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Metal carbonyl complexes of the ditertiary bismuthine p-$Ph_2BiC_6H_4BiPh_2$ and the effect of coordination upon bismuthine ligand geometry

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Abstract

Complexes of the type $[M(CO)_5(p\text{-}Ph_2BiC_6H_4BiPh_2)]$ and $[\{M(CO)_5\}_2(p\text{-}Ph_2BiC_6H_4BiPh_2)]$ (M = Cr or W) have been prepared and characterised by chemical analysis, ^1H- and $^{13}C\{^1H\}$-NMR and IR spectroscopies. The crystal structure of p-$Ph_2BiC_6H_4BiPh_2$ is reported. The reaction of $[CpFe(CO)_2(THF)]^+$ with p-$Ph_2BiC_6H_4BiPh_2$ in refluxing CH_2Cl_2 results in cleavage of one Bi–C bond to form $[CpFe(CO)_2(BiPh_3)]^+$ identified by an X-ray study. A survey of $BiPh_3$ and its compounds has established that the C–Bi–C angles increase upon complex formation. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Bismuthine; Chromium; Tungsten; X-ray structure

1. Introduction

The coordination chemistry of tertiary bismuthine ligands is very limited, a reflection both of the very weak σ-donor ability of the bismuth and the ease with which Bi–C bonds break in the presence of many metal centres [1,2]. Even for the commonest ligand, $BiPh_3$, only five complexes have been characterised by X-ray crystallography, namely -$[Cr(CO)_5(BiPh_3)]$ [3], $[M(CO)_5(BiPh_3)]$ (M = Mo or W) [4], $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(BiPh_3)]BF_4$ [5], and $[\{Cr(CO)_3(\eta^6\text{-}Ph)\}_2BiPh]$ [6], the last containing the bismuthine bonded to chromium η^6 via the phenyl rings not via the bismuth. Although potential ligands containing two bismuth atoms have been prepared, there are no reports of metal complexes [1]. There are also polydentates containing one bismuth centre in combination with P or As donors [1]. We report here attempts to prepare complexes of the ditertiary bismuthine p-$Ph_2BiC_6H_4BiPh_2$. We recently reported that coordination of $SbPh_3$ to metal centres resulted in an increase in the C–Sb–C bond angles and a decrease in the Sb–C bond distances [7], and we have used literature data to look for similar trends in bismuthine complexes.

2. Results and discussion

2.1. Reactions of $BiPh_3$ with metal carbonyls

In an attempt to extend the number of $BiPh_3$ complexes to support our search for systematic changes in the geometry at bismuth on coordination, we examined the reactions of $BiPh_3$ with $Ni(CO)_4$, $Co_2(CO)_8$, $Fe(CO)_5$, $Fe_2(CO)_9$/THF and $Mn_2(CO)_{10}$ using conditions which successfully produce the corresponding $SbPh_3$ complexes [1]. The reactions were monitored in situ by IR spectroscopy of the solutions in the carbonyl region. No reaction was apparent between $Ni(CO)_4$ and $BiPh_3$ in CH_2Cl_2, the reagents being recovered unchanged after several hours, consistent with the report of Benlian and Bigorgne [8]. In contrast, a mixture of $Co_2(CO)_8$ and $BiPh_3$ in CH_2Cl_2 darkened and decomposed over a few hours, but without any IR spectroscopic evidence for the formation of $Co_2(CO)_{8\text{-}n}(BiPh_3)_n$, the $\nu(C{=}O)$ of the binary carbonyl simply diminishing over time with no new bands appearing. No reaction was apparent between $Fe(CO)_5$ and $BiPh_3$ using $[\{CpFe(CO)_2\}_2]$ or $NaBH_4$ as catalyst, whilst photolysis in toluene resulted in decomposition. Decomposition also occurred using $Fe_2(CO)_9$/THF. It appears that the old report [9] of a (20e)

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$Fe(CO)_4(BiPh_3)_2$ is erroneous. We have recently prepared $[Mn_2(CO)_{10-n}(SbPh_3)_n]$ ($n = 1$ or 2) by photolysis of $Mn_2(CO)_{10}/SbPh_3$ in toluene or from $Mn_2(CO)_{10}/SbPh_3/Me_3NO$ [10]. In similar reactions using $BiPh_3$ only decomposition products were detected by in situ IR spectroscopic studies.

There is some disagreement in the literature about the $^{13}C\{^1H\}$-NMR spectrum of $BiPh_3$ concerning the assignment of the ipso-carbon resonance, which is variously described as δ 131.1, 134.1 or 155.4 ppm [11,12]. Similar uncertainties surround the ipso-carbon resonance positions in the metal complexes [4,5], and further confusion can be introduced by the facile decomposition of the metal complexes in solution. Clarification of this point was important in connection with the spectra of the dibismuthine complexes in Section 2.3. Our $^{13}C\{^1H\}$-NMR spectra of $BiPh_3$ (purified by repeated recrystallisations) confirm the report [12] that the ipso-carbon resonance is at δ 155.5 ($CHCl_3$ solution). In the complexes (recorded in $CH_2Cl_2/CDCl_3$ solutions at 250 K to minimise decomposition) the ipso-carbon resonances were observed at δ 156.3 $[Cr(CO)_5(BiPh_3)]$, 155.0 $[Mo(CO)_5(BiPh_3)]$, 156.7 $[W(CO)_5(BiPh_3)]$ and 156.0 $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(BiPh_3)]BF_4$.

2.2. The *p*-$Ph_2BiC_6H_4BiPh_2$ ligand

The *p*-$Ph_2BiC_6H_4BiPh_2$ was prepared as described by Zorn et al. [13] by reaction of *p*-$C_6H_4Br_2$, ^{n}BuLi and Ph_2BiCl, and purified by recrystallisation from propan-2-ol. After completion of our work, Matano et al. [14] reported the preparations of *m*- and *p*-$Ph_2BiC_6H_4BiPh_2$, and higher oligomers $Ph_2BiC_6H_4(BiPhC_6H_4)_nBiPh_2$ ($n = 1$ or 2). The latter syntheses used different reagents and reaction conditions, and in our preparations only $BiPh_3$ and *p*-$Ph_2BiC_6H_4BiPh_2$ were obtained in isolable amounts, although traces of $Ph_2BiC_6H_4BiPhC_6H_4BiPh_2$ were sometimes detected in the crude product by FAB MS. The *p*-$Ph_2BiC_6H_4BiPh_2$ was characterised by analysis, ^1H- and $^{13}C\{^1H\}$-NMR spectroscopy (Section 3). Notably the $^{13}C\{^1H\}$-spectrum contains six resonances, 155.4, 155.2 (ipso), 139.8 (C_6H_4), 137.9 (*o*-Ph), 130.8 (*m*-Ph), 128.0 (*p*-Ph). The X-ray crystal structure of the ligand was obtained and is shown in Fig. 1 and selected bond lengths and angles are given in Table 1. The structure consists of discrete centrosymmetric molecules with the expected pyramidal geometry at the Bi atom. The C–Bi–C angles are close to those found in $BiPh_3$ [15,16] and the Bi–C distances although not well determined fall in the expected range; other geometrical features are unexceptional.

2.3. *p*-$Ph_2BiC_6H_4BiPh_2$ complexes

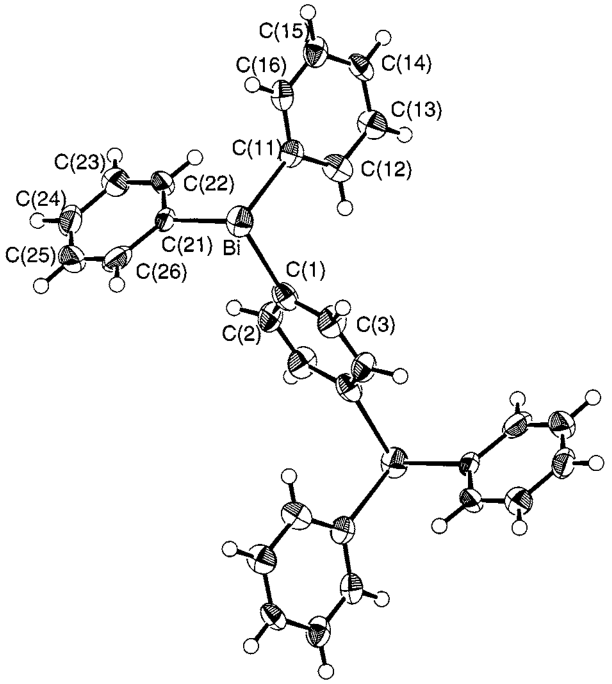

Fig. 1. Molecular structure of *p*-$Ph_2BiC_6H_4BiPh_2$ showing the atom numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

The reaction of *p*-$Ph_2BiC_6H_4BiPh_2$ with $[W(CO)_5(THF)]$ (generated in situ by photolysis of $W(CO)_6$ in THF) in 1:1 and 1:2 mole ratios, followed by removal of the THF in vacuo, and recrystallisation of the products by cooling a hexane solution produced yellow solids $[W(CO)_5(p\text{-}Ph_2BiC_6H_4BiPh_2)]$ (**1**) and $[\{W(CO)_5\}_2(p\text{-}Ph_2BiC_6H_4BiPh_2)]$ (**2**), respectively. The IR spectra in *n*-hexane solution are typical of $W(CO)_5$ groups with ν(C=O) at 2073, 1948 cm^{-1} (**1**) and 2075, 1950 cm^{-1} (**2**), which are as expected very similar to

Table 1
Selected bond lengths (Å) and angles (°) for *p*-$Ph_2BiC_6H_4BiPh_2$ [a]

Bond length (Å)			
Bi–C(1)	2.25(2)	C(1)–C(2)	1.35(2)
Bi–C(11)	2.24(2)	C(1)–C(3)	1.38(2)
Bi–C(21)	2.26(2)	C(2)–C(3i)	1.42(2)
C–C (phenyl)	1.36(2)–1.43(2)		
Bond angle (°)			
C(1)–Bi–C(11)	93.4(6)	C(2)–C(1)–C(3)	119(2)
C(1)–Bi–C(21)	93.9(6)	C(1)–C(2)–C(3i)	122(1)
C(11)–Bi–C(21)	94.3(6)	C(1)–C(3)–C(2i)	119(1)
C–C–C (phenyl)	118(2)–122(2)		
Torsional angle (°)			
C(1)–Bi–C(11)–C(12)	−5(1)	C(2)–C(1)–Bi–C(11)	−83(1)
C(1)–Bi–C(21)–C(22)	−96(1)	C(2)–C(1)–Bi–C(21)	11(1)

[a] Symmetry operation: (i) $1-x$, $-y$, $1-z$.

the frequencies observed for [W(CO)$_5$(BiPh$_3$)] (2074, 1945 cm^{-1}) [4]. The ^{1}H-NMR spectra are uninformative, but the ^{13}C{^{1}H}-NMR are more useful. NMR spectra were recorded from CH$_2$Cl$_2$/CDCl$_3$ solutions at 250 K to minimise decomposition. For the monotungsten complex (**1**), the δ(CO) were found at 198.4 {$^1J_{W-C} = 176$ Hz} and 197.5 {$^1J_{W-C} = 122$ Hz}, the ipso-Cs at 157.6, 156.0, 155.6, and 155.1, and seven other aromatic resonances between 140 and 128 ppm (by symmetry for an η^1 dibismuthine we expect 4 ipso-Cs and 8 others). The ditungsten complex **2** was less soluble and the ^{13}C{^{1}H}-NMR spectra had poorer signal/noise and the $^1J_{W-C}$ satellites were unclear on the δ(CO) resonances. However the aromatic regions are notably simpler than in complex **1** with two ipso-C resonances 156.0, 155.5, and four others. In contrast to [W(CO)$_5$(BiPh$_3$)] which exhibited a parent ion and stepwise loss of COs in the FAB mass spectrum, the dibismuthine complexes gave very weak FAB data dominated by lower mass fragments and are not useful. Despite many attempts we have been unable to obtain X-ray quality crystals of either tungsten complexes, even at low temperatures slow decomposition occurs in solution.

The chromium complexes of p-Ph$_2$BiC$_6$H$_4$BiPh$_2$ are less stable in solution than the tungsten analogues, although the powders appear stable at −20°C under nitrogen for some months. The reaction of [Cr(CO)$_5$(THF)] with p-Ph$_2$BiC$_6$H$_4$BiPh$_2$ in a 2:1 mole ratio, followed by rapid removal of the THF in vacuo, and recrystallisation by cooling a hexane solution, gave a poorly soluble greenish yellow powder, identified by analysis as [{Cr(CO)$_5$}$_2$(p-Ph$_2$BiC$_6$H$_4$BiPh$_2$)] (**3**). The filtrate contained the paler yellow [Cr(CO)$_5$(p-Ph$_2$BiC$_6$H$_4$BiPh$_2$)] (**4**) and Cr(CO)$_6$ which were again separated by crystallisation from hexane with cooling. Better yields of **4** were obtainable directly using a 1:1 ratio of [Cr(CO)$_5$(THF)]: p-Ph$_2$BiC$_6$H$_4$BiPh$_2$. The IR spectrum of complex **4** in n-hexane (ν(C=O) 2064, 1948 cm^{-1}) and its ^{13}C{^{1}H}-NMR spectrum, which was very similar to that of **1**, confirm it as having η^1-dibismuthine coordination. The freshly prepared n-hexane solution of complex **3** had a very similar IR spectrum (2064, 1948 cm^{-1}) to **4**, but its ^{13}C{^{1}H}-NMR spectrum was initially confusing, showing a complex aromatic region (at least 10 resonances), and three δ(CO) (212.0, 216.9, 221.1), and after recording the spectrum some precipitate was evident in the NMR tube. An IR spectrum obtained from the NMR solution after recording the NMR data revealed three ν(C=O) stretches, one of which corresponded to Cr(CO)$_6$. The ^{13}C{^{1}H}-NMR resonance at 212.0 can also be identified as the hexacarbonyl, and comparison of the aromatic region of the spectrum obtained from **3** showed it was very similar indeed to that of **4**. We conclude that, in solution at 250 K over a period of the few hours needed to record the ^{13}C{^{1}H}-NMR spectrum, **3** decomposes to **4** and Cr(CO)$_6$. Mass balance requires other products to form but these were not identified, presumably being in the observed precipitate. Decomposition/disproportionation is also a feature of the Group 6 carbonyl chemistry of distibines such as Ph$_2$SbCH$_2$SbPh$_2$ [17,18]. All attempts to isolate molybdenum carbonyl complexes of p-Ph$_2$BiC$_6$H$_4$BiPh$_2$ were unsuccessful, the reaction mixtures of [Mo(CO)$_5$(THF)] and the ligand rapidly turning brown and then black, and even at low temperatures no complex could be isolated. The solution stability of the Group 6 carbonyl complexes [M(CO)$_5$(BiPh$_3$)] is W > Cr ≫ Mo [4], and our results indicate a similar order for the p-Ph$_2$BiC$_6$H$_4$BiPh$_2$ complexes, although these are all less stable than the BiPh$_3$ analogues.

In an attempt to improve stability/solubility, we tried to prepare [(η^5-C$_5$H$_5$)Fe(CO)$_2$(p-Ph$_2$BiC$_6$H$_4$BiPh$_2$)]BF$_4$, from reaction of [(η^5-C$_5$H$_5$)Fe(CO)$_2$(THF)]$^+$ and the ligand. No reaction was apparent after stirring a suspension of the reagents in Et$_2$O overnight at room temperature (r.t.) Similarly no reaction (as monitored by IR spectroscopy) occurred in CH$_2$Cl$_2$ at r.t., but on refluxing the CH$_2$Cl$_2$ solution for several hours, the CO bands of the starting material disappeared, and were replaced by two new bands. Work up gave a quantity of brown/black material and an orange solid. Crystals of the latter were grown by the vapour diffusion of diethyl ether into a dichloromethane solution and found by an X-ray crystal structure determination to be the known complex [(η^5-C$_5$H$_5$)Fe(CO)$_2$(BiPh$_3$)]BF$_4$ [5] although as a different polymorph [19]. Cell reduction to the Niggli form established that the crystals were different, although the cell volumes are very similar and the geometry of the cation is very similar to that in the published structure [5]. The possibility that the crystal studied was unrepresentative of the whole was eliminated since the ^{13}C{^{1}H}-NMR and the IR spectra of other crystals from the batch and the bulk powder were identical, and in excellent agreement with literature data on the BiPh$_3$ complex [5]. Similarly the possibility that it results from BiPh$_3$ impurity in the p-Ph$_2$BiC$_6$H$_4$BiPh$_2$ was ruled out since, (a) the same batch used to obtain W and Cr complexes was used for the iron complex; and (b) the yield is not consistent with a minor impurity. The generation of BiPh$_3$ from p-Ph$_2$BiC$_6$H$_4$BiPh$_2$ requires only that one weak C–Bi bond on the bridging p-phenylene group breaks and a hydrogen atom is picked up by the carbon. Fission of C–Bi bonds in the presence of metals is well established, although often the decomposition products were not identified [1,2]. A closer example of ligand modification and coordination is in the formation of [Pd(AsMe$_2$Ph)$_3$Cl]BPh$_4$ on reaction of Bi(o-C$_6$H$_4$AsMe$_2$)$_3$ with PdCl$_2$(MeCN)$_2$ and NaBPh$_4$ [20].

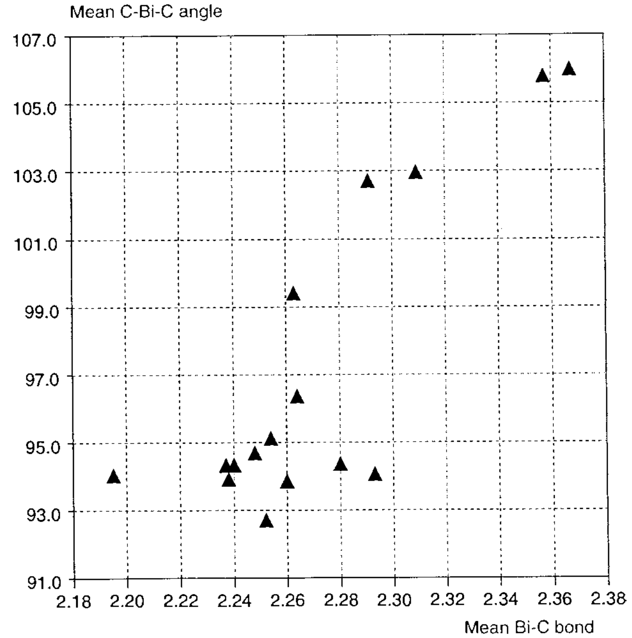

Fig. 2. Scattergram plot showing the average C–Bi–C angle (°) against the average Bi–C bond length (Å) for substituted aryl bismuthines BiR_3.

It is clear from the above results that p-$Ph_2BiC_6H_4BiPh_2$ is not well suited as a ligand with which to develop coordination chemistry of dibismuthines, in that in addition to very poor donor properties and the lack of substituents suited to NMR studies (both evident when the work was initiated), the complexes have poorer solubilities and are more prone to Bi–C fission than the $BiPh_3$ analogues. Future studies will focus on alkyl substituted dibismuthines.

2.4. The effect of coordination on bismuth ligand geometries

As indicated in Section 1, one object of this study was to obtain structural data on one or more complexes of p-$Ph_2BiC_6H_4BiPh_2$ and examine the bond angle/bond length changes that occur at the bismuth centre on coordination. Our failure to obtain crystallographic data on any of the complexes prevents this, but we have used literature data on $BiPh_3$ complexes as an alternative. Some five complexes of $BiPh_3$ have been structurally characterised including the Fe compound polymorph noted here and the ligand itself has been reported on two occasions [15,16] providing very small samples for any statistical inference to be drawn. In addition there is the dibismuthine reported here and the 3-coordinate Bi complex $[\{Cr(CO)_3(\eta^6\text{-}Ph)\}_2BiPh]$ [6], both of which have C–Bi–C angles close to those in $BiPh_3$. The poor donor properties of the bismuthines make it unlikely that there will be large numbers of examples available and we are forced to draw conclusions, albeit at lower confidence limits, with the small samples. As with $SbPh_3$ where the sample size is much larger, the effect of coordination at the Bi centre is to *increase* the C–Bi–C angle. For each complex a mean C–Bi–C angle was obtained and the mean of these (mean) angles was 99.1(9)°.[1] Similarly for the uncomplexed Bi ligand where we took the four examples gives a mean C–Bi–C angle of 93.9(1)°. (Using only the two $BiPh_3$ structures did not effect the conclusion.) In an attempt to quantify the difference in the means we used two statistical tests [21] (Student's t-test for two samples with different variances ($t = 12.5$, d.f. $= 4$) and ANOVA for a single factor ($F = 122$, d.f. $= 1, 7$)), which allows us to reject the Null Hypothesis (that is, that the two samples are drawn from a common population) at better than $\alpha = 0.01$. We also used the non-parametric Mann–Whitney U-test [22] and as expected found a similar result. With the usual caveats, we conclude that the effect of the increasing bond angle on coordination is statistically significant. No relationship between the C–Bi–C angle and the Bi–C distance analogous to that proposed [7] for Sb was found in the sample studied.

During this study we examined the pyramidal aryl substituted bismuthines $BiAr_3$ in the Cambridge structural database [23–25] and noted a positive correlation between the mean C–Bi–C angle and the mean Bi–C distance for 15 fragments. This is shown in Fig. 2 and the product–moment correlation coefficient (0.83) and the Spearman rank correlation coefficient (0.68) provide numerical support for the graphical display. Li et al [26] suggested such a trend based on four examples.

3. Experimental

Physical measurements were made as described previously [4].

3.1. Synthesis

3.1.1. p-$Ph_2BiC_6H_4BiPh_2$

p-$C_6H_4Br_2$ (3.14 g, 13.3 mmol) in diethyl ether (40 ml) and ^{n}BuLi (53.3 mmol) were refluxed together under nitrogen for 165 min. After cooling, $BiPh_2Br$ (11.8 g, 26.6 mmol) suspended in diethyl ether (60 ml) was added and the mixture stirred overnight and then refluxed under nitrogen for 9 h. After cooling, water (30 ml) was added and the organic layer separated, the solvent removed and propan-2-ol (50 ml) added to give a white solid, which was filtered and dried in vacuo.

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[1] In this and subsequent average values, an unweighted mean was used and the figure in parentheses represents the sample standard deviation.

Yield, 3.5 g, 33%. (Found: C, 45.1; H, 2.8. $C_{30}H_{24}Bi_2$ requires C, 44.9; H, 3.0%). ^{1}H-NMR ($CDCl_3$) 7.2(m), 7.8(m). $^{13}C\{^1H\}$-NMR ($CHCl_3$, 300 K) 155.4, 155.2, 139.8, 137.9, 130.8, 128.0.

3.1.2. *[W(CO)$_5$(p-Ph$_2$BiC$_6$H$_4$BiPh$_2$)] (**1**)*

$W(CO)_6$ (0.27 g, 0.75 mmol) in THF (30 ml) was photolysed for 160 min under nitrogen. *p*-$Ph_2BiC_6H_4BiPh_2$ (0.60 g, 0.75 mmol) was added and the mixture refluxed for 5 min. The solvent was then removed, the residue extracted into hexane, filtered, reduced in volume to ca. 5 ml and left in the freezer under nitrogen. The yellow solid which precipitated was filtered and dried in vacuo. (Found: C, 37.6; H, 2.3. $C_{35}H_{24}Bi_2O_5W$ requires C, 37.3; H, 2.1%). ^{1}H-NMR ($CDCl_3$) 7.2–7.9 (m). $^{13}C\{^1H\}$-NMR ($CH_2Cl_2/CDCl_3$, 250 K) 198.4 $\{^1J_{W-C} = 176$ Hz$\}$ and 197.5 $\{^1J_{W-C} = 122$ Hz$\}$, 157.6, 156.0, 155.6, 155.1, 140.0, 139.3, 138.0, 136.4, 131.5, 130.3, 128.3. IR (hexane)/cm^{-1} 2073, 1948.

3.1.3. *[{W(CO)$_5$}$_2$(p-Ph$_2$BiC$_6$H$_4$BiPh$_2$)] (**2**)*

Same as for **1** using *p*-$Ph_2BiC_6H_4BiPh_2$ (0.30 g, 0.37 mmol) and refluxing for 1 h. (Found: C, 33.4; H, 1.9. $C_{40}H_{24}Bi_2O_{10}W_2$ requires C, 33.1; H, 1.7%). ^{1}H-NMR ($CDCl_3$) 7.2–7.9 (m). $^{13}C\{^1H\}$ NMR ($CH_2Cl_2/CDCl_3$, 250 K) 197.9 and 197.7, 156.0, 155.5, 138.0, 136.2, 131.0, 130.1. IR (hexane)/cm^{-1} 2075, 1950.

3.1.4. *[{Cr(CO)$_5$}$_2$(p-Ph$_2$BiC$_6$H$_4$BiPh$_2$)] (**3**)*

Same as for **2** but using $Cr(CO)_6$ (0.17 g, 0.75 mmol). (Found: C, 40.0; H, 2.1. $C_{40}H_{24}Bi_2Cr_2O_{10}$ requires C, 40.5; H, 2.0%). ^{1}H-NMR ($CDCl_3$) 7.2–7.9 (m). $^{13}C\{^1H\}$-NMR ($CH_2Cl_2/CDCl_3$, 250 K) see text. IR (hexane)/cm^{-1} 2064, 1948.

3.1.5. *[Cr(CO)$_5$(p-Ph$_2$BiC$_6$H$_4$BiPh$_2$)] (**4**)*

Same as for **1** but using $Cr(CO)_6$ (0.17 g, 0.75 mmol). (Found: C, 42.5; H, 2.4. $C_{35}H_{24}Bi_2CrO_5$ requires C, 42.3; H, 2.4%). ^{1}H-NMR ($CDCl_3$) 7.2–7.9 (m). $^{13}C\{^1H\}$-NMR ($CH_2Cl_2/CDCl_3$, 250 K) 221.1, 216.9, 155.5, 155.2, 154.9, 139.9, 139.6, 139.3, 137.5, 130.5, 129.5, 127.8. IR (hexane)/cm^{-1} 2064, 1948. Yields for compounds **1** to **4** range from 10 to 20%.

3.2. *Crystallography*

Air-stable crystals were obtained by liquid diffusion of ethanol into a CH_2Cl_2 solution of *p*-$Ph_2BiC_6H_4BiPh_2$, and one (0.33 × 0.22 × 0.22 mm) was mounted on a glass fibre using the oil-film technique and held at 150 K using an Oxford Cryosystems low temperature device. Data (2519 observations, $2\theta_{max} = 50°$) were recorded using a Rigaku AFC7S diffractometer fitted with Mo–K$_\alpha$ radiation ($\lambda = 0.71073$ Å). After data processing there were 2321 unique observations ($R_{int} = 0.064$) and an empirical ψ-scan absorption was applied (Transmission: min. 0.612; max. 1.000) but no decay correction was required. The structure was solved by standard heavy atom procedures and refined to convergence by full-matrix least-squares refinement on F [27] to $R = 0.045$ [1431 observed reflections ($F > 4\sigma(F)$), 145 parameters, anisotropic (Bi, C) and isotropic atoms (H), $w^{-1} = \sigma^2(F_o)$, max. shift/Estimated S.D., 0.002, $S = 2.0$, $wR = 0.050$]. H atoms were included in the model in calculated positions (d(C–H) = 0.95 Å). The residual electron density was in the range 2.2 to −2.2 e Å^{-3}.

3.2.1. *Crystal data for p-Ph$_2$BiC$_6$H$_4$BiPh$_2$*

Molecular formula, $C_{30}H_{24}Bi_2$, $M_r = 802.48$, monoclinic, space group, $P2_1/a$ (no. 14), $a = 6.849(2)$, $b = 22.972(2)$, $c = 8.212(1)$ Å, $\beta = 97.07(2)°$, $V = 1282.2(4)$ Å^3, $Z = 2$, $D_{calc.} = 2.078$ g cm^{-3}, $F(000) = 740$, $\mu = 136.81$ cm^{-1}.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 114359 (ligand) and 114360 (Fe complex). Copies of these data can be obtained free of charge, on application to CCDC, 12 Union Rd., Cambridge CB2 1EZ, UK.

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