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Polyhetero-ferrocenes and -ruthenocenes derived from the 1,4,2-diphosphastibolyl ring anion $[P_2SbC_2Bu^t_2]^-$ †

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The complex $[RuCl_2(PPh_3)_3]$ reacted with the 1,4,2-diphosphastibolyl ring anion $[P_2SbC_2Bu^t_2]^-$ (containing *ca.* 25% of the 1,2,4-triphospholyl anion $[P_3C_2Bu^t_2]^-$) to produce a cocrystallised mixture (crystal structure) of two isomers of $[Ru(\eta^5\text{-}P_2SbC_2Bu^t_2)_2]$ with $[Ru(\eta^5\text{-}P_2SbC_2Bu^t_2)(\eta^5\text{-}P_3C_2Bu^t_2)]$. Variable-temperature $^{31}P\text{-}\{^1H\}$ NMR studies on the mixture show one of the isomers and the last complex to be fluxional at room temperature. It is believed that an interring Sb···Sb interaction in the other isomer restricts its fluxionality in solution. The reaction of $[P_2SbC_2Bu^t_2]^-$ with $FeCl_2$ yielded only one isomer of the heteroferrocene complex $[Fe(\eta^5\text{-}P_2SbC_2Bu^t_2)_2]$ which is also non-fluxional in solution and has a similar oxidation potential to that of ferrocene itself. The heteroruthenocene complexes $[Ru(\eta^5\text{-}P_2SbC_2Bu^t_2)(\eta^5\text{-}C_5R_5)]$ (R = H or Me) were prepared by treating $[Ru(\eta^5\text{-}C_5R_5)(MeCN)_3][PF_6]$ (R = H or Me) with $[P_2SbC_2Bu^t_2]^-$. The analogous ferrocene complex $[Fe(\eta^5\text{-}P_2SbC_2Bu^t_2)(\eta^5\text{-}C_5Me_5)]$ (crystal structure) was synthesized by treating a 1 : 1 mixture of $[P_2SbC_2Bu^t_2]^-$ and $Li(C_5Me_5)$ with half an equivalent of $FeCl_2$. Treatment of $[M(\eta^5\text{-}P_2SbC_2Bu^t_2)(\eta^5\text{-}C_5Me_5)]$ (M = Ru or Fe) with $[W(CO)_5(thf)]$ (thf = tetrahydrofuran) formed the secondary co-ordination complexes $[M(\eta^5\text{-}P_2SbC_2Bu^t_2)(\eta^5\text{-}C_5Me_5)\{W(CO)_5\}]$ (M = Ru or Fe) in which the $W(CO)_5$ fragment is η^1 ligated to the phosphorus centre adjacent to the ring antimony centre. A diphosphastibolyl-bridged cationic triple-decker complex $[(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}\eta^5{:}\,\eta^5\text{-}P_2SbC_2Bu^t_2)Ru(\eta^5\text{-}C_5Me_5)][PF_6]$ was the product of the reaction of $[P_2SbC_2Bu^t_2]^-$ with 2 equivalents of $[Ru(\eta^5\text{-}C_5Me_5)(MeCN)_3][PF_6]$.

The chemistry of phospha- and polyphospha-ferrocene and -ruthenocene sandwich complexes is now a well established area that is largely based on the use of monophospholyl anions as ligands. A range of complexes employing either 1,2- or 1,3-diphospholyl, or 1,2,4-triphospholyl ring anions have also been reported.[1] Representative examples of the latter include $[M(\eta^5\text{-}P_3C_2Bu^t_2)_2]$ (M = Fe **1**[2] or Ru **2**[3]), $[M(\eta^5\text{-}P_3C_2Bu^t_2)(\eta^5\text{-}P_2C_3Bu^t_3)]$ (M = Fe **3**[2] or Ru **4**[3]) and $[M(\eta^5\text{-}P_3C_2Bu^t_2)(\eta^5\text{-}C_5R_5)]$ (R = H, M = Fe **5**[4] or Ru **6**;[3] R = Me, M = Fe **7**[5] or Ru **8**[3]). In addition, several ferrocenes and ruthenocenes have been prepared from the pentaphospholyl anion, $[P_5]^-$.[1] A common feature of phosphorus-substituted ferrocenes is their ability to undergo secondary co-ordination through sterically available phosphorus lone pairs to neutral metal fragments; several examples of such complexes have been reported.[1]

Compared with the large volume of work dedicated to phospha-ferrocenes and -ruthenocenes relatively few studies have examined the chemistry of the arsenic, antimony and bismuth counterparts of these species. This can be attributed to the decreasing stability of unsaturated Group 15 element–carbon bonds with increasing molecular weight of the Group 15 element. Ashe and Al-Ahmed[6] have, however, produced at least one example of each of the ferrocenes, $[Fe(\eta^5\text{-}EC_4R_4)_2]$ **9** and $[Fe(\eta^5\text{-}EC_4R_4)(\eta^5\text{-}C_5H_5)]$ **10** (R = H or alkyl, E = As, Sb or Bi) which in the case of **9** (E = Sb or Bi, R = Me) show strong interring E···E interactions similar to the well known intermolecular solid-state E···E contacts in thermochromic distibanes and dibismuthanes. All crystallographically characterised examples of **9** and **10** show evidence of a high degree of aromatic delocalisation within the heterocyclic ligand which presumably accounts for the stability of these complexes.[6] It is noteworthy that several sandwich complexes, *e.g.* $[M(\eta^5\text{-}As_5)(\eta^5\text{-}C_5Me_5)]$ **11** (M = Fe or Ru), have also been prepared from the pentaarsolyl anion, $[As_5]^-$.[7]

It is only recently that this area of chemistry has been extended to hetero-ferrocenes and -ruthenocenes derived from heterocycles containing mixtures of Group 15 elements with the synthesis of $[Fe(\eta^5\text{-}PCHAsC_2Et_2)_2]$ **12**,[8] $[Fe(\eta^5\text{-}P_2AsC_2Bu^t_2)(\eta^5\text{-}C_5H_5)]$ **13**[9] and $[M(\eta^5\text{-}P_2AsC_2Bu^t_2)(\eta^5\text{-}C_5Me_5)]$ (M = Fe **14** or Ru **15**).[10] The diphosphaarsolyl rings in **13**–**15** were found to exist as inseparable mixtures of both the 1,2- and 2,4-diphospha isomers. Complex **13** has been used as a P-donor ligand in the preparation of the secondary co-ordination complex $[Fe(\eta^5\text{-}P_2AsC_2Bu^t_2)(\eta^5\text{-}C_5H_5)\{W(CO)_5\}]$ **16**,[9] whilst **14** and **15** have been utilised in the synthesis of the novel cationic triple-decker complex $[(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}\eta^5{:}\eta^5\text{-}P_2AsC_2Bu^t_2)Ru(\eta^5\text{-}C_5Me_5)][PF_6]$ **17**.[10] We have become interested in broadening this field to include ferrocenes and ruthenocenes employing mixed P, Sb-heterocyclic ligand systems. This has become possible with our recent regiospecific synthesis of the 1,4,2-diphosphastibolyl ring anion, $[P_2SbC_2Bu^t_2]^-$,[11] which we have utilised in the preparation of the ruthenocene complexes $[Ru(\eta^5\text{-}P_2SbC_2Bu^t_2)(\eta^5\text{-}C_5R_5)]$ (R = H **18** or Me **19**).[12] Herein we report the full extension of this preliminary report.

Results and Discussion

Treatment of $[Li(tmen)_2][P_2SbC_2Bu^t_2]$ (tmen = *N*,*N*,*N′N′*-tetramethylethane-1,2-diamine) with $[RuCl_2(PPh_3)_3]$ led to the formation of an orange, air-stable mixture of two isomers of $[Ru(\eta^5\text{-}P_2SbC_2Bu^t_2)_2]$ **20** and **21** with the compound $[Ru(\eta^5\text{-}P_2SbC_2Bu^t_2)(\eta^5\text{-}P_3C_2Bu^t_2)]$ **22** after chromatographic work-up (Kieselgel, hexane) (Scheme 1). The presence of **22** in the mixture is a result of the cosynthesis of the 1,2,4-triphospholyl ring anion $[P_3C_2Bu^t_2]^-$ (*ca.* 25%) in the preparation of the diphosphastibolyl precursor (*ca.* 75%), the anions being inseparable.[11] Rigorous attempts to separate **20**–**22** by fractional crystallisation or sublimation (150 °C, 0.04 mmHg) met with failure due to persistent cocrystallisation of these compounds (see below). By contrast, the reaction of $[Li(tmen)_2][P_2SbC_2Bu^t_2]$ with $FeCl_2$ yielded only one isomer of the mildly air-sensitive, brown heteroferrocene, $[Fe(\eta^5\text{-}P_2SbC_2Bu^t_2)_2]$ **23**, and none of the iron analogue of **22**, *viz.* $[Fe(\eta^5\text{-}P_2Sb\text{-}$

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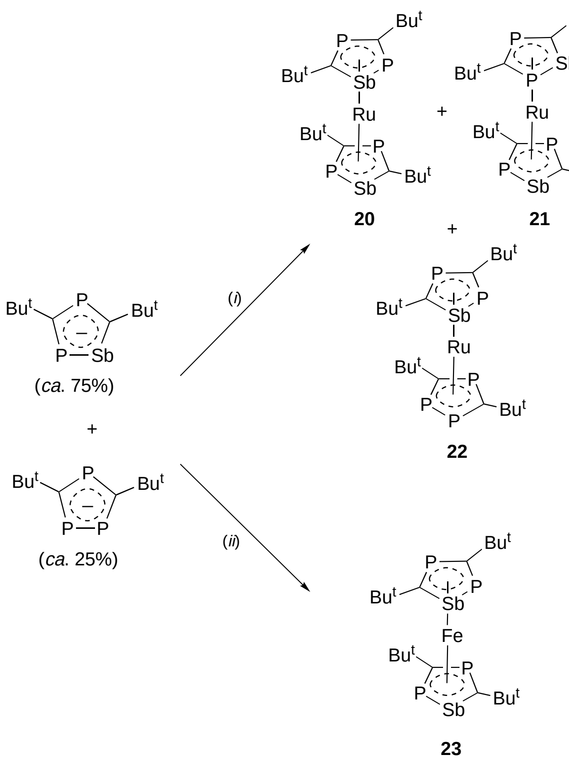
† *Non-SI units employed*: mmHg ≈ 133 Pa, eV ≈ 1.60×10^{-19} J.



Scheme 1 (*i*) [RuCl$_2$(PPh$_3$)$_3$], 1,2-dimethoxyethane (dme), 18 h, 25 °C; (*ii*) FeCl$_2$, dme, 18 h, 25 °C

$C_2Bu^t{}_2)(\eta^5$-$P_3C_2Bu^t{}_2)]$, after recrystallisation from hexane or sublimation (170 °C, 0.04 mmHg). A small amount of the triphospholyl impurity is, however, present in the crude reaction mixture but cannot be crystallised from it.

The variable-temperature ^{31}P-{^1H} NMR spectra for the mixture of compounds **20**–**22** are displayed in Fig. 1. It is clear that whilst **20** is non-fluxional in solution, **21** and **22** are undergoing fluxional processes at room temperature which can be attributed to a rotation, or partial rotation, of the heterocyclic rings about their metal–ring centroid axes. Such processes are common for sandwich complexes containing even heavily substituted cyclopentadienyl ligands[13] and have been observed for the closely related complex **2**.[3] It is difficult to calculate the energy barrier for these processes in **21** and **22** as the complexity of the ^1H NMR spectra of the mixture rules out the assignment of their coalesence temperatures. At −60 °C, however, the ^{31}P-{^1H} NMR spectra can be assigned as an $[AB]_2$ spin system for **20**, a superimposition of two [AX] systems for **21**, and the superimposition of an [AX] and an [AMX] system for **22**, the three high-field signals in the latter arising from the [AMX] system of the triphospholyl ring. There are no observed interring couplings for any of the compounds. These assignments were made by correlating mutual couplings, peak multiplicities and peak integrations to the structures of **20**–**22**. In addition, the low-temperature spectra of all three compounds have been successfully simulated using the PANIC program.[14] Unfortunately the complexity of both the ^1H and ^{13}C NMR spectra of the mixture of compounds did not allow their assignment although molecular-ion peaks displaying the correct isotopic distributions were observed for the isomers **20** and **21** and complex **22** in the mass spectrum of the mixture.

The ^{31}P-{^1H} NMR spectrum of the heteroferrocene **23** shows it to be non-fluxional in solution at room temperature as is its ruthenium analogue **20**. The spectrum has been assigned and successfully simulated as an [AA′BB′] spin system with characteristic two-bond intraring couplings (34 Hz) in addition to an interring coupling, $^2J(P_AP_{B'}) = J(P_{A'}P_B) = 8$ Hz $[J(P_AP_{A'}) = J(P_BP_{B'}) = 0$ Hz]. There is no observable change in the spectrum over the temperature range 25 ° to −60 °C. A similar interring coupling has been reported for the related complex **1**,[2] which was attributed to a through-space phosphorus–phosphorus interaction. It can be postulated that such an interaction also gives rise to the interring coupling in the present system which could explain why no such couplings are observed for **20** in which the interring distance is presumably larger. The ^1H and ^{13}C NMR spectra of **23** are as expected in that they highlight two sets of inequivalent tertiary butyl groups.

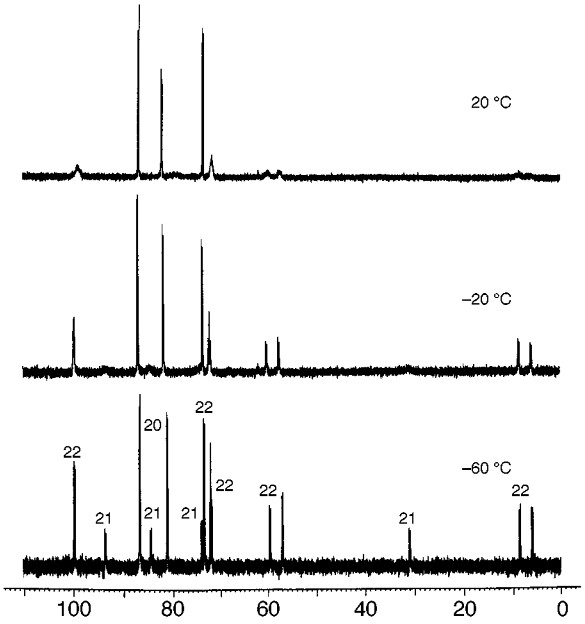


Fig. 1 Variable temperature ^{31}P-{^1H} NMR spectra for the cocrystallised mixture of compounds **20**–**22**

It is interesting that both compounds **20** and **23** appear to have 'rigid' structures in solution at room temperature while the isomeric form of **20**, *viz.* **21**, is fluxional even at −40 °C. It seems likely that this is due to strong Sb···Sb interring contacts in **20** and **23** similar to that previously reported for some distibaferrocenes **9**.[6] It is of course possible that **20** and **23** could exist as their 'equienergetic' P–P eclipsed conformers in solution. This, however, seems unlikely as **20** occurs solely as the Sb–Sb eclipsed conformer in the solid state (see below). The presence of such an Sb···Sb interaction in **21** is not plausible as this would necessitate the tertiary butyl groups from each ring being eclipsed by those on the opposing ring. Further evidence for the proposed Sb···Sb contact in **20** can be gained from its crystal structure.

The molecular structure of the cocrystallised mixture of compounds **20**–**22** is depicted in Fig. 2 (Table 1). The labelling scheme shown is for **20**. During the structural refinement it was found that the sites labelled Sb(1), Sb(2) and P(1) are partially occupied by phosphorus (51), phosphorus (13) and antimony (17%) respectively, while those labelled P(2), P(3) and P(4) all have a 100% phosphorus occupancy. This site disorder is consistent with the cocrystallisation of **20** and **21** (53% total) with **22** (47%) and is in line with the NMR spectra of the product mixture. The fact that P(2) has a 100% phosphorus occupancy confirms that **20** exists solely as its Sb–Sb eclipsed conformer in the cocrystallised mixture. The structural similarities between **20** and **22** have, no doubt, led to their ability to cocrystallise. Unfortunately any discussion of the bond lengths within the heterocyclic rings is precluded by the observed disorder, though the values for the cocrystallised mixture are shown in Table 1. It is evident, however, that the rings are essentially planar, almost parallel (dihedral angle 5.5°) and η^5-ligated to the ruthenium centre (centroid–Ru–centroid 170.5°, *cf.* 174.4° for **2**).[3] The distances of the two rings from the ruthenium centre are almost equivalent {1.825(2) [Sb(1) ring] and 1.812(2) Å [Sb(2)

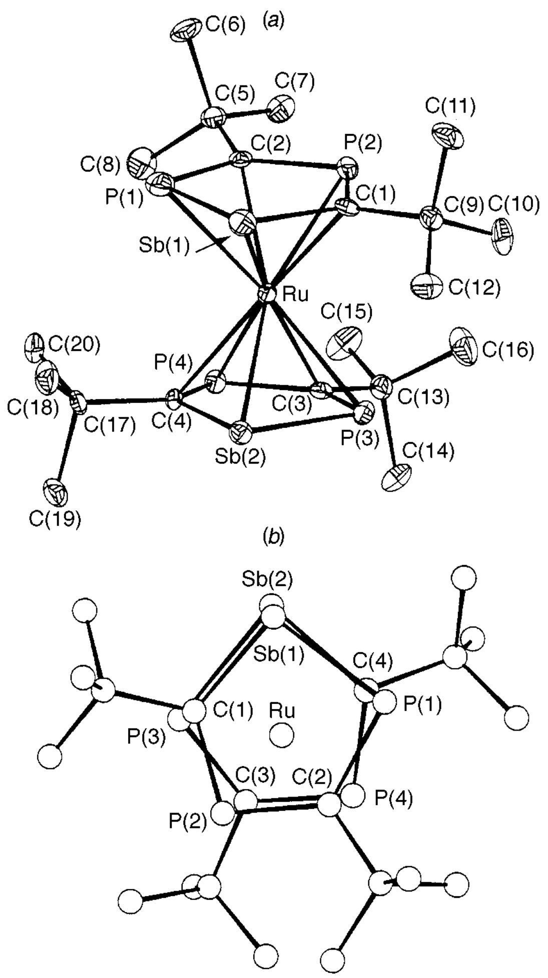


Fig. 2 Molecular structure of the cocrystallised mixture of compounds **20**–**22** (atomic labels represent **20**)

Table 1 Selected intramolecular distances (Å) and angles (°) for the cocrystallised mixture of compounds **20**–**22** with estimated standard devictions (e.s.d.s) in parentheses

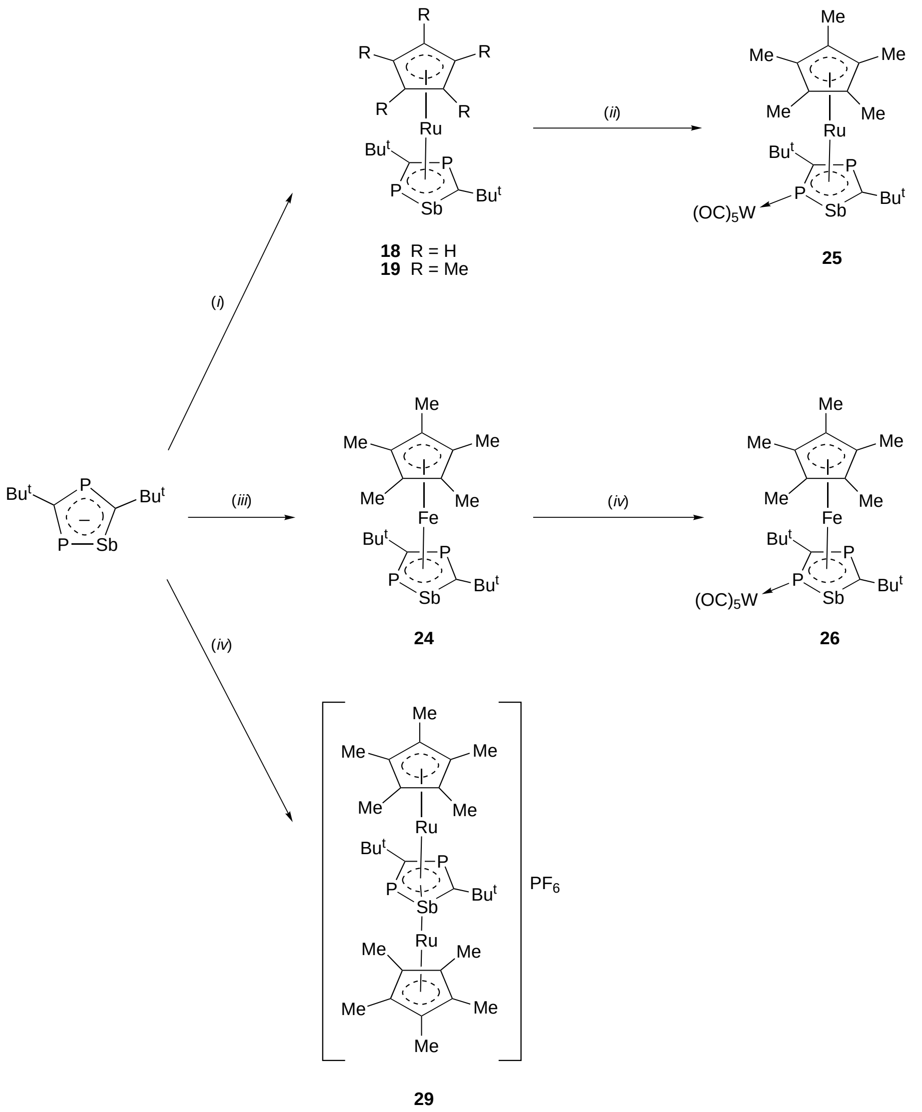
Sb(1)–C(1)	2.045(6)	Sb(1)–P(1)	2.312(1)
Sb(1)–Ru	2.674(1)	Sb(2)–C(4)	2.096(5)
Sb(2)–P(3)	2.420(2)	Sb(2)–Ru	2.729(1)
Ru–C(1)	2.292(5)	Ru–C(3)	2.298(6)
Ru–C(4)	2.312(5)	Ru–C(2)	2.331(5)
Ru–P(2)	2.441(1)	Ru–P(4)	2.442(2)
Ru–P(3)	2.488(2)	Ru–P(1)	2.587(1)
P(1)–C(2)	1.914(6)	P(2)–C(1)	1.755(6)
P(2)–C(2)	1.774(6)	P(3)–C(3)	1.770(6)
P(4)–C(4)	1.748(5)	P(4)–C(3)	1.768(6)
C(1)–C(9)	1.549(8)	C(2)–C(5)	1.556(8)
C(3)–C(13)	1.558(8)	C(4)–C(17)	1.559(7)
C(1)–Sb(1)–P(1)	92.8(2)	C(4)–Sb(2)–P(3)	87.7(2)
C(3)–Ru–C(4)	72.1(2)	C(1)–Ru–C(2)	72.2(2)
C(1)–Ru–P(2)	43.39(13)	C(2)–Ru–P(2)	43.57(14)
C(3)–Ru–P(4)	43.7(2)	C(4)–Ru–P(4)	43.04(13)
C(3)–Ru–P(3)	43.20(14)	C(4)–Ru–P(3)	81.59(13)
P(4)–Ru–P(3)	79.22(5)	C(1)–Ru–P(1)	80.5(2)
C(2)–Ru–P(1)	45.43(14)	P(2)–Ru–P(1)	80.31(5)
C(1)–Ru–Sb(1)	47.88(14)	C(2)–Ru–Sb(1)	80.01(14)
P(2)–Ru–Sb(1)	81.72(4)	P(1)–Ru–Sb(1)	52.11(3)
C(3)–Ru–Sb(2)	80.61(13)	C(4)–Ru–Sb(2)	48.28(12)
P(4)–Ru–Sb(2)	82.05(4)	P(3)–Ru–Sb(2)	55.04(4)
Sb(1)–Ru–Sb(2)	81.33(2)	C(2)–P(1)–Sb(1)	99.2(2)
C(1)–P(2)–C(2)	101.1(3)	C(3)–P(3)–Sb(2)	101.4(2)
C(4)–P(4)–C(3)	101.1(3)	C(9)–C(1)–P(2)	118.7(4)
C(9)–C(1)–Sb(1)	117.0(4)	P(2)–C(1)–Sb(1)	123.5(3)
C(5)–C(2)–P(2)	118.2(4)	C(5)–C(2)–P(1)	118.1(4)
P(2)–C(2)–P(1)	123.2(3)	C(13)–C(3)–P(4)	117.0(4)
C(13)–C(3)–P(3)	117.4(4)	P(4)–C(3)–P(3)	125.3(3)
C(17)–C(4)–P(4)	117.8(4)	C(17)–C(4)–Sb(2)	117.4(3)
P(4)–C(4)–Sb(2)	124.2(3)		

ring]} and similar to that observed in the related complex **2**, 1.814 Å.[3]

It is clear from Fig. 2(*b*) that the rings are eclipsed and arranged in such a fashion as to minimise the interring interaction of the tertiary butyl groups. The crystal structures of the triphospholyl-ferrocene and -ruthenocene complexes **1**[2] and **2**[3] show an identical arrangement of ligands about the metal centre. Although it is not valid to comment on the lengths of the interring Sb···Sb contacts in the structure of **20**, it is obvious that it will be well within the sum of the van der Waals radii for two antimony centres (4.40 Å)[14] and that an interaction should exist as predicted from the ^{31}P NMR studies. Considering the smaller covalent radius of iron (1.17 Å) over ruthenium (1.24 Å),[15] it seems likely that any Sb···Sb contacts in **23** should be stronger than in **20** which may explain the absence of any other isomers in its preparation.

Since the heteroferrocene **23** could be obtained in a pure state its electrochemistry was examined by cyclic voltammetry. These studies determined that **23** undergoes a pseudo-reversible one-electron oxidation with an $E_{\frac{1}{2}}$ value of 78 mV relative to ferrocene. Similar studies have been carried out on the heteroferrocenes $[Fe(EC_4R_4)_2]$ (E = P, As, Sb or Bi) with the conclusion that when R = H the diphospha- and diarsa-ferrocenes are harder to oxidise than ferrocene itself, the distibaferrocene is slightly easier to oxidise than ferrocene and the dibismaferrocene is considerably easier to oxidise.[6] When the heteroferrocenes were substituted with alkyl groups their oxidation became increasingly facile, presumably due to the electron-donating ability of the alkyl groups. These results suggested to the authors that P and As have greater effective π electronegativities than that of C, the π electronegativity of Sb is close to that of C and Bi is considerably more π electropositive than is C. Interestingly, the present system, **23**, is only marginally more difficult to oxidise than is ferrocene. It is possible that this is due to a balance of the electron-withdrawing abilities of the phosphorus centres and the electron-donating ability of the tertiary butyl groups relative to the unsubstituted carbon centres in ferrocene. From the previous studies it would be expected that the antimony centres should not affect this balance significantly. Obviously further electrochemical studies will need to be carried out on a range of related polyheteroferrocenes to confirm this hypothesis.

As reported in a preliminary communication,[12] treatment of $[Li(tmen)_2][P_2SbC_2Bu^t{}_2]$ with $[Ru(C_5R_5)(MeCN)_3][PF_6]$ affords (Scheme 2) moderate yields of the ruthenocenes $[Ru(\eta^5\text{-}P_2SbC_2Bu^t{}_2)(\eta^5\text{-}C_5R_5)]$ (R = H **18** or Me **19**) which cocrystallise with small amounts (*ca.* 10%) of the known triphospholyl complexes **6** and **8**, respectively, due to the aforementioned contamination of $[P_2SbC_2Bu^t{}_2]^-$ with $[P_3C_2Bu^t{}_2]^-$. Full synthetic details for **18** and **19** are reported herein. The ferrocene analogue of **19**, $[Fe(\eta^5\text{-}P_2SbC_2Bu^t{}_2)(C_5Me_5)]$ **24**, can also be prepared in good yield by the reaction of $FeCl_2$ with a 1 : 1 mixture of $[Li(tmen)_2][P_2SbC_2Bu^t{}_2]$ and $Li(C_5Me_5)$ in dme. This air-stable, brown complex can be partially purified by crystallisation from hexane but the product always cocrystallises with small amounts (*ca.* 15%) of the known triphospholyl complex **7**,[5] which could not be separated despite repeated attempts at fractional recrystallisation. The triphospholyl contamination of **18**, **19** and **24** has precedent in the synthesis of the closely related diphosphaarsolyl complexes **13**–**15** which all cocrystallise with their triphospholyl counterparts.[9,10] Several attempts were made to prepare the iron counterpart of **18**, *viz.* $[Fe(\eta^5\text{-}P_2SbC_2Bu^t{}_2)(C_5H_5)]$, by the reaction of $FeCl_2$ with $Li(C_5H_5)$ and $[Li(tmen)_2][P_2SbC_2Bu^t{}_2]$ in a 1 : 1 ratio however this only yielded $[Fe(C_5H_5)_2]$ and **23** after work-up. This situation presumably arises due to a higher reactivity of $Li(C_5H_5)$ relative to $[P_2Sb$-



Scheme 2 (*i*), $[Ru(C_5R_5)(MeCN)_3][PF_6]$ (R = H or Me), dme, 18 h, 25 °C; (*ii*) $[W(CO)_5(thf)]$, thf, 18 h, 25 °C; (*iii*) $FeCl_2$, $Li(C_5Me_5)$, dme, 18 h, 25 °C; (*iv*) $[W(CO)_5(thf)]$, thf, 18 h, 25 °C; (*v*) $2[Ru(C_5Me_5)(MeCN)_3][PF_6]$, dme, 18 h, 25 °C

$C_2Bu^t{}_2]^-$ which facilitates the preferential consumption of $Li(C_5H_5)$, *i.e.* ferrocene formation, in the early stages of the reaction.

The spectroscopic data for compounds **18** and **19** have been reported in the preliminary communication and support their proposed structures.[12] The ^{31}P-{^1H} NMR spectrum of **24** is similar to its ruthenium analogue **19** in that it displays an [AX] pattern with characteristic $^2J(P_AP_X)$ couplings (44 Hz). Interestingly, however, both signals are shifted downfield (*ca.* 20 ppm) with respect to those in the spectrum of **19**. In addition, the low-field signal is significantly broadened which suggests it arises from the ring phosphorus atom adjacent to the quadrupolar antimony centre. Both the ^1H and ^{13}C NMR spectra of **24** also resemble those of **19**.

The molecular structure of compound **24** (Fig. 3, Table 2) is isomorphous to that of **19** which was also reported in the preliminary communication.[12] During refinement it was found that the site labelled Sb is partially occupied by phosphorus (15%) while the sites P(1) and P(2) have 100% phosphorus occupancy. This observation is consistent with the solution NMR data and confirms that the known triphospholyl complex **7** (15%) cocrystallises with **24** (85%). Owing to this site disorder it is not valid to comment on the bond lengths and angles within the diphosphastibolyl ring. However, it is clear that both rings are planar, η^5-ligated to the Fe and almost parallel [dihedral angle 2.1(1)°, *cf.* 2° in **19**).[12] The distance from the iron atom to the heterocycle centroid [1.661(2) Å] is significantly less than to the C_5Me_5 ring centroid [1.711(2) Å], the centroid–Fe–centroid angle being approximately linear at 176° (*cf.* centroid–Ru–centroid 177° in **19**[12]). As in the structure of **19**, the unit cell of **24** contains two molecules which have a close intermolecular contact between centrosymmetrically related P(2) centres [3.515(3) Å, *cf.* 3.467(3) Å in **19**[12]] which is significantly less than the sum of the van der Waals radii for two phosphorus centres (3.8 Å).[14] This generates a pseudo-dimeric structure binding both enantiomers of **24**.

In an attempt to utilise compounds **19** and **24** as ligands in the formation of secondary co-ordination complexes they were treated with tetrahydrofuran (thf) solutions of $[W(CO)_5(thf)]$ at room temperature to afford the orange-yellow crystalline complexes $[M(\eta^5\text{-}P_2SbC_2Bu^t{}_2)(\eta^5\text{-}C_5Me_5)\{W(CO)_5\}]$ (M = Ru **25** or Fe **26**). Again **25** and **26** cocrystallise with small amounts (*ca.* 15–20%) of their triphospholyl counterparts $[M(\eta^5\text{-}P_3C_2Bu^t{}_2)(\eta^5\text{-}C_5Me_5)\{W(CO)_5\}]$ (M = Ru **27** or Fe **29**) respectively, which originate from the triphospholyl impurities, **7** and **8**, in the starting materials, **19** and **24**. A similar contamination has been reported for the η^5: η^1-diphosphaarsolyl complex **16** which also cocrystallises with its triphospholyl analogue $[Fe(\eta^5\text{-}P_3C_2Bu^t{}_2)(\eta^5\text{-}C_5H_5)\{W(CO)_5\}]$.[9] The contaminants **27** and **29** could not be separated from the major products despite repeated attempts at fractional recrystallisation.

The spectroscopic data for the tungsten pentacarbonyl com-

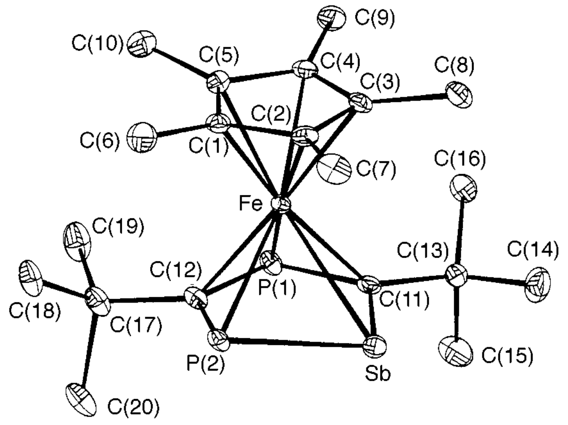


Fig. 3 Molecular structure of the cocrystallised mixture of compounds **24** and **7** (atomic labels represent **24**)

plexes **25** and **26** can be easily assigned despite the presence of the cocrystallised impurities **27** and **29**. The ^{31}P-{^1H} NMR spectrum for each shows an [AX] pattern with characteristic $^2J(P_AP_X)$ couplings. In addition, the signals corresponding to the phosphorus centres adjacent to the antimony centres display ^{183}W satellites with couplings indicative of one-bond interactions. These signals are also shifted considerably upfield relative to the corresponding signals of the parent molecules **19** and **24**. Therefore, it can be concluded that co-ordination to the tungsten pentacarbonyl fragments occurs solely through the phosphorus centres in the 1 positions of the rings which is not surprising considering the steric inaccessibility of the P in the 4 positions and the expected higher s character of the antimony lone pairs. The ^1H and ^{13}C NMR spectra for **25** and **26** are consistent with this assignment, the latter showing normal *cis*- and *trans*- two-bond P–C couplings between the 1-phosphorus centres and the carbonyl carbons. Molecular ion peaks with the correct isotopic distributions were observed in the FAB mass spectra of both compounds.

An examination of the use of $[P_2SbC_2Bu^t_2]^-$ in the formation of a triple-decker complex analogous to the diphosphaarsolyl-bridged species **17**[10] was also undertaken. To this end $[Ru(C_5Me_5)(MeCN)_3][PF_6]$ was treated with half an equivalent of $[P_2SbC_2Bu^t_2]^-$ to afford low yields of the orange crystalline compound $[(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}\eta^5\text{: }\eta^5\text{-}P_2SbC_2Bu^t_2)Ru(\eta^5\text{-}C_5Me_5)][PF_6]$ **29** after recrystallisation from CH_2Cl_2–hexane. The contamination of the ring precursor $[P_2SbC_2Bu^t_2]^-$ with $[P_3C_2Bu^t_2]^-$ resulted in a small amount (*ca.* 3%) of the known triphospholyl-bridged triple-decker complex $[(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}\eta^5\text{:}\eta^5\text{-}P_3C_2Bu^t_2)Ru(\eta^5\text{-}C_5Me_5)][PF_6]$ **30**[10] cocrystallising with **29**. The ^{31}P NMR spectrum of **29** displays an [AX] $[^2J(P_AP_X) = 32\text{ Hz}]$ pattern shifted *ca.* 80 ppm upfield from that of the parent complex **19**, in addition to a septet for the PF_6 counter anion. Three singlets that integrate in the ratio 30:9:9 are seen in the ^1H NMR spectrum of **29** and correspond to the Me groups of the two C_5Me_5 ligands and the two inequivalent tertiary butyl groups of the heterocyclic ligand respectively. The base peak for the positive-ion FAB mass spectrum corresponds to the triple-decker cation and exhibits the correct isotopic distribution.

Conclusion

A range of polyhetero-ferrocene and -ruthenocene complexes have been prepared from the 1,4,2-diphosphastibolyl ring anion $[P_2SbC_2Bu^t_2]^-$. These complexes display similar properties to those of their counterparts derived from the 1,2,4-triphospholyl anion $[P_3C_2Bu^t_2]^-$ with the exception of $[Ru(\eta^5\text{-}P_2SbC_2Bu^t_2)_2]$ **20** which shows evidence for strong interring Sb···Sb contacts both in solution and the solid state. We have also demonstrated the utility of the η^5-co-ordinated diphosphastibolyl ring as an η^1 ligand in the formation of two heterobimetallic, secondary co-ordination complexes. The remarkable stability of all the prepared complexes is presumably due to a high degree of aromaticity within the metal-co-ordinated diphosphastibolyl ring. This stability has prompted us to extend the current study to an examination of the co-ordination chemistry of the analogous 1,4,2-diphosphabismolyl ring anion $[P_2BiC_2Bu^t_2]^-$ which we have recently synthesized.[16] The results of these studies will be reported in forthcoming publications.

Table 2 Selected intramolecular distances (Å) and angles (°) for the cocrystallised mixture of compounds **24** and **7** with e.s.d.s in parentheses

Sb–C(11)	2.088(5)	Sb–P(2)	2.4135(13)
Sb–Fe	2.6415(8)	Fe–C(3)	2.085(4)
Fe–C(2)	2.090(4)	Fe–C(4)	2.100(5)
Fe–C(1)	2.109(4)	Fe–C(5)	2.116(5)
Fe–C(12)	2.173(4)	Fe–C(11)	2.216(4)
Fe–P(1)	2.3196(14)	Fe–P(2)	2.3611(14)
P(1)–C(11)	1.754(5)	P(1)–C(12)	1.763(5)
P(2)–C(12)	1.780(5)	C(1)–C(2)	1.433(6)
C(1)–C(5)	1.435(7)	C(1)–C(6)	1.499(6)
C(2)–C(3)	1.436(6)	C(2)–C(7)	1.500(7)
C(3)–C(4)	1.418(7)	C(3)–C(8)	1.499(6)
C(4)–C(5)	1.434(6)	C(4)–C(9)	1.505(7)
C(5)–C(10)	1.487(7)	C(11)–C(13)	1.560(6)
C(12)–C(17)	1.549(6)		
C(11)–Sb–P(2)	88.28(13)	C(3)–Fe–C(2)	40.2(2)
C(3)–Fe–C(4)	39.6(2)	C(2)–Fe–C(4)	66.9(2)
C(3)–Fe–C(1)	67.1(2)	C(2)–Fe–C(1)	39.9(2)
C(4)–Fe–C(1)	66.7(2)	C(3)–Fe–C(5)	66.9(2)
C(2)–Fe–C(5)	67.0(2)	C(4)–Fe–C(5)	39.8(2)
C(1)–Fe–C(5)	39.7(2)	C(12)–Fe–C(11)	76.4(2)
C(12)–Fe–P(1)	46.06(12)	C(11)–Fe–P(1)	45.42(12)
C(12)–Fe–P(2)	45.99(13)	C(11)–Fe–P(2)	86.68(12)
P(1)–Fe–P(2)	84.52(5)	C(12)–Fe–Sb	84.59(13)
C(11)–Fe–Sb	49.98(12)	P(1)–Fe–Sb	86.05(4)
P(2)–Fe–Sb	57.36(3)	C(11)–P(1)–C(12)	101.1(2)
C(12)–P(2)–Sb	100.9(2)	C(2)–C(1)–C(5)	108.1(4)
C(1)–C(2)–C(3)	107.7(4)	C(4)–C(3)–C(2)	108.1(4)
C(3)–C(4)–C(5)	108.6(4)	C(4)–C(5)–C(1)	107.5(4)
C(13)–C(11)–P(1)	116.1(3)	C(13)–C(11)–Sb	118.9(3)
C(1)–C(11)–Sb	123.8(2)	C(17)–C(12)–P(1)	117.3(3)
C(17)–C(12)–P(2)	116.9(3)	P(1)–C(12)–P(2)	125.4(3)

Experimental

General remarks

All manipulations were carried out using standard Schlenk and glove-box techniques under an atmosphere of high-purity argon or dinitrogen. The solvents tetrahydrofuran, 1,2-dimethoxyethane and hexane were distilled over Na/K alloy then freeze/thaw degassed prior to use. Dichloromethane was distilled from CaH_2 prior to use. The ^1H, ^{13}C and ^{31}P NMR spectra were recorded on either a Bruker WM-250 or AM 400 spectrometer in C_6D_6, $[^2H_8]$toluene, CD_2Cl_2 or $CDCl_3$ and were referenced to the residual ^1H resonances of the solvent used (^1H NMR), the ^{13}C resonance of the deuteriated solvent (^{13}C NMR) or to external 85% H_3PO_4 (δ 0.0, ^{31}P NMR) respectively. Mass spectra were recorded using VG 12-253 quad [70 eV, electron/chemical ionisation (EI/CI)], or VG-autospec [Cs^+ ions, 25 kV, 3-nitrobenzyl alcohol matrix (FAB)] instruments and conditions. Cyclic voltammetry was performed with electrochemical equipment from EG & G Princeton Applied Research and a model 273 potentiostat/galvanostat. The electrochemical cell was operated under an atmosphere of argon with platinum working and auxiliary electrodes and an Ag–AgCl reference electrode, in a MeCN–dme (1:1) solvent mixture (1 mmol dm^{-3} solution of complex **23**). A 0.1 mol dm^{-3} solution of $[NBu_4][ClO_4]$ was used as supporting electrolyte. Microanalyses were obtained from the University of Wales, Cardiff Microanalytical

Service. Melting points were determined in sealed glass capillaries under argon, and are uncorrected. Those for cocrystallised mixtures are included for the benefit of experimenters wishing to repeat the syntheses of these mixtures. Quoted approximate percentage yields for one component of a cocrystallised mixture were calculated by relating the integration of the ^{1}H NMR spectrum of the mixture to the total weight yield on the basis of the transition-metal precursor. Quoted infrared data are for the most prominent absorbances for all components of the cocrystallised mixture if present. Microanalytical data could not be obtained for compounds that cocrystallised with triphospholyl impurities. The starting materials $[\mathrm{Li(tmen)_2}][\mathrm{P_2SbC_2Bu^t_2}]$,[11] $\mathrm{Li(C_5Me_5)}$,[17] $[\mathrm{RuCl_2(PPh_3)_3}]$,[18] $[\mathrm{Ru(C_5H_5)(MeCN)_3}][\mathrm{PF_6}]$[19] and $[\mathrm{Ru(C_5Me_5)(MeCN)_3}][\mathrm{PF_6}]$[20] were prepared by published procedures. All other reagents were used as received.

Syntheses

$[\mathrm{Ru}(\eta^5\text{-}\mathrm{P_2SbC_2Bu^t_2})_2]$ 20, 21 and $[\mathrm{Ru}(\eta^5\text{-}\mathrm{P_2SbC_2Bu^t_2})(\eta^5\text{-}\mathrm{P_3C_2Bu^t_2})]$ 22. The salt $[\mathrm{Li(tmen)_2}][\mathrm{P_2SbC_2Bu^t_2}]$ (0.86 g, 1.55 mmol) in dme (10 cm^3) was added over 15 min to a suspension of $[\mathrm{RuCl_2(PPh_3)_3}]$ (730 mg, 0.77 mmol) in dme (5 cm^3) at −40 °C. The mixture was warmed to room temperature and stirred for 18 h. Volatiles were removed *in vacuo* and the residue was purified by column chromatography (60 mesh silica, hexane eluent) and subsequent crystallisation from hexane to afford a cocrystallised mixture of compounds **20**–**22**, yield 110 mg, m.p. 154 °C. ^{31}P-{^{1}H} NMR (101.4 MHz, [^{2}H$_8$]toluene, 213 K): δ **20**, 80 (d, $^2J_{\mathrm{PP}} = 32$) and 85 (d, $^2J_{\mathrm{pp}} = 32$); **21**, δ 29 (d, $^2J_{\mathrm{PP}} = 37$), 73 (d, $^2J_{\mathrm{PP}} = 35$), 83 (d, $^2J_{\mathrm{PP}} = 37$) and 92 (d, $^2J_{\mathrm{PP}} = 35$); **22** δ 5 (dd, $^1J_{\mathrm{PP}} = 413$, $^2J_{\mathrm{PP}} = 39$), 56 (dd, $^1J_{\mathrm{PP}} = 413$, $^2J_{\mathrm{PP}} = 39$), 70 (virtual t, $^2J_{\mathrm{PP}} = 39$, $^2J_{\mathrm{PP}} = 39$), 71 (d, $^2J_{\mathrm{PP}} = 36$) and 98 (d, $^2J_{\mathrm{PP}} = 36$ Hz). EI mass spectrum for the mixture (70 kV): *m/z* 746 (**20**, **21**$^+$, 3), 656 (**22**$^+$, 14), 69 ($\mathrm{CBu^{t+}}$, 38) and 57 ($\mathrm{Bu^{t+}}$, 100%). IR (for the mixture): ṽ/cm^{-1} 750m, 1230m, 1359m and 1378m.

$[\mathrm{Fe}(\eta^5\text{-}\mathrm{P_2SbC_2Bu^t_2})_2]$ 23. The salt $[\mathrm{Li(tmen)_2}][\mathrm{P_2SbC_2Bu^t_2}]$ (1.1 g, 1.98 mmol) in dme (10 cm^3) was added over 15 min to a suspension of $\mathrm{FeCl_2}$ (130 mg, 1.03 mmol) in dme (5 cm^3) at −40 °C. The mixture was warmed to room temperature and stirred for 18 h. Volatiles were removed *in vacuo* and the residue was extracted with hexane (30 cm^3) and filtered. The filtrate was reduced in volume to *ca.* 5 cm^3 and placed at −20 °C overnight to yield brown-black crystals of compound **23** (113 mg, 16%), m.p. 165–169 °C. NMR ($\mathrm{C_6D_6}$, 298 K): ^{1}H (400 MHz), δ 1.31 (s, 9 H, $\mathrm{Bu^t}$) and 1.86 (s, 9 H, $\mathrm{Bu^t}$); ^{13}C (100.6 MHz), δ 36.9 [virtual t, $\mathrm{C(\mathit{C}H_3)_3}$, $^3J_{\mathrm{PC}} = 9$], 37.2 [d, $\mathrm{C(\mathit{C}H_3)_3}$, $^3J_{\mathrm{PC}} = 9$], 43.1 [virtual t, $\mathrm{\mathit{C}(CH_3)_3}$, $^2J_{\mathrm{PC}} = 19$, $^2J_{\mathrm{PC}} = 19$ Hz], 43.3 [d, $\mathrm{\mathit{C}(CH_3)_3}$, $^2J_{\mathrm{PC}} = 18$], 148.4 [d, SbCP, $^1J_{\mathrm{PC}} = 82$], 159.9 (dd, PCP, $^1J_{\mathrm{PC}} = 82$, 106); ^{31}P-{^{1}H} (101.4 MHz), δ 76.3 (dd, $^2J_{\mathrm{PP}} = 34$, interring $^2J_{\mathrm{PP}} = 8$) and 95.9 (dd, $^2J_{\mathrm{PP}} = 34$, interring $^2J_{\mathrm{PP}} = 8$ Hz). EI mass spectrum (70 kV): *m/z* 700 (M^+, 50), 562 ($M^+ - 2\mathrm{CBu^t}$, 19), 81 ($\mathrm{C_2Bu^t{}_2{}^+}$, 100), 69 ($\mathrm{CBu^t}$, 68) and 57 ($\mathrm{Bu^{t+}}$, 76%). IR: ṽ/cm^{-1} 720m, 1220w and 1480w (Found: C, 34.85; H, 6.1. Calc. for $\mathrm{C_{20}H_{36}FeP_4Sb_2}$: C 34.3; H, 5.2%).

$[\mathrm{Ru}(\eta^5\text{-}\mathrm{P_2SbC_2Bu^t_2})(\eta^5\text{-}\mathrm{C_5H_5})]$ 18. The salt $[\mathrm{Li(tmen)_2}][\mathrm{P_2SbC_2Bu^t_2}]$ (1.1 g, 1.98 mmol) in dme (10 cm^3) was added over 15 min to a suspension of $[\mathrm{Ru(C_5H_5)(MeCN)_3}][\mathrm{PF_6}]$ (880 mg, 2.02 mmol) in dme (10 cm^3) at −40 °C. The mixture was warmed to room temperature and stirred for 18 h. Volatiles were removed *in vacuo* and the residue was extracted with hexane (30 cm^3) and filtered. The filtrate was reduced in volume to *ca.* 5 cm^3 and placed at −20 °C overnight to yield orange cocrystals of compounds **18** (*ca.* 90%) and **6** (*ca.* 10%) (363 mg, 38%), m.p. 86 °C. NMR ($\mathrm{C_6D_6}$, 298 K) for **18**: ^{1}H (250 MHz), δ 1.24 (s, 9 H, $\mathrm{Bu^t}$), 1.44 (s, 9 H, $\mathrm{Bu^t}$) and 4.65 (s, 5 H, $\mathrm{C_5H_5}$); ^{13}C (100.6 MHz), δ 36.6 [d of d, $\mathrm{C(\mathit{C}H_3)_3}$, $^3J_{\mathrm{PC}} = 10.5$ and 10.5] 38.6 [d, $\mathrm{C(\mathit{C}H_3)_3}$, $^3J_{\mathrm{PC}} = 10.6$], 40.2 [d of d, $\mathrm{\mathit{C}(CH_3)_3}$, $^2J_{\mathrm{PC}} = 19.4$ and 15.4], 40.9 [d, $\mathrm{\mathit{C}(CH_3)_3}$, $^2J_{\mathrm{PC}} = 16.9$], 76.6 (s, $\mathrm{C_5H_5}$), 140.7 (d of d, PCP, $^1J_{\mathrm{PC}} = 86.2$ and 110.7) and 149.6 (d, SbCP, $^1J_{\mathrm{PC}} = 84.3$); ^{31}P-{^{1}H} (101.4 MHz), δ 27.8 (d, CPC, $^2J_{\mathrm{PP}} = 35.6$ Hz) and 64.7 (d, SbPC). EI mass spectrum (70 kV): *m/z* 488 (M^+, 10), 350 ($M^+ - 2\mathrm{CBu^t}$, 48%) and 57 ($\mathrm{Bu^{t+}}$, 100%). IR: ṽ/cm^{-1} 810s, 1220m, 1780w and 1690w.

$[\mathrm{Ru}(\eta^5\text{-}\mathrm{P_2SbC_2Bu^t_2})(\eta^5\text{-}\mathrm{C_5Me_5})]$ 19. The salt $[\mathrm{Li(tmen)_2}][\mathrm{P_2SbC_2Bu^t_2}]$ (1.0 g, 1.8 mmol) in dme (10 cm^3) was added over 15 min to a suspension of $[\mathrm{Ru(C_5Me_5)(MeCN)_3}][\mathrm{PF_6}]$ (900 mg, 1.79 mmol) in dme (10 cm^3) at −40 °C. The mixture was warmed to room temperature and stirred for 18 h. Volatiles were removed *in vacuo* and the residue was extracted with hexane (30 cm^3) and filtered. The filtrate was reduced in volume to *ca.* 5 cm^3 and placed at −20 °C overnight to yield orange cocrystals of compound **19** (*ca.* 90%) and **8** (*ca.* 10%) (385 mg, 37%), m.p. 123 °C. NMR ($\mathrm{C_6D_6}$, 298 K) for **19**: ^{1}H (250 MHz), δ 1.45 (s, 9 H, $\mathrm{Bu^t}$), 1.60 (s, 9 H, $\mathrm{Bu^t}$) and 1.83 (s, 15 H, $\mathrm{C_5Me_5}$); ^{13}C (100.6 MHz), δ 13.9 [s, $\mathrm{C_5(\mathit{C}H_3)_5}$], 36.8 [d of d, $\mathrm{C(\mathit{C}H_3)_3}$, $^3J_{\mathrm{PC}} = 10.7$ and 10.7], 38.6 [d, $\mathrm{C(\mathit{C}H_3)_3}$, $^3J_{\mathrm{PC}} = 10.8$], 41.2 [d of d, $\mathrm{\mathit{C}(CH_3)_3}$, $^2J_{\mathrm{PC}} = 19.1$ and 15.7], 41.9 [d, $\mathrm{\mathit{C}(CH_3)_3}$, $^2J_{\mathrm{PC}} = 17.7$], 93.1 (s, $\mathrm{\mathit{C}_5Me_5}$), 142.1 (d of d, PCP, $^1J_{\mathrm{PC}} = 83.5$ and 108.2 Hz) and 152.9 (d, SbCP, $^1J_{\mathrm{PC}} = 82.3$); ^{31}P-{^{1}H} (101.4 MHz), δ 30.1 (d, CPC, $^2J_{\mathrm{PP}} = 41.4$ Hz) and 80.0 (d, SbPC). EI mass spectrum (70 kV): *m/z* 558 (M^+, 10), 420 ($M^+ - 2\mathrm{CBu^t}$, 12) and 57 ($\mathrm{Bu^{t+}}$, 100%). IR: ṽ/cm^{-1} 720m, 1040w and 1210w.

$[\mathrm{Fe}(\eta^5\text{-}\mathrm{P_2SbC_2Bu^t_2})(\eta^5\text{-}\mathrm{C_5Me_5})]$ 24. A mixture of $[\mathrm{Li(tmen)_2}][\mathrm{P_2SbC_2Bu^t_2}]$ (1.0 g, 1.8 mmol) and $\mathrm{Li(C_5Me_5)}$ (0.25 g, 1.8 mmol) in dme (20 cm^3) was added over 15 min to a suspension of $\mathrm{FeCl_2}$ (230mg, 1.8 mmol) in dme (10 cm^3) at −40 °C. The mixture was warmed to room temperature and stirred for 18 h. Volatiles were removed *in vacuo* and the residue was extracted with hexane (20 cm^3) and filtered. The filtrate was reduced to *ca.* 5 cm^3 and placed at −20 °C overnight to yield brown crystals of compounds **24** (*ca.* 85%) and **7** (*ca.* 15%) (280 mg, 26%), m.p. 124 °C. NMR ($\mathrm{C_6D_6}$, 298 K) for **24**: ^{1}H (250 MHz), δ 1.64 (s, 9 H, $\mathrm{Bu^t}$), 1.78 (s, 9 H, $\mathrm{Bu^t}$) and 1.80 (s, 15 H, $\mathrm{C_5Me_5}$); ^{13}C (100.6 MHz), δ 13.7 [s, $\mathrm{C_5(\mathit{C}H_3)_5}$], 36.8 [virtual t, $\mathrm{C(\mathit{C}H_3)_3}$, $^3J_{\mathrm{PC}} = 10$ and 10], 39.0 [d, $\mathrm{C(\mathit{C}H_3)_3}$, $^3J_{\mathrm{PC}} = 11$], 42.3 [d of d, $\mathrm{\mathit{C}(CH_3)_3}$, $^2J_{\mathrm{PC}} = 17$ and 20], 43.1 [d, $\mathrm{\mathit{C}(CH_3)_3}$, $^2J_{\mathrm{PC}} = 18$], 86.0 (s, $\mathrm{\mathit{C}_5Me_5}$), 152.1 (d of d, PCP, $^1J_{\mathrm{PC}} = 79$ and 104) and 165.2 (d, SbCP, $^1J_{\mathrm{PC}} = 79$); ^{31}P-{^{1}H} (101.4 MHz), δ 49.0 (d, CPC, $^2J_{\mathrm{PP}} = 44$) and 100.0 (d, SbPC, $^2J_{\mathrm{PP}} = 44$ Hz). EI mass spectrum (70 kV): *m/z* 513 (M^+, 10), 457 ($M^+ - \mathrm{Bu^t}$, 3), 375 ($M^+ - 2\mathrm{CBu^t}$, 19) and 57 ($\mathrm{Bu^{t+}}$, 100%). IR: ṽ/cm^{-1} 700m and 1020m.

$[\mathrm{Ru}(\eta^5\text{-}\mathrm{P_2SbC_2Bu^t_2})(\eta^5\text{-}\mathrm{C_5Me_5})\{\mathrm{W(CO)_5}\}]$ 25. The compound $[\mathrm{W(CO)_6}]$ (310 mg, 0.88 mmol) in thf (75 cm^3) was irradiated (254 nm) for 6 h. Compound **19** (220 mg, 0.4 mmol) in thf (5 cm^3) was added to the resulting yellow solution and the mixture stirred overnight. Volatiles were removed *in vacuo* and the residue purified by column chromatography (Kieselgel, hexane). The pale orange band was collected and concentrated to *ca.* 3 cm^3 to yield orange cocrystals of compounds **25** (79%) and **27** (21%) (60 mg, 14%), m.p. 157 °C (decomp.). NMR ($\mathrm{CD_2Cl_2}$, 298 K) for **25**: ^{1}H (250 MHz), δ 1.39 (s, 9 H, $\mathrm{Bu^t}$), 1.57 (s, 9 H, $\mathrm{Bu^t}$) and 2.10 (s, 15 H, $\mathrm{C_5Me_5}$); ^{13}C (100.6 MHz), δ 11.5 [s, $\mathrm{C_5(\mathit{C}H_3)_5}$], 34.4 [dd, $\mathrm{C(\mathit{C}H_3)_3}$, $^3J_{\mathrm{PC}} = 6$ and 12], 36.0 [d, $\mathrm{C(\mathit{C}H_3)_3}$, $^3J_{\mathrm{PC}} = 12$], 38.5 [d of d, $\mathrm{\mathit{C}(CH_3)_3}$, $^2J_{\mathrm{PC}} = 17$ and 5], 40.2 [d, $\mathrm{\mathit{C}(CH_3)_3}$, $^2J_{\mathrm{PC}} = 18$], 93.4 (s, $\mathrm{\mathit{C}_5Me_5}$), 126.8 (d of d, PCP, $^1J_{\mathrm{PC}} = 73$ and 88), 152.4 (d, SbCP, $^1J_{\mathrm{PC}} = 83$), 196.0 [d, W(CO), $^2J_{\mathrm{PC}} = 5$, $^1J_{\mathrm{WC}} = 127$] and 198.5 (d, $^2J_{\mathrm{PC}} = 28$ Hz); ^{31}P-{^{1}H} (101.4 MHz), δ 33.3 (d, SbPC, $^2J_{\mathrm{PP}} = 52$, $^1J_{\mathrm{PW}} = 212$) and 36.7 (d, CPC, $^2J_{\mathrm{PP}} = 52$ Hz). FAB mass spectrum (25 kV): *m/z* 882 (M^+, 5), 828 ($M^+ - 2\mathrm{CO}$, 11), 772 ($M^+ - 4\mathrm{CO}$, 16), 742 ($M^+ - 5\mathrm{CO}$, 34) and 558 [$M^+ - \mathrm{W(CO)_5}$, 29%]. IR: ṽ/cm^{-1} 1941s (sh), 2066s.

$[\mathrm{Fe}(\eta^5\text{-}\mathrm{P_2SbC_2Bu^t_2})(\eta^5\text{-}\mathrm{C_5Me_5})\{\mathrm{W(CO)_5}\}]$ 26. The compound $[\mathrm{W(CO)_6}]$ (157 mg, 0.45 mmol) in thf (40 cm^3) was irradiated

Table 3 Crystal data for the cocrystallised mixtures $[Ru(\eta^5\text{-}P_2SbC_2Bu^t{}_2)_2]$ **20**, **21**, $[Ru(\eta^5\text{-}P_2SbC_2Bu^t{}_2)(\eta^5\text{-}P_3C_2Bu^t{}_2)]$ **22** and $[Fe(\eta^5\text{-}P_2SbC_2Bu^t{}_2)(\eta^5\text{-}C_5Me_5)]$ **24**, $[Fe(\eta^5\text{-}P_3C_2Bu^t{}_2)(\eta^5\text{-}C_5Me_5)]$ **7**

	20–22	**24**, **7**
Chemical formula	$C_{20}H_{36}P_{4.47}RuSb_{1.53}$	$C_{20}H_{33}FeP_{2.15}Sb_{0.85}$
M	702.27	499.39
Space group	$P2_1/n$	$P\bar{1}$
Crystal system	Monoclinic	Triclinic
a/Å	16.638(2)	8.578(1)
b/Å	9.9790(7)	10.465(1)
c/Å	17.341(2)	13.889(1)
α/°		96.75(1)
β/°	112.890(6)	106.51(2)
γ/°		109.97(2)
U/Å^3	2652.4(4)	1091.2(2)
Z	4	2
D_c/g cm^{-3}	1.759	1.520
μ(Mo-Kα) cm^{-1}	23.91	18.79
Absorption correction, T_{max}, T_{min}	1.18, 0.85	1.21, 0.82
F(000)	1380	509
Reflections collected	7001	4392
No. unique reflections	3652	3031
Crystal size/mm	0.28 × 0.24 × 0.18	0.32 × 0.22 × 0.20
θ Range/°	2–25	2–25
R [a] (on F)	0.0446	0.0380
wR [b] (on F^2 for all data)	0.0937	0.0797
x in weighting scheme [c]	0.0483	0.0314

[a] $\Sigma(\Delta F)/\Sigma(F_o)$. [b] $[\Sigma w(\Delta F^2)^2/\Sigma w(F_o{}^2)^2]^{\frac{1}{2}}$. [c] $w = 1/[\sigma^2(F_o{}^2) + (xP)^2]$ where $P = [\max(F_o{}^2) + 2(F_c{}^2)]/3$.

(254 nm) for 6 h. Compound **24** (88 mg, 0.2 mmol) in thf (5 cm^3) was added to the resulting yellow solution and the mixture stirred overnight. Volatiles were removed *in vacuo* and the residue was purified by column chromatography (Kieselgel, hexane). The pale orange band was collected and concentrated to *ca.* 3 cm^3 to yield orange cocrystals of compounds **26** (86%) and **28** (14%) (56 mg, 35%), m.p. 165 °C (decomp.). NMR (CDCl$_3$, 298 K) for **26**: ^{1}H (250 MHz), δ 1.45 (s, 9 H, Bu^t), 1.61 (s, 9 H, Bu^t) and 1.92 (s, 15 H, C$_5$Me$_5$); ^{13}C (100.6 MHz), δ 13.3 [s, $C_5(CH_3)_5$], 36.4 [dd, $C(CH_3)_3$, $^3J_{PC} = 6$ and 12], 38.2 [d, $C(CH_3)_3$, $^3J_{PC} = 11$], 40.8 [d of d, $C(CH_3)_3$, $^2J_{PC} = 19$ and 6], 43.0 [d, $C(CH_3)_3$, $^2J_{PC} = 18$], 87.6 (s, C_5Me_5), 133.6 (d of d, PCP, $^1J_{PC} = 71$ and 85), 165.3 (d, SbCP, $^1J_{PC} = 79$), 197.2 [d, W(CO), $^2J_{PC} = 6$, $^1J_{WC} = 127$] and 200.0 (d, $^2J_{PC} = 28$ Hz); ^{31}P-{^{1}H} (101.4 MHz), 46.0 (d, SbPC, $^2J_{PP} = 54$, $^1J_{PW} = 214$) and 47.8 (d, CPC, $^2J_{PP} = 52$ Hz). FAB mass spectrum (25 kV): *m/z* 836 (M^+, 15), 782 ($M^+ - 2CO$, 8), 754 ($M^+ - 3CO$, 13) and 512 [$M^+ - W(CO)_5$, 61%]. IR: $\tilde{\nu}$/cm^{-1} 1940s, 1975s and 2067m.

$[(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}\eta^5\text{:}\eta^5\text{-}P_2SbC_2Bu^t{}_2)Ru(\eta^5\text{-}C_5Me_5)][PF_6]$ 29. The salt $[Li(tmen)_2][P_2SbCBu^t{}_2]$ (0.96 g, 1.7 mmol) in dme (10 cm^3) was added over 15 min to a suspension of $[Ru(C_5Me_5)(MeCN)_3][PF_6]$ (1.60 g, 3.2 mmol) in dme (10 cm^3) at −40 °C. The mixture was warmed to room temperature and stirred for 18 h. Volatiles were removed *in vacuo* and the residue was extracted with thf (20 cm^3) and filtered through a 5 cm pad of neutral alumina. Volatiles were removed from the filtrate *in vacuo* and the residue was taken up in CH$_2$Cl$_2$ (0.5 cm^3) and layered with hexane (5 cm^3) to yield orange cocrystals of compounds **29** (97%) and **30** (3%) (30 mg, 2%), m.p. 225 °C (decomp.). NMR (CDCl$_3$, 298 K) for **29**: ^{1}H (250 MHz), δ 1.27 (s, 9 H, Bu^t), 1.54 (s, 9 H, Bu^t) and 1.74 (s, 30 H, C$_5$Me$_5$); ^{13}C (100.6 MHz), δ 12.2 [s, $C_5(CH_3)_5$], 38.2 [d of d, $C(CH_3)_3$, $^2J_{PC} = 11$ and 14], 39.1 [virtual t, $C(CH_3)_3$, $^3J_{PC} = 10$ and 10], 39.2 [d, $C(CH_3)_3$, $^2J_{PC} = 15$], 41.0 [d, $C(CH_3)_3$, $^3J_{PC} = 10$], 93.2 (s, C_5Me_5) and 119.5 (d, SbCP, $^1J_{PC} = 108$); ^{31}P-{^{1}H} (101.4 MHz), δ 1.2 (d, $^2J_{PP} = 32$), −49.7 (d, $^2J_{PP} = 32$) and −143.9 (spt, PF$_6$, $^1J_{PF} = 713$ Hz). FAB mass spectrum (25 kV): *m/z* 794 ($M^+ - PF_6$, 100) and 420 ($M^+ - PF_6 - 2CBu^t$, 42%). IR: $\tilde{\nu}$/cm^{-1} 1680w (br).

Crystallography

Cocrystals of compounds **20**–**22** and **24** and **7** suitable for structure determination were grown from hexane and mounted in oil. Intensity data were measured on a FAST[21] area-detector diffractometer at 150(2) K using Mo-Kα radiation (λ 0.710 69 Å). Both structures were solved by heavy-atom methods (SHELXS 86[22]) and refined by least squares using the SHELXL 93[23] program. The structures were refined on F^2 using all data. Neutral-atom complex scattering factors were employed.[24] Empirical absorption corrections were carried out by the DIFABS method.[25] Crystal data, details of the data collections and refinement are given in Table 3.

Anisotropic thermal parameters were refined for all non hydrogen atoms. The hydrogen atoms in both structures were included in calculated positions (riding model). During refinement of the structure of (**20**–**22**) a site disorder was found to exist in which the sites labelled Sb(1), Sb(2) and P(1) are partially occupied by phosphorus (51), phosphorus (13) and antimony (17%) respectively. A site disorder is also present in the structure of **24** and **7** in which the site labelled Sb is partially occupied by phosphorus (15%).

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/497.

Acknowledgements

We gratefully acknowledge financial support from The Leverhulme Trust (to S. J. B.), The University of Wales, Swansea (studentship for M. D. F.), The Nuffield Foundation and Johnson Matthey for a loan of ruthenium salts. We also thank Professor M. B. Hursthouse and Mr. D. E. Hibbs (EPSRC Crystallography Service, Cardiff) for the X-ray data collection and many helpful discussions.

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Received 6*th February* 1997; *Paper* 7/00869D