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Full Paper

Nucleophilic Aromatic Substitution of Bis(pentafluorophenyl)mercury with Various Bulky Nucleophiles and the Structures of $[Hg(C_6F_4X\text{-}4)_2]$ ($X = \textit{cyclo}\text{-}C_5H_{10}N, OCH(CH_3)_2, OC(CH_3)_3$)

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Reactions of bis(pentafluorophenyl)mercury with piperidine, sodium *iso*-propoxide or sodium *tert*-butoxide have yielded the corresponding 4-substituted tetrafluorophenylmercurials, $[Hg(C_6F_4X\text{-}4)_2]$ ($X = \textit{cyclo}\text{-}C_5H_{10}N$ (**1**), $OCH(CH_3)_2$ (**2**), $OC(CH_3)_3$ (**3**)), in reasonable yields but the bulkier nucleophiles, *cis*-2,6-dimethylpiperidine and 2,6-di-*iso*-propylphenolate (from sodium 2,6-di-*iso*-propylphenolate) decomposed the mercurial into pentafluorobenzene. Treatment of bis(pentafluorophenyl)mercury with another bulky nucleophile, 2,6-diphenylphenolate (from sodium 2,6-diphenylphenolate), in methanol, resulted in the unexpected formation of $[Hg(C_6F_4(OMe)\text{-}4)_2]$ (**4**). The structures of all the mercurials have linear C–Hg–C stereochemistry with two coplanar aryl rings. Amongst a complex series of supramolecular interactions, $Hg\cdots O$ bonding is observed for the alkoxy substituted mercurials but there are no $Hg\cdots N$ interactions in the structure of bis(2,3,5,6-tetrafluoro-4-piperidinophenyl)mercury.

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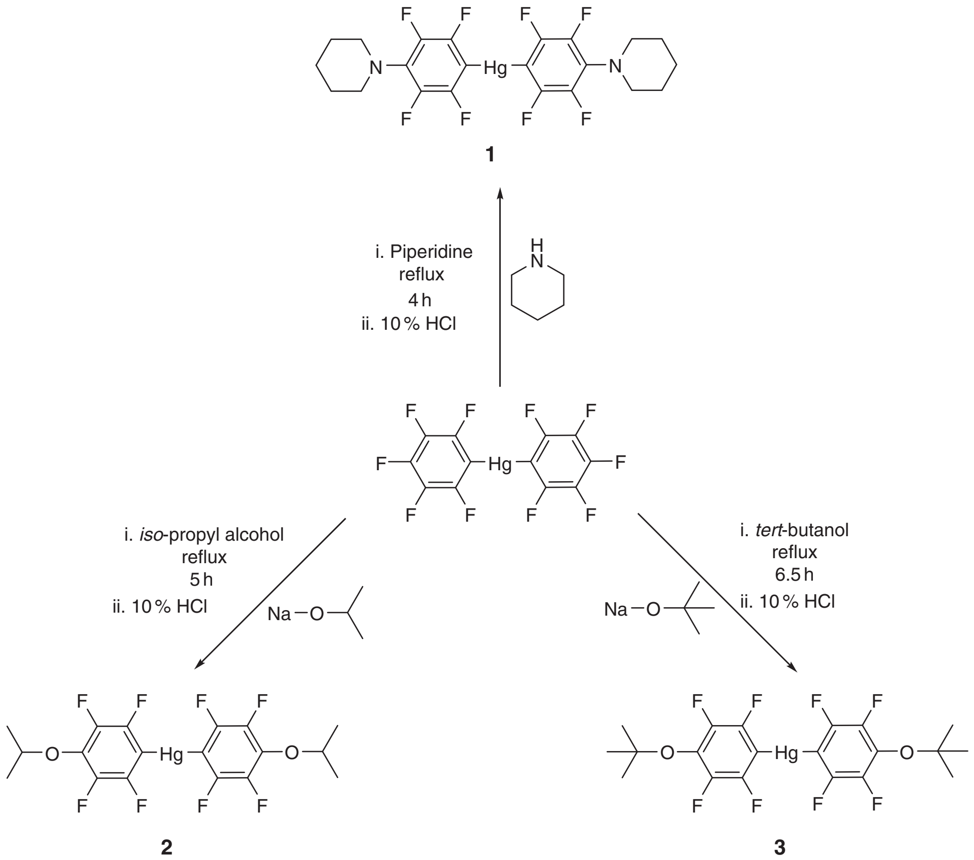
Introduction

Nucleophilic aromatic substitution reactions of polyfluoroarenes, with the displacement of a fluorine substituent, have been an extensively studied topic.[1–3] Much less studied are these types of reactions with polyfluoroarylorganometallics (and organometalloids) and only $[Hg(C_6F_5)_2]$, $[Hg(C_6F_5)Cl]$, $[Cr(CO)_3C_5H_4F]$, $[Si(C_6F_5)(CH_3)_3]$, $[Li(C_6F_5)]$, and $[S(C_6F_5)_2O_2]$ appear to have been investigated.[4–8] In an early study, the mercury compound $[Hg(C_6F_5)_2]$ was shown to give good yields of $[Hg(C_6F_4X\text{-}4)_2]$ ($X = OH$, OMe, $NHNH_2$) on reaction with KOH, NaOMe, or hydrazine, respectively, although the reaction with hydrazine also yielded a considerable amount of Hg metal. By contrast, methyllithium gave (pentafluorophenyl)lithium and $[Hg(CH_3)_2]$. Reactions of $[Hg(C_6F_5)Cl]$ were more complex. Thus, hydrazine caused symmetrisation into Hg metal and $[Hg(C_6F_5)_2]$, and sodium methoxide produced $[Hg(C_6F_4(OMe)\text{-}4)_2]$ from a combination of nucleophilic substitution and symmetrisation.[4] The nucleophiles used for these previous studies are relatively small and not likely to inhibit substitution at an aromatic carbon.[4] We now report the effect of steric bulk on reactions of $[Hg(C_6F_5)_2]$ from investigations of treatment with various bulky nucleophiles (piperidine, *cis*-2,6-dimethylpiperidine, *iso*-propoxide ($^{-}O^iPr$), *tert*-butoxide ($^{-}O^tBu$), 2,6-di-*iso*-propylphenolate ($^{-}$Odip), and 2,6-diphenylphenolate ($^{-}$Odpp). The last four nucleophiles are from their sodium derivatives.).

In addition, the structural aspects of new bis(polyfluorophenyl)mercury compounds are of interest, in view of reports of different rotations of the aryl rings (0°–90°) in structures of such compounds.[9–18] Simple explanations in terms of electronic or steric effects are ruled out on considering the sequence $[Hg(C_6F_5)_2]$ (dihedral angle: 58.4°),[17,18] $[Hg(C_6H_2F_3\text{-}2,4,6)_2]$ (coplanar rings),[11] $[Hg(C_6H_3F_2\text{-}2,6)_2]$ (dihedral angle: 88°),[11] and $[Hg(C_6F_4(NO_2)\text{-}2)_2]$ (coplanar).[16] Accordingly, it has been proposed that the rotation angles may be influenced by supramolecular interactions, which lead to different crystal packing assemblies.[16] As two rotamers of $[Hg(C_6F_4(NO_2)\text{-}3)_2]$, with twist angles of 87° and 59°, can be crystallised from the same solvent at room temperature and −10°C, respectively, the interconversion energy must be low and this is borne out by calculations.[16] The supramolecular interactions and crystal packing of the two rotamers are different.[16] Thus, the structures of the new mercurials, $[Hg(C_6F_4X\text{-}4)_2]$ ($X = \textit{cyclo}\text{-}C_5H_{10}N$, ($O^iPr$), ($O^tBu$), prepared in this study have been determined and are discussed together with their supramolecular interactions.

Results and Discussion

The mercurials $[Hg(C_6F_4X\text{-}4)_2]$ ($X = \textit{cyclo}\text{-}C_5H_{10}N$ (**1**), (O^iPr) (**2**), (O^tBu) (**3**)) were synthesised by treating $[Hg(C_6F_5)_2]$ with piperidine, sodium *iso*-propoxide, and sodium *tert*-butoxide, respectively (Scheme 1). In order to determine the reaction times required, the reaction mixtures were tracked at 1 h intervals using $^{19}F\{^1H\}$ NMR spectroscopy. Complete reaction was indicated when the three resonances of $[Hg(C_6F_5)_2]$ were



Scheme 1. Reaction scheme for the synthesis of **1**–**3**.

Table 1. Reaction conditions used to synthesise 1–3

Product	Amount of $[Hg(C_6F_5)_2]$ used [mmol]	Nucleophile (amount used [mmol])	Solvent (amount used [mL])	Reaction time [h]	Yield [%] (recrystallisation solvent)
1	0.75	Piperidine^A (40)	–	4	36 (chloroform)
2	0.93	$^-O^iPr^B$ (3.8)	*iso*-propyl alcohol (15)	5	67 (ethanol)^C
3	0.47	$^-O^tBu^B$ (5.4)	*tert*-butanol (25)	6.5	32 (acetone)

^{A}Piperidine used as both the nucleophile and solvent.
^{B}From sodium derivative.
^{C}Crude product was recrystallised twice.

completely replaced by the two signals of the desired product, with one exhibiting mercury satellites.

The synthesis of **1** was initially attempted using ethanol as the solvent, following a report of the nucleophilic aromatic substitution of bromopentafluorobenzene with piperidine in ethanol.[19] However, this proved ineffective with $[Hg(C_6F_5)_2]$, as only a small signal corresponding to the desired product was present in the $^{19}F\{^1H\}$ NMR spectrum despite a long reaction time (Fig. S1A in the Supplementary Material). As $[Hg(C_6F_5)_2]$ dissolves readily in piperidine, which has a higher boiling point than ethanol, the synthesis was then tried with piperidine as the solvent as well as a reactant. After four hours the $^{19}F\{^1H\}$ NMR signals of **1** replaced those of the mercurial reactant. The $^{19}F\{^1H\}$ NMR spectrum of **1** is shown in Fig. S1B in the Supplementary Material.

The synthesis of complexes **2** and **3** required longer reactions times than for **1**. The amounts of reactants, reaction times, and solvents used for these reactions are listed in Table 1. A representative ^{199}Hg NMR spectrum was obtained for **1** which exhibited a pentet at −774.34 ppm with a $^3J_{Hg-F}$ coupling constant (410 Hz) which corresponds well to that observed in the $^{19}F\{^1H\}$ NMR spectrum (406 Hz). The chemical shift of **1** is higher than for $[HgPh_2]$ (−799 ppm),[20] in contrast to other bis(polyfluoroaryl)mercurials ($[Hg(C_6F_5)_2]$ (−953 ppm)[21] and $[Hg(C_6F_4H\text{-}4)_2]$ (−946 ppm))[20] with the exception of $[Hg(C_6H_3F_2\text{-}2,6)_2]$ (−780 ppm).[20] This may be attributed to the electron donating properties of the *cyclo*-$C_5H_{10}N$ substituent.

Bulkier nucleophiles (*cis*-2,6-dimethylpiperidine, $^-$Odip and $^-$Odpp) were also examined to determine the limits of steric bulk on these type of nucleophilic aromatic substitutions. The reactions involving the nucleophiles *cis*-2,6-dimethylpiperidine (reaction 1, Table 2) and $^-$Odip (reaction 2, Table 2) gave pentafluorobenzene[22] as the fluorocarbon product and possibly a trace amount of $[Hg(C_6F_4(Odip)\text{-}4)_2]$. Although $[Hg(C_6F_5)_2]$ has been recrystallised unchanged from concentrated sulfuric acid,[23] it is susceptible to nucleophilic attack at the mercury

Table 2. Reaction conditions for the attempted substitution reactions

Reaction	Amount of $[Hg(C_6F_5)_2]$ used [mmol]	Nucleophile (amount used [mmol])	Solvent (amount used [mL])	Reaction time	Products
1^A	0.47	*cis*-2,6-dimethylpiperidine (300)	–	10.5 h	C_6F_5H
2	0.47	$^-$Odip^B (3.7)	dipOH (20)	10 h	C_6F_5H $[Hg(Odip)_2]^C$ $[Hg(C_6H_2(CH(CH_3)_2(ONa))(Odip)]^C$
3	0.47	$^-$Odpp^B (0.92)	methanol (25)	3 weeks	**4** and HOdpp

^{A}*cis*-2,6-dimethylpiperidine is used as both the nucleophile and solvent.
^{B}From the sodium derivative.
^{C}On the basis of mass spectra.

centre giving $C_6F_5^-$ and then C_6F_5H, e.g. by iodide ions or $(Ph_2P)_2NH$.[24,25] The reaction mixture from an attempted synthesis (reaction 2, Table 2) also gave products with mercury isotope patterns in the mass spectrum. One peak at *m*/*z* 663 may correspond to $\{[Hg(Odip)\text{-}4)_2] + OH^- + 5H_2O\}^-$, while the peak at *m*/*z* 713 could be assigned to the mercuration product $\{[Hg(C_6H_2(CH(CH_3)_2ONa)(Odip)] + OH^- + 2H_2O + 2MeCN\}^-$. Sodium 2,6-di-*iso*-propylphenolate is activated with regards to electrophilic mercuration. The formation of C_6F_5H in attempted syntheses (reactions 1 and 2) suggests that it is also inert to *cis*-2,6-dimethylpiperidine and $^-$Odip. In order to confirm this, C_6F_5H was treated with *cis*-2,6-dimethylpiperidine on an NMR scale. After prolonged sonication, no reaction was observed. The solution was then left standing for a week at room temperature and the $^{19}F\{^1H\}$ NMR spectrum showed mainly C_6F_5H but also trace amounts of the potential product by resonances at −141.9 and −152.0 ppm (1 : 1). In addition, a new peak at −139.9 ppm may correspond to 1,2,4,5-tetrafluorobenzene.[22] Thus, C_6F_5H is also resistant to this bulky nucleophile.

As HOdpp is a solid, it was not used as a reaction medium for the reaction of $[Hg(C_6F_5)_2]$ with NaOdpp (reaction 3, Table 2). The reaction was attempted in methanol. Unexpectedly, the known[4,9] compounds $[Hg(C_6F_4(OMe)\text{-}4)_2]$ (**4**) and 2,6-diphenylphenol (HOdpp) were isolated from hand-picked crystals. Despite the relative acidities of methanol and HOdpp, the excess methanol and the thermodynamic sink provided by the nucleophilic substitution of $[Hg(C_6F_5)_2]$ by methoxide ions have driven this outcome. Overall, *cis*-2,6-dimethylpiperidine, $^-$Odip, and $^-$Odpp are too bulky to displace a fluorine atom by nucleophilic substitution.

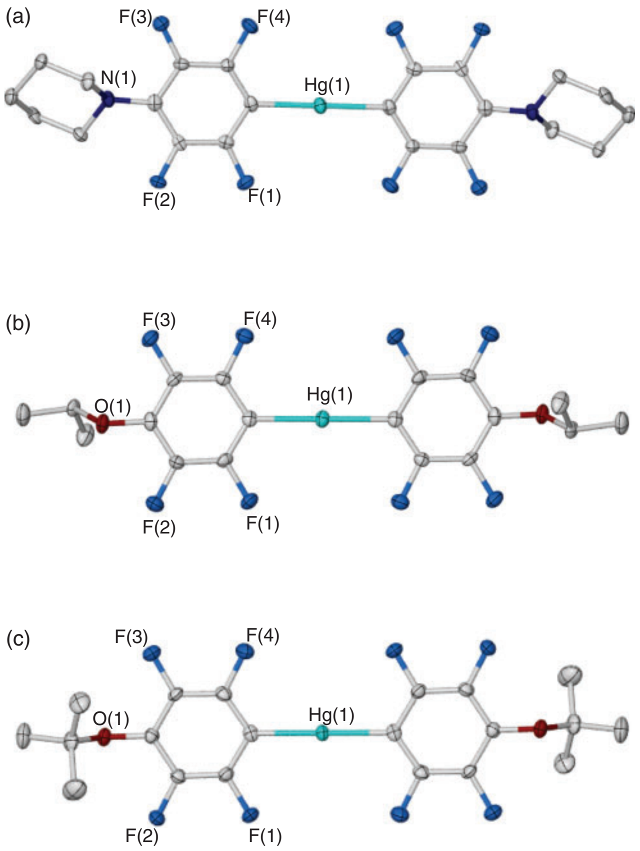


Fig. 1. X-ray crystal structures of (a) **1**, (b) **2** and (c) **3** showing 50 % probability thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

Structural Determinations

The molecular structures were determined for three complexes (**1**–**3**, Fig. 1), with crystals prepared by slow evaporation from chloroform, ethanol, and acetone, respectively. The crystal data of these compounds are given in Table 3 and selected bond lengths and angles are given in Table 4. These compounds are monomeric at the molecular level with the mercury metal centres having a characteristic coordination number of two.[26] Complex **1** has the piperidinyl substituent in a chair configuration. Interestingly, the aromatic rings of all these compounds have a coplanar arrangement (Fig. 1), with a C–Hg–C angle of 180° (Table 2). The aryl twist angle of **1**–**3** (0°) contrasts those of $[Hg(C_6F_4(NH_2)\text{-}4)_2]$ (62.2°) and $[Hg(C_6F_4(OMe)\text{-}4)_2]$ (52.9°), which contain less bulky 4-substituents.[9] There have been several reports of diarylmercury compounds with a planar orientation,[10,11] notably diphenylmercury,[12–14] even though calculations favour 90°.[14] Although the contrast between the present results and the structures of $[Hg(C_6F_4X\text{-}4)_2]$ ($X = NH_2$ and OMe)[9] might suggest that coplanar rings are associated with bulky *para*-substituents, $[Hg(C_6F_4H\text{-}4)_2]$ also has coplanar rings.[11]

The Hg–C distances of **1**–**3** are comparable to those of other similar reported structures.[9–11,15–18] The N–C(Ar) and O–C(Ar) bond lengths lie between those of N(O)–C and N(O)=C[27] indicating partial double bond character. This is attributed to the partial conjugation of the lone pairs of the nitrogen or oxygen atoms of the NC_5H_{10}, O^iPr, and O^tBu substituents into the aryl ring. Other related complexes, such as $[Hg(C_6F_4(NH_2)\text{-}4)_2]$ and $[Hg(C_6F_4(OMe)\text{-}4)_2]$ show comparable N–C(OAr) and O–C(Ar) bond lengths.[9]

Different supramolecular assemblies are observed in these three structures and may contribute to their coplanar

Table 3. Crystallographic data for 1–3

Parameter	1	2	3
Empirical formula	$C_{22}H_{20}F_8HgN_2$	$C_{18}H_{14}F_8HgO_2$	$C_{20}H_{18}F_8HgO_2$
Molecular weight	664.99	614.88	642.93
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	P-1	$P2_1/c$
Crystal colour	Colourless	Colourless	Colourless
Crystal size [mm^3]	0.12 × 0.1 × 0.1	0.2 × 0.1 × 0.1	0.12 × 0.05 × 0.04
a [Å]	12.3696(17)	6.7648(4)	10.4453(6)
b [Å]	10.2968(15)	7.1018(5)	10.8951(6)
c [Å]	8.2449(12)	10.6119(6)	9.2388(5)
α [deg.]	90	71.292(4)	90
β [deg.]	98.324(5)	85.555(3)	93.230(3)
γ [deg.]	90	77.176(3)	90
V [Å^3]	1039.1(3)	470.83(5)	1049.73(10)
Z	2	1	2
Density (calc.) [g cm^{-3}]	2.125	2.169	2.034
R_1 ($I > 2\sigma(I)$)	0.0584 (0.0328)	0.0255 (0.0255)	0.0258 (0.0152)
F_{000}	636	290	612
λ [Å]	0.71073	0.71073	0.71073
$2\theta_{max}$ [deg.]	55.0	55.0	55.0
Final GoF	1.018	1.124	1.015
wR_2 ($I > 2\sigma(I)$)	0.0797 (0.0701)	0.0476 (0.0476)	0.0426 (0.0381)
μ [mm^{-1}]	7.491	8.260	7.416

Table 4. Selected bond lengths and angles for 1–3

Bonds/atoms	1	2	3
		Bond distances [Å]	
Hg–C	2.064(5)	2.069(4)	2.057(2)
C(4)–N(O)	1.390(7)	1.367(4)	1.364(3)
Hg···N(O)	4.559(5)	3.3147(2)	2.981(2)
		Bond angles [deg.]	
C–Hg–C	180.0(1)	180.0(3)	180.0(2)
		Deviations from the ring plane [Å]	
Hg	0.076(8)	0.104(6)	0.077(5)
N(O)	0.100(9)	0.125(6)	0.109(5)

arrangement. For **1**, each of the aromatic rings exhibits a π–π interaction with one other ring (Fig. 2 and Fig. S2 in the Supplementary Material). The π–π stacking of these rings is in a parallel offset face-to-face arrangement with an interplanar distance of 3.286(8) Å, much shorter than the sum (3.46 Å) of the van der Waals radii of two aryl rings.[28] A minimum C–C contact of 3.314(8) Å between pairs of carbons (C(2)···C(3′), C(2′)···C(3)) of these rings is observed. The packing of this molecule can be described as a herringbone structure, and the offset pairs lie near perpendicular (85.2(3)°) to their neighbouring pairs (Fig. 2).

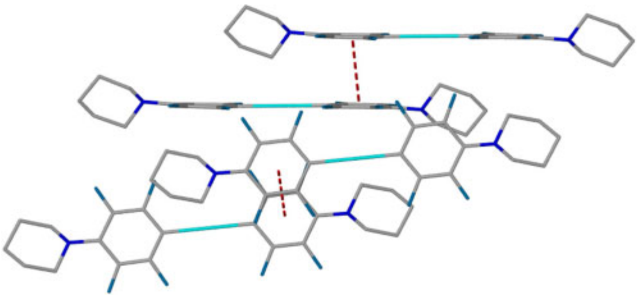


Fig. 2. A simplified representation showing the rotation of the π-stacked pairs of **1**.

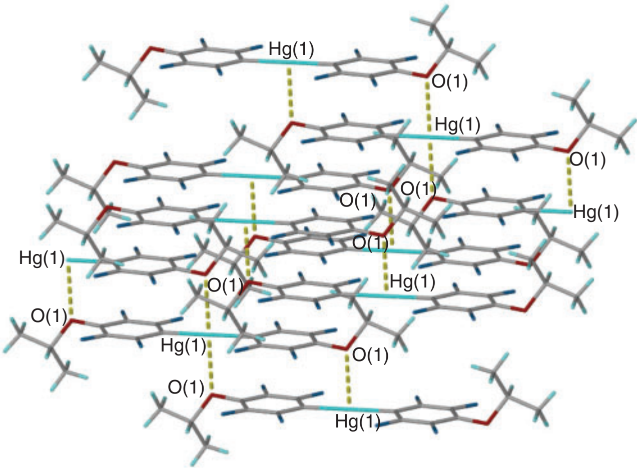


Fig. 3. The crystal packing diagram of **2** highlighting the Hg···O interactions.

In contrast to its less sterically hindered derivative [Hg($C_6F_4(NH_2)$-4)$_2$],[9] **1** exhibits no Hg···N interactions as the separation (4.559(5) Å) is well outside the van der Waals radii for mercury (1.73 Å[29–33] and can be up to 2.1–2.2 Å,[9,34,35] particularly when perpendicular to a strong bonding axis) and nitrogen (1.55 Å).[36] A possible explanation for this could be the deviation of the nitrogen (0.100(9) Å) from the plane of the aromatic rings away from the mercury atom, whereas in [Hg($C_6F_4(NH_2)$-4)$_2$] the nitrogen is bent towards the mercury atom and is therefore in a better position to donate electron density to mercury. Analysis of the [Hg($C_6F_4(NH_2)$-4)$_2$] structure revealed another feature that differs from **1** which may also contribute to the different ring rotation angle of 62.2°. An intermolecular hydrogen bonding interaction between the NH_2 groups and a F substituent is present in this particular structure, and may contribute to the twist of the aryl rings despite them being locked in a π–π interaction.[9]

While these hydrogen bonds (NH_2···F) and Hg···N interactions are absent in **1**, other possible interactions are observed. These include a weak intermolecular F(2)···Hg contact at a distance of 3.451(3) Å, a value which lies just outside the sum of the van der Waals radii of fluorine (1.47 Å)[36] and mercury (1.73 Å minimum value) but is within the limit using higher proposed values for mercury.[29–33] Interestingly, a short halogen–halogen contact can be observed between the same F(2) of one molecule and F(1) of another. The distance between these two atoms (2.785(5) Å) is within the sum of two van der Waals radii of fluorine (2.94 Å).[36] It appears that this interaction may contribute to the offset pairs lying near perpendicular to each other, as the aromatic ring of F(1) is rotated almost 90° relative to the aryl ring containing F(2) of this interaction.

Although **2** showed a less complex assembly, major interactions can still be observed such as π–π interactions and F···H non-classical hydrogen bonding, the latter not a feature of **1**. The interplanar distance between the aromatic rings is 3.273(4) Å with a C(1)–C(5′) contact of 3.281(6) Å. This π–π stacking is also arranged in an offset face-to-face manner and represents a sandwich herringbone structure. In contrast to the assembly of **1**, the π–π interactions do not exist as perpendicular pairs of pairs but instead as sets of parallel pairs. Moreover, there is also plausible evidence of a Hg···O interaction (Fig. 3) at a distance

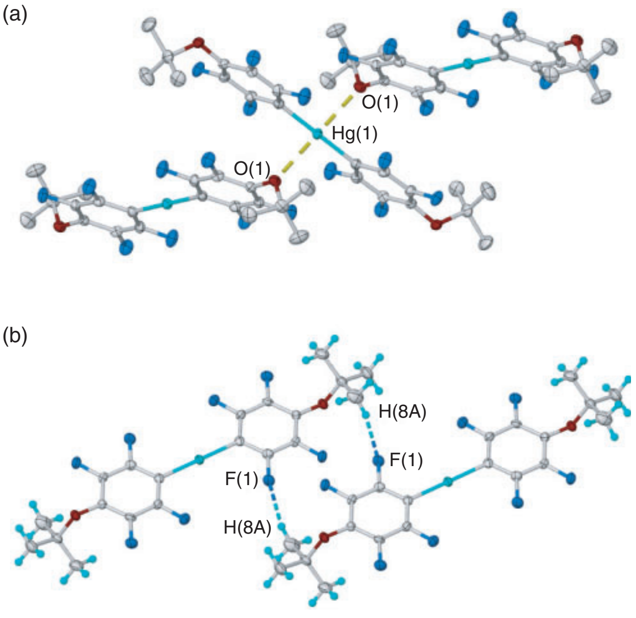


Fig. 4. The (a) Hg···O and (b) F···H interactions of **3**.

of 3.315(3) Å, which is near the sum of the van der Waals radii of mercury (minimum value) and oxygen (3.25 Å).[29–33,36] However, there have been credible reports of stacking bonding distances of 3.30–3.40 Å for Hg···O, implying a mercury van der Waals radius of 1.9–2.0 Å.[29,34,35] Thus, phenylmercuric quinolin-8-olate and 2-methylquinolin-8-olate have intermolecular association in the liquid and gas phase[37] while the intermolecular Hg···O distances in the solid state are in the range 3.3–3.4 Å.[35] In the structures of **4** (Hg···O: 3.313 Å) and [$Hg(C_6H_4(OMe)\text{-}4)(C_6F_5)$] (Hg···O: 3.411 Å), Hg···O interactions are proposed.[9,38] Consequently a Hg···O interaction is plausible. Furthermore, the oxygen atom is displaced out of the plane of the aromatic ring (0.126(7) Å) towards the mercury atom, consistent with an interaction.

Such an interaction is more apparent with **3** as the Hg···O distance is 2.981(2) Å (Fig. 4a), which is well within the sum of van der Waals radii with the minimum value for mercury.[29–33,36] Similar to **2**, the oxygen atoms of **3** are also displaced out of the plane of the aryl ring towards the mercury atom by 0.109(5) Å.

Apart from the Hg···O interaction, the assembly of this structure contains similar interactions to **1**, such as π–π stacking interactions (interplanar distance: 3.072(4) Å) and F···F interactions (2.830(3) Å). However, an intermolecular H···F interaction can also be observed in this assembly (Fig. 4b) at a distance of 2.576 Å, fitting within the sum of van der Waals radii of 2.67 Å.[36] These interactions may also play a role in the coplanarity of the structure.

Comparison of **2** and **3** with **4**, which contains the less bulky 4-OMe substituent, revealed some similar interactions such as π–π stacking, Hg···O interactions, and F···H non-classical hydrogen bonding.[9] However, unlike the coplanar complexes **2** and **3**, the dihedral angle of **4** is 52.9°.[9] One contributing factor to this difference in angles may be the F···H(CH_3) non-classical hydrogen bonding. Complexes **2** and **3** contain more than one methyl substituent at different angles compared with **4**, enabling hydrogen bonding without twisting of the rings, whereas rotation may be required in **4** in order for the F···H bonding to occur. In addition, the methyl groups in **2** and **3** have more flexibility than in the OMe substituent of **4**. Hydrogen bonding for these complexes is summarised in Table 5.

Table 5. Hydrogen bonding data for 2, 3, and 4

Complex	D	H	A	$d_{D–H}$ [Å]	$d_{H–A}$ [Å]	$d_{D–A}$ [Å]	$<_{DHA}$ [deg.]
2	C9	H9B	F(1)	0.98	2.55	3.273(6)	130.25
3	C8	H8A	F(1)	0.96	2.58	3.219(4)	124.72
4	C5	H1	F(1)	0.88	2.63	3.3272(9)	136.12

Conclusions

Three new organomercury compounds **1**–**3** have been synthesised by nucleophilic aromatic substitution reactions through treatment of [$Hg(C_6F_5)_2$] with piperidine, $NaO^{i}Pr$ or $NaO^{t}Bu$. The bulkier nucleophiles used in attempted reactions 1–3 (Table 2) proved unsuitable due to their steric bulk preventing access to the ring carbons. The mercurials from the successful reactions have crystal structures with co-planar ring arrangements. In the crystal packing different assemblies and supramolecular interactions were observed. The major features were π–π stacking, and Hg···O and F···H interactions, which may contribute to the planar configurations of these structures.

Experimental

General

All reactions, except for the synthesis of **1**, were performed under a nitrogen atmosphere using standard Schlenk procedures for air-sensitive compounds but the isolated mercurials are air-stable. Methanol, isopropyl alcohol, and *tert*-butanol were dried over calcium oxide and then distilled. 2,6-Dimethylpiperidine and 2,6-di-*iso*-propylphenol were dried over KOH and 4 Å molecular sieves, respectively, and then distilled. [$Hg(C_6F_5)_2$], [$NaO^{i}Pr$], [$NaO^{t}Bu$], and [NaOdpp] were synthesised by literature methods.[39–42] All other reagents were used without further purification. All NMR spectra were recorded using a Bruker DPX300 spectrometer and the Top Spin NMR software on a Windows NT workstation. The solvents used were either deuterated chloroform or deuterated acetone. The proton chemical shifts were calibrated using the residual proton peak from the deuterated solvents and the fluorine chemical shifts were calibrated using trichlorofluoromethane as an external reference. The mercury chemical shift was calibrated using 1 M $HgCl_2$ in DMSO-d_6 at −1501.6 ppm.[43]

An electrothermal IA6304 apparatus was used to measure the melting points of all the complexes and was calibrated against benzoic acid (mp 122°C). The infrared spectra of the compounds were recorded with a Cary 630 FTIR spectrometer using ATR measurements in a range of 4000–600 cm^{-1}. All the electrospray ionisation mass spectrometry (ESI MS) measurements were performed using a Micromass Platform II ESI-MS linked with a Waters 2690 HPLC system. Each of the reported peaks of Hg-containing ions correspond to the main peak (containing ^{202}Hg) of a cluster with the expected isotopic pattern, as determined by the program *Molecular Weight Calculator*. The microanalysis for **1** was conducted by the Campbell Microanalytical Laboratories, University of Otago, Dunedin, New Zealand, while the other two complexes were analysed by the Elemental Analysis Service, London Metropolitan University.

X-Ray Crystallography

Single crystals were loaded onto a fine glass fibre or cryoloop using viscous hydrocarbon oil with the collections kept at 123 K using an open-flow N_2 Oxford Cryosystem. A Bruker X8 Apex II diffractometer was used to collect the data, which were processed using the *SAINT*[44] program. Each dataset was empirically corrected for absorption (*SADABS*)[45] and then merged. The structures were solved using direct methods and refined by full-matrix least-squares on all F^2 data using *SHELX-97*[46] for **3** and *SHELX-2013*[46] for **1** and **2** with the X-Seed graphical interface.[47] All the hydrogen atoms attached to carbon were placed in idealised positions and allowed to ride on the atom to which they were attached. Crystal and refinement data are in Table 3.

General Procedure

$[\mathrm{Hg(C_6F_5)_2}]$ was added to a three necked round bottom flask containing the appropriate nucleophile and solvent. The mixture was then heated at reflux under N_2. Once cooled, the reaction mixture was poured into 10 mL of HCl (10 %) and then extracted with diethyl ether (30 mL) three times. The ether layers were then combined, dried with anhydrous magnesium sulfate, and then evaporated to dryness. The amounts of reagents and reaction times used for each reaction are listed in Table 1 and Table 2.

$[\mathrm{Hg(C_6F_4(}$cyclo-$\mathrm{NC_5H_{10})\text{-}4)_2}]$ **1**

This synthesis was performed without a N_2 atmosphere.

Colourless crystals (0.18 g, 36 %), mp 167–169°C. $\nu_{\max}$ (ATR)/cm^{-1} 2943 (m), 2852 (m), 2814 (m), 2707 (w), 1633 (m), 1451 (vs), 1380 (s), 1354 (s), 1319 (s), 1276 (m), 1224 (s), 1152 (m), 1098 (s), 1069 (s), 1032 (m), 1000 (s), 950 (vs), 904 (s), 873 (m), 850 (m), 828 (m), 777 (m), 717 (m). δ_{H} (300 MHz, $\mathrm{CDCl_3}$) 1.67 (m, 12H, 3 × $\mathrm{CH_2}$ overlapping), 3.23 (m, 8H, N–$\mathrm{CH_2}$). $\delta_{\mathrm{F}\{^1\mathrm{H}\}}$ (282.4 MHz, $\mathrm{CDCl_3}$) −122.3 (m, with ^{199}Hg satellites $^3J_{(\mathrm{Hg–F})}$ 406, 4F, F(2,6)), −149.3 (m, 4F, F(3,5)). $\delta_{^{199}\mathrm{Hg}}$ (71.6 MHz, $\mathrm{CDCl_3}$) −774.3 (p, $^3J_{(\mathrm{Hg–F})}$ 410). *m/z* (ESI$^+$) 667 (100 %, $[\mathrm{M+H}]^+$). Anal. Calc. for $\mathrm{C_{22}H_{20}F_8N_2Hg}$: C 39.74, H 3.03, N 4.21. Found: C 40.00, H 2.95, N 4.12 %.

Attempted Synthesis of $[\mathrm{Hg(C_6F_4(NC_5H_8Me_2\text{-}2,6)\text{-}4)_2}]$

A $^{19}\mathrm{F}\{^1\mathrm{H}\}$ NMR spectrum of the reaction mixture was recorded and the signals observed indicated the formation of $\mathrm{C_6F_5H}$;[22] no Hg satellites were observed.

$[\mathrm{Hg(C_6F_4(O^iPr)\text{-}4)_2}]$ **2**

Colourless crystals (0.38 g, 67 %), mp 121–122°C. $\nu_{\max}$ (ATR)/cm^{-1} 2986 (m), 2926 (m), 2883 (m), 1633 (m), 1470 (vs), 1367 (s), 1337 (s), 1268 (w), 1177 (m), 1145 (m), 1080 (vs), 956 (vs), 901 (s), 865 (w), 824 (s), 797 (s), 733 (m), 693 (w), 659 (w). δ_{H} (300 MHz, $\mathrm{CDCl_3}$) 1.39 (d, $^3J_{(\mathrm{H–H})}$ 6, 12H, $\mathrm{CH_3}$), 4.60 (s, $^3J_{(\mathrm{H–H})}$ 6, 2H, CH). $\delta_{\mathrm{F}\{^1\mathrm{H}\}}$ (282.4 MHz, $\mathrm{CDCl_3}$) −122.0 (dm, $^3J_{(\mathrm{F–F})}$ 15, with ^{199}Hg satellites $^3J_{(\mathrm{Hg–F})}$ 413, 4F, F(2,6)), −153.7 (dm, $^3J_{(\mathrm{F–F})}$ 16, 4F, F(3,5)). *m/z* (ESI$^-$) 207 (100 %, $\mathrm{C_6F_4O^iPr^-}$), 651 (28, $[\mathrm{M+Cl}]^-$). Anal. Calc. for $\mathrm{C_{18}H_{14}F_8O_2Hg}$: C 35.16, H 2.29. Found: C 35.17, H 2.02 %.

$[\mathrm{Hg(C_6F_4(O^tBu)\text{-}4)_2}]$ **3**

Colourless crystals (0.096 g, 32 %), mp 210–212°C. $\nu_{\max}$ (ATR)/cm^{-1} 2982 (m), 2839 (w), 2185 (w), 1631 (m), 1463 (vs), 1396 (m), 1368 (s), 1262 (m), 1161 (m), 1078 (vs), 952 (vs), 842 (vs), 807 (s), 765 (w), 717 (m), 665 (w). δ_{H} (300 MHz, $\mathrm{(CD_3)_2CO}$) 1.18 (s, $\mathrm{CH_3}$). $\delta_{\mathrm{F}\{^1\mathrm{H}\}}$ (282.4 MHz, $\mathrm{(CD_3)_2CO}$) −122.5 (m, with ^{199}Hg satellites $^3J_{(\mathrm{Hg–F})}$ 430, 4F, F(2,6)), −151.3 (m, 4F, F(3,5)). *m/z* (ESI$^-$): 221 (100 %, $\mathrm{C_6F_4O^tBu^-}$), 645 (2, $[\mathrm{M+H}]^-$), 679 (8, $[\mathrm{M+Cl}]^-$). Anal. Calc. for $\mathrm{C_{20}H_{18}F_8O_2Hg}$: C 37.36, H 2.82. Found: C 37.37, H 2.74 %.

Attempted Synthesis of $[\mathrm{Hg(C_6F_4(Odip)\text{-}4)_2}]$

A solution of NaOdip was made by treating sodium metal (0.090 g, 3.7 mmol) with dried (4 Å molecular sieves) 2,6-di-*iso*-propylphenol (15 mL). The $^{19}\mathrm{F}\{^1\mathrm{H}\}$ NMR spectrum of the reaction mixture showed signals for $\mathrm{C_6F_5H}$;[22] no Hg satellites were observed. The solid product was recovered by evaporation under vacuum.

m/z (ESI$^-$) mercury containing cluster 663 (10 %, $[([\mathrm{Hg(Odip)\text{-}4)_2}] + \mathrm{OH^-} + 5\mathrm{H_2O})]^-$, 713 (100, $[([\mathrm{Hg(Odip)(C_6H_2(CH(CH_3)_2)ONa)}] + \mathrm{OH^-} + 2\mathrm{H_2O} + 2\mathrm{MeCN})]^-$.

Attempted Synthesis of $[\mathrm{Hg(C_6F_4(Odpp)\text{-}4)_2}]$

Once the reaction had been performed (reaction 3, Table 2), the resulting crude products were recrystallised from acetone and the crystals were handpicked to obtain compounds **4** and 2,6-diphenylphenol. The ^{1}H NMR signals matched the spectrum of the starting material 2,6-diphenylphenol[48] and the $^{19}\mathrm{F}\{^1\mathrm{H}\}$ NMR spectrum corresponded well to the literature data for **4**.[49]

Hand-picked single crystals were identified by unit cell measurements.

2,6-Diphenylphenol unit cell: *a* 11.65 Å, *b* 18.399 Å, *c* 6.368 Å, $\alpha = \beta = \gamma = 90°$, *V* 1308.145 Å^3; **4** unit cell: *a* 14.2692 Å, *b* 7.0972 Å, *c* 14.7601 Å, $\alpha = \gamma = 90°$, β 105.91°, *V* 1437.52 Å^3. Both are in agreement with reported data.[9,50]

Attempted Synthesis of $\mathrm{HC_6F_4(NC_5H_8Me_2\text{-}2,6)\text{-}4}$

$\mathrm{C_6F_5H}$ (0.1 mL) and 1 mL of *cis*-2,6-dimethylpiperidine were placed in an NMR tube and sonicated. A $^{19}\mathrm{F}\{^1\mathrm{H}\}$ NMR spectrum of the reaction mixture was recorded at 1 h intervals for 3 h and then the solution was left to sonicate overnight and only $\mathrm{C_6F_5H}$ was detected. The NMR tube was then taken out and left standing at room temperature for one week and was heated for 3 h at 80°C.

The same spectra were observed after one week of standing and then after 3 h of heating:

$\delta_{\mathrm{F}\{^1\mathrm{H}\}}$ (282.4 MHz, $\mathrm{(CD_3)_2CO}$): −139.0 (m, 2F, F(2,6) ($\mathrm{C_6F_5H}$)), −139.9 (m, 1F, ($\mathrm{C_6F_4H_2}$-*p*)), −141.9 (m, 0.016F, F(2,6) ($\mathrm{HC_6F_4(NC_5H_8Me_2\text{-}2,6)\text{-}4}$)), −152.0 (m, 0.018F, F(3,5) −152.0 ($\mathrm{HC_6F_4(NC_5H_8Me_2\text{-}2,6)\text{-}4}$)), −154.0 (m, 1F, F(4) ($\mathrm{C_6F_5H}$)), −162.5 (m, 2F, F(3,5) ($\mathrm{C_6F_5H}$)).

Crystallographic Data

X-Ray data have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. **1** 936417, **2** 936418 and **3** 936416. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax +44-1223-336-033; email deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk.)

Supplementary Material

The $^{19}\mathrm{F}\{^1\mathrm{H}\}$ NMR spectra obtained for both **1** and the initial attempt to syntheses **1** in ethanol, as well as the crystal packing diagram for **1** are available on the Journal's website.

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References

[1] M. Hudlicky, *Chemistry of Organic Fluorine Compounds: A Laboratory Manual with Comprehensive Literature Coverage* **1970** (Ellis Horwood: Chichester).
[2] R. D. Chambers, *Fluorine in Organic Chemistry* **2004** (Wiley-Blackwell: Oxford).
[3] R. E. Banks, B. E. Smart, J. C. Tatlow, *Organofluorine Chemistry, Principals and Commercial Application* **1994** (Plenum Press: New York, NY).
[4] J. Burdon, P. L. Coe, M. Fulton, J. C. Tatlow, *J. Chem. Soc.* **1964**, 2673. doi:10.1039/JR9640002673
[5] C. Baldoli, P. DelButtero, E. Licandro, S. Maiorana, *Gazz. Chim. Ital.* **1988**, *118*, 409.
[6] F. W. G. Fearon, H. Gilman, *J. Organomet. Chem.* **1967**, *10*, 535. doi:10.1016/S0022-328X(00)83184-8
[7] R. D. Chambers, J. A. Cunningham, D. A. Pyke, *Tetrahedron* **1968**, *24*, 2783. doi:10.1016/S0040-4020(01)82550-3
[8] R. D. Chambers, J. A. Cunningham, D. J. Spring, *J. Chem. Soc. C* **1968**, 1560. doi:10.1039/J39680001560
[9] G. B. Deacon, C. M. Forsyth, D. M. M. Freckmann, G. Meyer, D. Stellfeldt, *Z. Anorg. Allg. Chem.* **2000**, *626*, 540. doi:10.1002/(SICI)1521-3749(200002)626:2<540::AID-ZAAC540>3.0.CO;2-M
[10] D. S. Brown, A. G. Massey, D. A. Wickens, *J. Organomet. Chem.* **1980**, *194*, 131. doi:10.1016/S0022-328X(00)86660-7
[11] D. Naumann, F. Schulz, *Z. Anorg. Allg. Chem.* **2005**, *631*, 122. doi:10.1002/ZAAC.200400244
[12] B. Ziolkovska, R. M. Myasnikova, A. I. Kitaigorodskii, *J. Struct. Chem.* **1965**, *5*, 678. doi:10.1007/BF00744055
[13] D. Grdenić, B. Kamenar, A. Nagl, *Acta Crystallogr. B* **1977**, *33*, 587. doi:10.1107/S056774087700418X
[14] C. Glidewell, J. N. Low, J. L. Wardell, *Acta Crystallogr. C* **2005**, *61*, m107. doi:10.1107/S0108270104034134
[15] G. B. Deacon, P. W. Felder, P. C. Junk, K. Müller-Buschbaum, T. J. Ness, C. C. Quitmann, *Inorg. Chim. Acta* **2005**, *358*, 4389. doi:10.1016/J.ICA.2005.05.014
[16] G. B. Deacon, C. M. Forsyth, P. C. Junk, E. I. Izgorodina, T. J. Ness, G. Meyer, I. Pantenburg, *CrystEngComm* **2011**, *13*, 88. doi:10.1039/C0CE00258E
[17] N. R. Kunchur, M. Mathew, *Chem. Commun.* **1966**, 71.
[18] D. L. Wilkinson, J. Riede, G. Müller, *Z. Naturforsch B* **1991**, *46*, 285.
[19] V. V. Bardin, L. S. Pressman, L. N. Rogoza, G. G. Furin, *J. Fluor. Chem.* **1991**, *53*, 213. doi:10.1016/S0022-1139(00)82342-8
[20] N. J. Barassi, G. B. Deacon, J. A. Weigold, *Z. Anorg. Allg. Chem.* **1994**, *620*, 993. doi:10.1002/ZAAC.19946200607
[21] W. McFarlane, *J. Chem. Soc. A* **1968**, 2280. doi:10.1039/J19680002280
[22] M. I. Bruce, *J. Chem. Soc. A* **1968**, 1459. doi:10.1039/J19680001459
[23] R. D. Chambers, G. E. Coates, J. G. Livingstone, W. K. R. Musgrave, *J. Chem. Soc.* **1962**, 4367. doi:10.1039/JR9620004367
[24] H. B. Albrecht, G. B. Deacon, M. J. Tailby, *J. Organomet. Chem.* **1974**, *70*, 313. doi:10.1016/S0022-328X(00)83362-8
[25] M. L. Cole, G. B. Deacon, P. C. Junk, K. Konstas, P. W. Roesky, *Eur. J. Inorg. Chem.* **2005**, 1090. doi:10.1002/EJIC.200400932
[26] D. Grdenić, *Q. Rev. Chem. Soc.* **1965**, *19*, 303. doi:10.1039/QR9651900303
[27] L. E. Sutton, *Tables of Interatomic Distances and Configuration in Molecules and Ions* **1958**, Spec. Publ. No. 11 (The Chemical Society: London).
[28] L. Pauling, *The Nature of the Chemical Bond and the Structure of Molecules and Crystals* **1960** (Cornell University Press: Ithaca, NY).
[29] A. J. Canty, G. B. Deacon, *Inorg. Chim. Acta* **1980**, *45*, L225. doi:10.1016/S0020-1693(00)80155-3
[30] P. Pyykkö, M. Straka, *Phys. Chem. Chem. Phys.* **2000**, *2*, 2489. doi:10.1039/B001171L
[31] M. Tsunoda, F. P. Gabbai, *J. Am. Chem. Soc.* **2000**, *122*, 8335. doi:10.1021/JA0016598
[32] M. R. Haneline, M. Tsunoda, F. P. Gabbai, *J. Am. Chem. Soc.* **2002**, *124*, 3737. doi:10.1021/JA0166794
[33] M. R. Haneline, R. E. Taylor, F. P. Gabbai, *Chem. – Eur. J.* **2003**, *9*, 5188. doi:10.1002/CHEM.200305109
[34] K. R. Flower, V. J. Howard, S. Naguthney, R. G. Pritchard, J. E. Warren, A. T. McGown, *Inorg. Chem.* **2002**, *41*, 1907. doi:10.1021/IC010881Q
[35] C. L. Raston, B. W. Skelton, A. H. White, *Aust. J. Chem.* **1978**, *31*, 537. doi:10.1071/CH9780537
[36] A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441. doi:10.1021/J100785A001
[37] R. J. Bertino, G. B. Deacon, J. M. Miller, *Aust. J. Chem.* **1978**, *31*, 527. doi:10.1071/CH9780527
[38] G. B. Deacon, P. C. Junk, *J. Chem. Crystallogr.* **2003**, *33*, 605. doi:10.1023/A:1024945826698
[39] G. B. Deacon, J. E. Cosgriff, E. T. Lawrenz, C. M. Forsyth, D. L. Wilkinson, in *Hermann-Brauer Synthetic Methods of Organometallic and Inorganic Chemistry* (Ed. W. A. Herrmann) **1997**, Vol. 6 (Ed. F. T. Edelmann), pp. 48–49 (G. Thieme: Stuttgart).
[40] A. Agarwal, K. Srivastava, S. K. Puri, P. M. Chauhan, *Bioorg. Med. Chem. Lett.* **2005**, *15*, 3133. doi:10.1016/J.BMCL.2005.04.011
[41] F. Montanari, P. Tundo, *J. Org. Chem.* **1982**, *47*, 1298. doi:10.1021/JO00346A027
[42] D. J. Darensbourg, J. C. Yoder, G. E. Struck, M. W. Holtcamp, J. D. Draper, J. H. Reibenspies, *Inorg. Chim. Acta* **1998**, *274*, 115. doi:10.1016/S0020-1693(97)05962-8
[43] M. A. Sens, N. K. Wilson, P. D. Ellis, J. D. Odom, *J. Magn. Reson.* **1975**, *19*, 323.
[44] Bruker AXS, *Apex2 v 2.0-2005* **2005** (Bruker AXS: Madison, WI).
[45] G. M. Sheldrick, *SADABS: Program for Scaling and Absorption Correction of Area Detector Data* **1997** (Universität Göttingen: Göttingen).
[46] G. M. Sheldrick, *Acta Crystallogr. A* **2008**, *64*, 112. doi:10.1107/S0108767307043930
[47] L. J. Barbour, *J. Supramol. Chem.* **2001**, *1*, 189. doi:10.1016/S1472-7862(02)00030-8
[48] D.-H. Lee, J.-Y. Jung, M.-J. Jin, *Chem. Commun.* **2010**, *46*, 9046. doi:10.1039/C0CC03535A
[49] G. B. Deacon, D. Tunaley, *J. Organomet. Chem.* **1978**, *156*, 403. doi:10.1016/S0022-328X(00)93546-0
[50] K. Nakatsu, H. Yoshioka, K. Kunimoto, T. Kinugasa, S. Ueji, *Acta Crystallogr. B* **1978**, *34*, 2357. doi:10.1107/S0567740878008183