined with a riding model with thermal parameter 20% greater than U_{iso} of the carrier atom. Crystal data and refinement details are given in Table 1.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported here have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 147452 and 147453 for **2** and **4**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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