Half sandwich complexes derived from a 2,4-diphosphastibolyl ring anion

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Abstract

The reaction of the hetero-ring anion $[C_2Bu^t_2P_2Sb]^-$ with $[\{M(\eta^4\text{-}1,5\text{-}C_8H_{12})Cl\}_2]$, M = Rh, Ir, leads to the formation of $[M(\eta^5\text{-}C_2Bu^t_2P_2Sb)(\eta^4\text{-}1,5\text{-}C_8H_{12})]$, M = Rh **7**, Ir **8**. Treatment of $CoCl_2$ with either an equimolar mixture of $[C_2Bu^t_2P_2Sb]^-$ and $[C_5Me_5]^-$, or two equivalents of $[C_2Bu^t_2P_2Sb]^-$ affords the compounds $[Co(\eta^5\text{-}C_5Me_5)(\eta^4\text{-}C_2Bu^t_2HP_2Sb)]$, **11**, and $[Co(\eta^5\text{-}C_2Bu^t_2P_2Sb)(\eta^4\text{-}C_2Bu^t_2HP_2Sb)]$, **12**, which represent the first examples of diphosphastibacyclopentadiene complexes; the X-ray crystal structures of **7** and **11** are reported.

Keywords: Diphosphastibolyl; Diphosphastibacyclopentadiene; Low coordination; Antimony; Phosphorus

1. Introduction

Cyclopentadienyl ring anions substituted with one or more of the heavier Group 15 elements are proving to be versatile ligands toward both transition and main group metals. The most studied of these are the mono- and polyphospholyl anions $[C_nR_nP_{5-n}]^-$ ($n = 0$–4), which display a wide variety of coordination modes [1]. Especially relevant to the work reported here is the 1,2,4-triphospholyl ring, $[C_2Bu^t_2P_3]^-$, **1**, the organometallic chemistry of which has been extensively studied by Nixon [2]. Heterocyclopentadienyl anions derived from As, Sb or Bi have not been as closely investigated, though Ashe and Al-Ahmad [3] have had considerable success in preparing complexes from ring anions of the type $[C_4R_4E]^-$ (E = As, Sb, Bi; R = H, alkyl). In addition, some work has been carried out by Scherer and coworkers with the pentaarsolyl anion, As_5^- [4]. Only recently has this area been extended to hetero-cycles containing mixtures of Group 15 elements with the synthesis of the 2,4- and 3,4-diphosphaarsolyls, $[C_2Bu^t_2P_2As]^-$ (**2** and **3** respectively) [5], and the 3-phosphaarsolyls, $[C_3R_2HPAs]^-$ (R = Me, Et, Ph) [6], all of which form transition metal complexes. We have become interested in broadening this field to mixed P,

Sb heterocyclic systems which we have achieved with the high yield, regiospecific synthesis of the 2,4-diphos-phastibolyl ring anion $[C_2Bu^t_2P_2Sb]^-$ **4** [7]. Early work with this ligand has enabled us to incorporate it into the air-stable sandwich complexes, $[Ru(\eta^5\text{-}C_5R_5)(\eta^5\text{-}C_2Bu^t_2P_2Sb)]$ (R = H **5**, Me **6**), one of which, **6**, displays intermolecular $P \cdots P$ interactions in the solid state [8]. These results have prompted us to examine the preparation of half sandwich complexes derived from **4** which we describe herein. The preparation and charac-terisation of the first diphosphastibacyclopentadiene complexes by protonation of cobalt complexes of **4** are also reported.
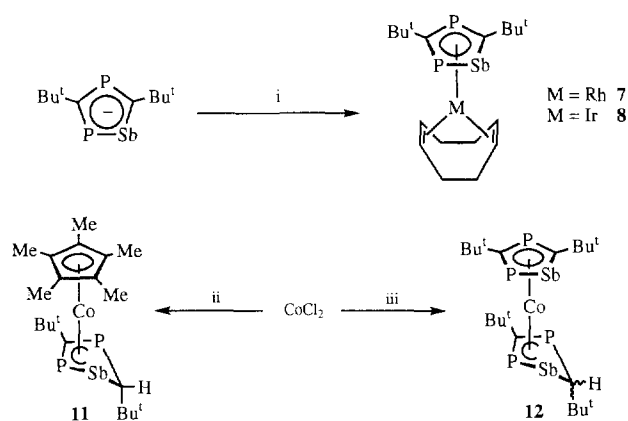

E = P   E' = P   **1**
E = As E' = P   **2**
E = P   E' = As **3**
E = Sb E' = P   **4**

R = H   **5**
R = Me **6**

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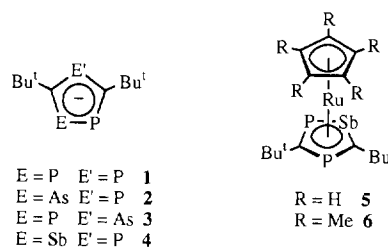
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2. Results and discussion

Treatment of [4][Li(tmeda)$_2$] with [{M(η^4-1,5-C$_8$H$_{12}$)Cl}$_2$], M = Rh, Ir, leads to the formation of the air- and moisture-stable complexes, [M(η^5-C$_2$Bu$^t_2$P$_2$Sb)(η^4-1,5-C$_8$H$_{12}$)], M = Rh 7, Ir 8 (Scheme 1). Both complexes could be partially purified by column chromatography (60 mesh silica, hexane eluent) and subsequent crystallisation from diethyl ether, though contamination with small amounts (ca. 10%) of the analogous triphospholyl complexes, [M(η^5-C$_2$Bu$^t_2$P$_3$)(η^4-1,5-C$_8$H$_{12}$)], M = Rh 9 [9], Ir 10, was unavoidable. These impurities are a result of the co-synthesis of the triphospholyl ring anion, 1 (ca. 25%), in the preparation of the diphosphastibolyl precursor, 4 (ca. 75%) [7]; the mixture being inseparable. Rigorous attempts to purify 7 and 8 met with failure due to their persistent co-crystallisation with 9 and 10 respectively. Analytical data could not be obtained for the same reason. The approximate yields of 7 (26%) and 8 (22%) were determined by relating the integration of the ^{31}P NMR spectra of the mixtures (7 and 9) and (8 and 10) to the total weight yield and are calculated on the transition metal precursor. Complexes 7 and 8 possess remarkable thermal stability (dec. > 200 °C for the mixture) which is most likely a result of considerable heterocyclic ring aromaticity, as has been proposed for related half sandwich complexes derived from [C$_4$R$_4$E]$^-$ (E = As, Sb, Bi) [3].

Treatment of CoCl$_2$ with either an equimolar mixture of [4][Li(tmeda)$_2$] and Li[C$_5$Me$_5$], or two equivalents of [4][Li(tmeda)$_2$] in DME afforded low to moderate yields of the air- and moisture-stable diamagnetic complexes, [Co(η^5-C$_5$Me$_5$)(η^4-C$_2$Bu$^t_2$HP$_2$Sb)], 11 (8%, m.p. 127 °C), and [Co(η^5-C$_2$Bu$^t_2$P$_2$Sb)(η^4-C$_2$Bu$^t_2$HP$_2$Sb)], 12 (18%, m.p. 138 °C) (Scheme 1). Both compounds were purified by column chromatography (60 mesh silica, hexane) and recrystallised from ether. Interest-

ingly, no contamination of 11 or 12 with their 1,2,4-triphosphacyclopentadiene analogues, [Co(η^5-C$_5$Me$_5$)(η^4-C$_2$Bu$^t_2$HP$_3$)] 13 and the previously reported [Co(η^5-C$_2$Bu$^t_2$P$_3$)(η^4-C$_2$Bu$^t_2$HP$_3$)] 14 [10], was observed, despite the aforementioned co-synthesis of the precursor ring anion 4 with 1. This situation arose due to significantly different column retention times for the contaminants relative to the major products.

The spectroscopic data for 7 and 8 support the proposed half sandwich structures. Their ^{31}P{^{1}H} NMR spectra show AMX and AX patterns respectively with $^2J_{P(A)P(X)}$ coupling constants in the characteristic range. The broadness of the low field signal in 7 and the high field signal in 8 suggest these arise from the phosphorus atoms adjacent to the quadrupolar antimony centres. In addition, compound 7 shows $^1J_{Rh(M)P(A \text{ and } X)}$ couplings of 6.5 Hz. It is noteworthy that similar $^1J_{RhP}$ couplings of 6.7 Hz are also displayed by the impurity, 9, though these were not described in the previous report on this compound [9]. The triphospholyl impurity, 10, in the synthesis of 8 has not been previously reported but exhibits an AX$_2$ pattern (δ 83.6 (d), 101.9 (tr), $^2J_{PP}$ = 44.2 Hz) as expected. Solution ^{1}H and ^{13}C NMR data could not be assigned due to the complexity of the spectra of the mixtures (7 and 9) and (8 and 10). The mass spectra of 7 and 8 exhibit molecular ion peaks with the correct isotopic distribution.

The spectroscopic data for 11 and 12 are consistent with both proposed structures having protonated ring carbons which lie between an antimony and a phosphorus centre. Interestingly, there is no evidence for the corresponding 1,4-diphospha-2-stibacyclopentadiene complexes that would arise from the protonation of the ring carbons adjacent to two phosphorus centres. Consistent with this is the fact that both the saturated ring carbons and their proton substituents appear as doublets (^{13}C and ^{1}H NMR respectively) being coupled to only one phosphorus and having $^1J_{PC}$ and $^2J_{PH}$ coupling constants in the characteristic range. Unfortunately, it is not possible to tell from the ^{1}H NMR spectra of 11 and 12 if the ring protons are in the exo- or endo-positions, though the presence of only one signal for each confirms that one isomer is exclusively formed.

The ^{31}P{^{1}H} NMR spectrum of 11 displays an AX pattern with characteristic $^2J_{P(A)P(X)}$ couplings. The broadness of the high field signal implies that this originates from the phosphorus adjacent to the antimony centre. Four broad, widely spaced multiplets were observed in the ^{31}P{^{1}H} NMR spectrum of 12 which did not resolve sufficiently at −60 °C to allow the assignment of these signals. Presumably this broadness arises from either inter-ring P–P coupling, quadrupolar broadening due to antimony, rotation of the η^5-diphosphastibolyl ring relative to the η^4-diphosphastibacyclopentadiene ligand or a combination of more than one of these factors. The mass spectra of both compounds

Scheme 1. Reagents and conditions: (i) [{M(η^4-1,5-C$_8$H$_{12}$)Cl}$_2$], M = Rh, Ir, DME, 24h, 25 °C; (ii) [4][Li(tmeda)$_2$], Li[C$_5$Me$_5$], DME, 25 °C, 18h; (iii) [4][Li(tmeda)$_2$], DME, 25 °C, 18h.

exhibit molecular ion peaks with the correct isotopic distribution. It is noteworthy that **11** and **12** contain the first examples of metal-coordinated antimony-substituted butadiene fragments. For sake of comparison, one of us has recently reported the first uncoordinated antimony substituted butadiene, viz. [{(2,4,6-Bu$_3^t$Ph)(Me$_3$SiO)C=Sb}$_2$] [11].

With regards to a mechanism for the formation of **11** and **12**, it seems plausible that both are formed via the paramagnetic intermediates, [Co(η^5-C$_5$Me$_5$)(η^5-C$_2$Bu$_2^t$P$_2$Sb)] and [Co(η^5-C$_2$Bu$_2^t$P$_2$Sb)(η^5-C$_2$Bu$_2^t$P$_2$Sb)], which most likely abstract protons from the reaction solvent. A similar argument has been put forward to explain the formation of the closely related complex, **14** [10].

The molecular structure of **7** is depicted in Fig. 1 (see Tables 1 and 2). During refinement it was found that the sites labelled Sb(1) and P(1) were partially occupied by phosphorus (25%) and antimony (7%) respectively, whilst P(2) had a 100% phosphorus occupancy. This site disorder is consistent with the co-crystallisation of a racemic mixture of both enantiomers of **7** (82%) with the by-product triphospholyl complex **9** (18%) and is in line with the NMR of the product mixture (vide supra). Repeated attempts to fractionally crystallise complex **7** from the mixture proved fruitless, which is not surprising given the structural similarities between **7** and **9** which, no doubt, leads to their ability to co-crystallise.

Table 1

Crystal data for the co-crystallised mixture of [Rh(η^5-C$_2$Bu$_2^t$P$_2$Sb)(η^4-1,5-C$_8$H$_{12}$)] **7** and [Rh(η^5-C$_2$Bu$_2^t$P$_3$)(η^4-1,5-C$_8$H$_{12}$)] **9**, and [Co(η^5-C$_5$Me$_5$)(η^4-C$_2$Bu$_2^t$HP$_2$Sb)] **11**

	7 and 9	11
Chemical formula	C$_{18}$H$_{30}$P$_{2.18}$RhSb$_{0.82}$	C$_{20}$H$_{34}$CoP$_2$Sb
Fw	516.68	517.09
Space group	P2$_1$/n	P2$_1$/c
a (Å)	8.6080(9)	29.131(9)
b (Å)	18.4110(14)	15.788(7)
c (Å)	12.6110(7)	9.725(2)
α (°)	90.0	90.0
β (°)	100.350(9)	90.500(10)
γ (°)	90.0	90.0
V (Å^3)	1966.1(3)	4473(3)
Z	4	8
T (K)	150(2)	150(2)
λ (Å)	0.71069	0.71069
ρ$_{calcd}$ (g cm^{-1})	1.746	1.536
μ (MoK$_\alpha$) (cm^{-1})	21.44	20.93
F(000)	1030	2096
Reflections collected	5663	15159
No. unique reflections	2543	6188
Crystal size (mm^3)	0.18×0.22×0.28	0.2×0.31×0.12
θ range(°)	2–25	2–25
R ^{a} (on F)	0.0484	0.0586
wR' ^{b} (on F^2 for all data)	0.0825	0.0846

^{a} $R = \Sigma(\Delta F)/\Sigma(F_o)$.
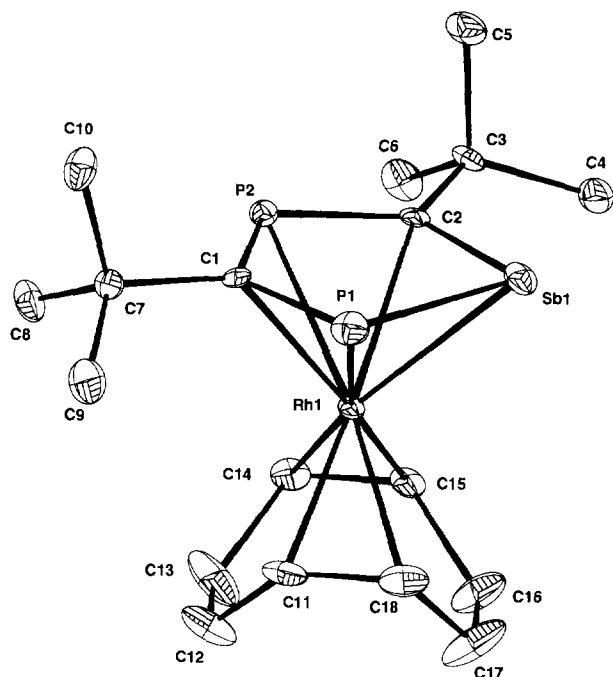^{b} $wR = [\Sigma\{w(\Delta F^2)^2\}/\Sigma\{w(F_o^2)^2\}]^{1/2}$.

Fig. 1. Molecular structure of the co-crystallised mixture of **7** and **9**. Selected bond lengths (Å) and angles (°): Sb(1)–C(2) 2.078(7), Sb(1)–P(1) 2.4001(14), P(1)–C(1) 1.834(7), P(2)–C(1) 1.745(7), P(2)–C(2) 1.770(6), C(2)–Sb(1)–P(1) 88.9(2), C(1)–P(1)–Sb(1) 101.7(2), C(1)–P(2)–C(2) 102.7(3), P(2)–C(1)–P(1) 123.2(3), P(2)–C(2)–Sb(1) 123.5(3).

Table 2

Fractional atomic coordinates (× 10^4) and equivalent isotropic thermal parameters (Å^2 × 10^3) for the co-crystallised mixture of **7** and **9**. U$_{eq}$ is defined as one-third of the trace of the orthogonalised U$_{ij}$ tensor

	x	y	z	U$_{eq}$
Sb(1) ^{a}	−1053(1)	1068(1)	497(1)	23(1)
Rh(1)	1681(1)	1782(1)	1190(1)	14(1)
P(1) ^{b}	−759(2)	2330(1)	96(2)	27(1)
P(2)	212(2)	2186(1)	2616(2)	18(1)
C(1)	−88(7)	2710(3)	1445(6)	17(2)
C(2)	−246(7)	1298(3)	2115(6)	17(2)
C(3)	−213(7)	698(3)	2959(7)	20(2)
C(4)	−156(8)	−6(3)	2465(7)	31(2)
C(5)	−1760(8)	764(3)	3392(7)	30(2)
C(6)	1162(8)	771(3)	3915(7)	32(2)
C(7)	138(7)	3548(3)	1584(6)	20(2)
C(8)	1451(8)	3718(3)	2545(7)	31(2)
C(9)	528(9)	3919(3)	582(7)	43(2)
C(10)	−1423(8)	3849(3)	1814(7)	30(2)
C(11)	3176(8)	2336(3)	254(7)	31(2)
C(12)	4727(9)	2541(5)	923(9)	66(3)
C(13)	5145(8)	2189(4)	1969(9)	57(3)
C(14)	3920(7)	1690(3)	2299(7)	29(2)
C(15)	3539(7)	1028(3)	1826(7)	26(2)
C(16)	4265(10)	693(4)	926(8)	48(3)
C(17)	3918(11)	1029(4)	−102(9)	60(3)
C(18)	2791(8)	1663(3)	−220(7)	33(2)

^{a} Site occupied with phosphorus (25%).
^{b} Site occupied with antimony (7%).

It is certain, however, that the crystal structure determination does confirm the presence of both compounds in the one crystal. Unfortunately, any discussion of the bond lengths and angles within the heterocyclic ring is precluded by the observed disorder. However, bond lengths for the co-crystallised mixture are shown in Fig. 1, from which it is obvious that the ring is essentially planar and η^5-ligated to the rhodium centre (Rh(1)–centroid 1.846(2) Å; Rh(1)–centroid–ring plane 90.0(2)°). The geometry of the coordinated 1,5-cyclooctadiene ligand is similar to that in related complexes, e.g. **9** [9].

Complex **11** crystallises with two independent molecules in the asymmetric unit with no significant geometric differences between them. It is apparent from the molecular structure of one of these (Fig. 2, see Tables 1 and 3) that the SbPCP fragment of the diphosphastibacyclopentadiene ring is planar and η^4-ligated to the Co centre (Co(1)–centroid 1.660(2) Å). The planar η^5-C$_5$Me$_5$ ligand is more distant (Co(1)–centroid 1.700(3) Å) and is almost parallel to the hetero-butadiene fragment (dihedral angle 3.3(3)°, centroid–Co(1)–centroid 175.1(2)°). The dihedral angle formed between the hetero-butadiene fragment and the plane defined by Sb(1)–C(1)–P(1) is 49.9(2)°. As in the related complex, **14** [10], the hetero-butadiene ligand is largely delocalised, as evidenced by the equivalence of the P(2)–C(11) and P(1)–C(11) bond lengths, both of which lie in the normal range for delocalised P–C double bonds
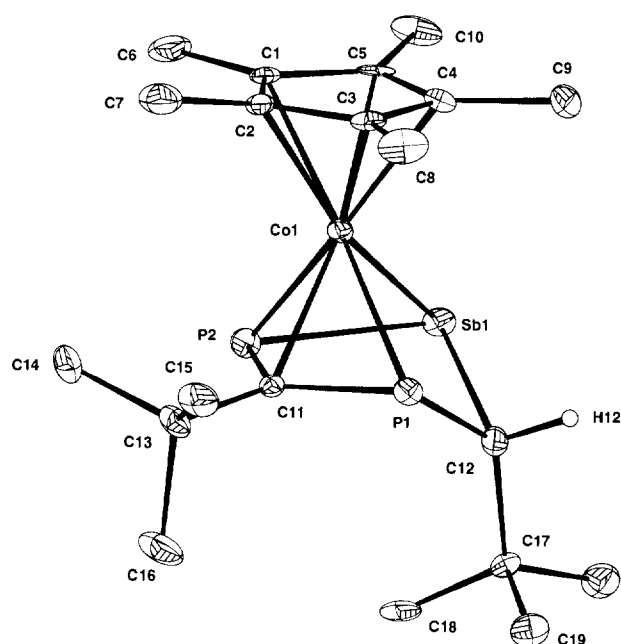

Fig. 2. Molecular structure of one of the crystallographically independent molecules of **11**. Selected bond lengths (Å) and angles (°): Sb(1)–P(2) 2.457(2), Sb(1)–C(12) 2.179(6), P(2)–C(11) 1.781(6), P(1)–C(11) 1.780(5), P(1)–C(12) 1.859(7), C(12)–Sb(1)–P(2) 93.1(2), C(11)–P(2)–Sb(1) 95.3(2), C(11)–P(1)–C(12) 105.8(3), P(1)–C(11)–C(12) 120.5(3), P(1)–C(12)–Sb(1) 97.9(3).

Table 3
Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters (Å$^2 \times 10^3$) for both crystallographically independent molecules of **11**. U_{eq} is defined as one-third of the trace of the orthogonalised U_{ij} tensor

	x	y	z	U_{eq}
Sb(1)	555(1)	5962(1)	29(1)	20(1)
Sb(2)	4114(1)	4389(1)	1723(1)	27(1)
Co(1)	1374(1)	5340(1)	−254(1)	15(1)
Co(2)	3774(1)	4416(1)	4173(1)	15(1)
P(1)	1190(1)	5762(1)	−2429(2)	18(1)
P(2)	749(1)	4476(1)	−439(2)	21(1)
P(3)	3971(1)	5800(1)	3825(2)	16(1)
P(4)	3304(1)	4582(1)	2329(2)	29(1)
C(1)	1717(2)	4870(3)	1489(6)	18(2)
C(2)	2022(2)	4853(4)	365(6)	22(2)
C(3)	2062(2)	5691(4)	−147(7)	21(2)
C(4)	1788(2)	6221(4)	674(6)	18(2)
C(5)	1579(2)	5718(4)	1705(6)	21(2)
C(6)	1584(3)	4125(4)	2353(7)	47(2)
C(7)	2316(3)	4112(4)	−52(8)	44(2)
C(8)	2370(2)	5982(4)	−1280(7)	37(2)
C(9)	1760(3)	7182(3)	537(7)	34(2)
C(10)	1301(3)	6019(4)	2884(7)	36(2)
C(11)	1090(2)	4698(3)	−1908(6)	14(2)
C(12)	645(2)	6339(3)	−2107(6)	23(2)
C(13)	1287(2)	3945(4)	−2748(7)	25(2)
C(14)	1357(3)	3158(3)	−1855(7)	37(2)
C(15)	1738(2)	4189(4)	−3458(7)	35(2)
C(16)	930(3)	3734(4)	−3886(7)	41(2)
C(17)	245(2)	6315(3)	−3135(6)	16(2)
C(18)	0(2)	5461(4)	−3141(6)	26(2)
C(19)	431(2)	6490(4)	−4596(6)	28(2)
C(20)	−103(3)	7000(4)	−2742(7)	33(2)
C(21)	3577(2)	4001(4)	6173(7)	23(2)
C(22)	3505(2)	3343(4)	5185(7)	26(2)
C(23)	3931(2)	3160(3)	4570(6)	19(2)
C(24)	4264(2)	3711(3)	5171(6)	16(2)
C(25)	4035(2)	4237(3)	6147(6)	16(2)
C(26)	3238(3)	4304(4)	7207(7)	42(2)
C(27)	3059(3)	2876(4)	4939(8)	45(2)
C(28)	4019(3)	2456(3)	3571(6)	33(2)
C(29)	4778(2)	3676(4)	4936(7)	33(2)
C(30)	4269(3)	4862(4)	7087(6)	31(2)
C(31)	4296(2)	5696(3)	2207(6)	18(2)
C(32)	3403(2)	5451(3)	3455(6)	20(2)
C(33)	2983(2)	5916(4)	4078(7)	25(2)
C(34)	3111(3)	6362(4)	5444(7)	34(2)
C(35)	2830(3)	6598(4)	3039(7)	47(2)
C(36)	2570(3)	5339(4)	4333(8)	42(2)
C(37)	4264(2)	6386(4)	1069(6)	23(2)
C(38)	4672(2)	6249(4)	95(6)	31(2)
C(39)	4311(3)	7272(3)	1762(6)	33(2)
C(40)	3811(2)	6366(4)	267(6)	29(2)

[12]. It is noteworthy that the Sb(1)–P(2) interaction (2.457(2) Å) in **11** is the shortest fully ordered Sb–P bond length yet reported, whilst the Sb(1)–C(12) and P(1)–C(12) bond lengths are close to the means for single bonds (2.20 Å [13] and 1.857 Å [14] respectively). Interestingly, the ring proton, H(12), in **11** occupies the *exo*-position which contrasts to the *endo*-proton in the related complex, **14** [10].

3. Experimental details

All manipulations were carried out using standard Schlenk and glove box techniques under an atmosphere of high purity argon or dinitrogen. Solvents were distilled over Na–K alloy then freeze–thaw degassed prior to use. ^{1}H and ^{31}P NMR spectra were recorded on a Bruker WM-250 spectrometer in deuterated benzene and were referenced to the residual ^{1}H resonances of the solvent (7.15 ppm) and 85% H_3PO_4 (0.0 ppm) respectively. ^{13}C NMR spectra were recorded in deuterated benzene on a Bruker AM 400 spectrometer using broad band proton decoupling and were referenced to the ^{13}C resonances of the deuterated solvent (δ 128.00). Melting points were determined in sealed glass capillaries under argon, and are uncorrected.

3.1. Synthesis of $[Rh(\eta^5\text{-}C_2Bu^t_2P_2Sb)(\eta^4\text{-}1,5\text{-}C_8H_{12})]$ 7

[4][Li(tmeda)$_2$] (1.0 g, 1.8 mmol) in DME (15 ml) was added over 15 min to a suspension of [{Rh(η^4-1,5-C$_8$H$_{12}$)Cl}$_2$] (418 mg, 1.8 mmol) in DME (5 ml) at −40 °C. The mixture was warmed to room temperature and stirred for 18 h. Volatiles were removed in vacuo and the residue purified by column chromatography (60 mesh silica, hexane eluent) and subsequent crystallisation from diethyl ether to afford a mixture of 7 (ca. 90%) and 9 (ca. 10%). (yield 280 mg, m.p. 154 °C for the mixture). 7: ^{31}P{^{1}H} NMR (1001.4 MHz, C$_6$D$_6$, 298 K) δ: 142 (d of d, CPC, $^2J_{PP}$ = 35.2 Hz, $^1J_{PRh}$ = 6.5 Hz), 166 (d of d, SbPC, $^2J_{PP}$ = 35.2 Hz, $^1J_{PRh}$ = 6.5 Hz); EI-MS (70 kV) 532 (M$^+$, 10%), 108 (COD$^-$, 15%), 67 (100%).

3.2. Synthesis of $[Ir(\eta^5\text{-}C_2Bu^t_2P_2Sb)(\eta^4\text{-}1,5\text{-}C_8H_{12})]$ 8

[4][Li(tmeda)$_2$] (1.0 g, 1.8 mmol) in DME (15 ml) was added over 15 min to a suspension of [{Ir(η^4-1,5-C$_8$H$_{12}$)Cl}$_2$] (580 mg, 1.8 mmol) in DME (5 ml) at −40 °C. The mixture was warmed to room temperature and stirred for 18 h. Volatiles were removed in vacuo and the residue purified by column chromatography (60 mesh silica, hexane eluent) and subsequent crystallisation from diethyl ether to afford a mixture of 8 (ca. 80%) and 10 (ca. 20%) (yield 312 mg, m.p. 133 °C for the mixture). 8: ^{31}P{^{1}H} NMR δ: (101.4 MHz, C$_6$D$_6$) δ: 117 (d, CSbP, $^2J_{PP}$ = 38.1 Hz), 125 (d, CPC, $^2J_{PP}$ = 38.1 Hz); EI-MS (70 kV) 622 (M$^+$, 5%), 484 (M$^+$ − 2CBu^t, 5%) 57 (Bu^{t+}, 100%).

3.3. Synthesis of $[Co(\eta^5\text{-}C_5Me_5)(\eta^4\text{-}C_2Bu^t_2HP_2Sb)]$ 11

A mixture of [4][Li(tmeda)$_2$] (1.0 g, 1.7 mmol) and Li(C$_5$Me$_5$) (241 mg, 1.7 mmol) in DME (20 ml) was added over 15 min to a suspension of CoCl$_2$ (212 mg, 1.7 mmol) in DME (15 ml) at −40 °C. The mixture was

warmed to room temperature and stirred for 18 h. Volatiles were removed in vacuo and the residue purified by column chromatography (60 mesh silica, hexane eluent) and subsequent crystallisation from diethyl ether to afford 11 (yield 8%, m.p. 127 °C). ^{1}H NMR (400 MHz, C$_6$D$_6$, SiMe$_4$) δ 0.75 (s, 9H, Bu^t), 1.33 (d, 1H, CH, $^2J_{PH}$ = 58.1 Hz), 1.56 (s, 9H, Bu^t), 1.71 (s, 15H, C$_5$Me$_5$); ^{13}C NMR (100.6 MHz, C$_6$D$_6$), δ 11.9 (s, C$_5$(CH$_3$)$_5$), 30.0 (d, C(CH$_3$)$_3$, $^3J_{PC}$ = 5.0 Hz), 32.8 (d, C(CH$_3$)$_3$, $^2J_{PC}$ = 23.2 Hz), 35.1 (d of d, C(CH$_3$)$_3$, $^3J_{PC}$ = 9.6 and 9.3 Hz), 42.1 (d of d, C(CH$_3$)$_3$, $^2J_{PC}$ = 24.1 and 25.3 Hz), 52.5 (d, Sb(CHBu^t)P, $^1J_{PC}$ = 53 Hz), 93.5 (s, C$_5$Me$_5$), 143.0 (d of d, PCP, $^1J_{PC}$ = 106.7 and 107 Hz); ^{31}P{^{1}H} NMR (101.4 MHz, C$_6$D$_6$) δ 1.4 (d, SbPC, $^2J_{PP}$ = 29.1 Hz), 68.1 (d, CPC, $^2J_{PP}$ = 29.1 Hz); EI-MS (70 kV) 516 (M$^+$, 60%), 459 (M$^+$ − Bu^t, 100%), 57 (Bu^t, 50%).

3.4. Synthesis of $[Co(\eta^5\text{-}C_2Bu^t_2P_2Sb)(\eta^4\text{-}C_2Bu^t_2HP_2Sb)]$ 12

[4][Li(tmeda)$_2$] (1.0 g, 1.8 mmol) in DME (20 ml) was added over 15 min to a suspension of [CoCl$_2$] (106 mg, 0.85 mmol) in DME (5 ml) at −40 °C. The mixture was warmed to room temperature and stirred for 18 h. Volatiles were removed in vacuo and the residue purified by column chromatography (60 mesh silica, hexane eluent) and subsequent crystallisation from diethyl ether to afford 12 (yield 18%, m.p. 138 °C). ^{1}H NMR (400 MHz, C$_6$D$_6$, SiMe$_4$) δ 1.02 (s, 9H, Bu^t), 1.13 (s, 9H, Bu^t), 1.34 (d, 1H, CH, $^2J_{PH}$ = 47.1 Hz), 1.55 (s, 9H, Bu^t), 1.76 (s, 9H, Bu^t); ^{13}C NMR (100.6 MHz, C$_6$D$_6$), δ 32.1 (d, C(CH$_3$)$_3$, $^3J_{PC}$ = 8.0 Hz), 32.8 (d of d, C(CH$_3$)$_3$, $^3J_{PC}$ = 6.0 and 7.1 Hz), 36.5 (d, C(CH$_3$)$_3$, $^3J_{PC}$ = 8.2 Hz), 37.1 (d of d, C(CH$_3$)$_3$, $^3J_{PC}$ = 7.0 and 7.9 Hz), 42.2 (d of d, C(CH$_3$)$_3$, $^2J_{PC}$ = 15.3 and 16.2 Hz), 43.1 (d of d, C(CH$_3$)$_3$, $^2J_{PC}$ = 18.0 and 19.1 Hz), 43.8 (d, C(CH$_3$)$_3$, $^2J_{PC}$ = 17.0 Hz), 44.1 (d, C(CH$_3$)$_3$, $^2J_{PC}$ = 16.8 Hz), 47.5 (d, Sb(CHBu^t)P, $^1J_{PC}$ = 58.4 Hz), 145.4 (d, SbCP, $^1J_{PC}$ = 83.1 Hz), 148.9 (d of d, PCP, $^1J_{PC}$ = 110.1 and 87.2 Hz), 161.6 (d of d, PCP, $^1J_{PC}$ = 102.2 and 86.4 Hz); ^{31}P{^{1}H} NMR (101.4 MHz, C$_6$D$_6$), δ 24.2 (broad), 93.5 (broad), 141.1 (broad), 160.3 (broad); EI-MS (70 kV) 704 (M$^+$, 5%) 67 (100%) 57 (Bu^t, 50%).

4. Structure determinations

Crystals suitable for X-ray structure determination were mounted in oil. Intensity data were measured using a FAST [15] area detector diffractometer using Mo Kα radiation. The structures were solved by the heavy atoms, 7, or direct, 11, methods (SHELXS-86 [16]) and refined by least squares using the SHELXL-93 [17] program. The structures were refined on F^2 using all

data. Neutral-atom complex scattering factors were employed [18]. Empirical absorption corrections were carried out by the DIFABS method [19]. Crystal data, details of data collections and refinement are given in Table 1. Molecular structures are shown in Figs. 1 and 2. Anisotropic thermal parameters were refined for all non-hydrogen atoms. The hydrogen atoms in both structures were included in calculated positions (riding model). Atom coordinates, thermal parameters, hydrogen atom parameters and full lists of bond lengths and angles have been deposited as supplementary material. Further details of the crystal structure investigations are available on request from the director of the Cambridge Crystallographic Data Centre.

Acknowledgements

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