Lithioalkynyl Iron(II) or Ruthenium(II) Complexes as Precursors of Novel Alkynyl and Vinylidene Derivatives: Heterobimetallic Complexes containing a Bridging Ethynediyl System†

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Deprotonation of ethynyl complexes [Fe(C≡CH)(η^5-C_5H_5)(dppm)] **1a** (dppm = $Ph_2PCH_2PPh_2$) and [Ru(C≡CH)(η^5-C_9H_7)L_2] [L_2 = 2PPh$_3$ **1b**, $Ph_2PCH_2CH_2PPh_2$(dppe) **1c** or (PMe_3)(PPh_3) **1d**] with LiBu^t at −78 °C gave the lithiated complexes [Fe(C≡CLi)(η^5-C_5H_5)(dppm)] **2a** and [Ru(C≡CLi)(η^5-C_9H_7)L_2] **2b**–**2d**, respectively. These species have been used *in situ* as precursors of novel alkynyl and vinylidene complexes by reactions with electrophiles. Treatment of complexes **2a**–**2d** with $MeOSO_2CF_3$ at −78 °C gave vinylidene complexes [Fe(=C=CMe$_2$)(η^5-C_5H_5)(dppm)][CF_3SO_3] **3a** and [Ru(=C=CMe$_2$)(η^5-C_9H_7)L_2][CF_3SO_3] [L_2 = 2PPh$_3$ **3b**, dppe **3c** or (PPh_3)(PMe_3) **3d**]. Iodoalkynyl complexes [Ru(C≡CI)(η^5-C_9H_7)L_2] (L_2 = 2PPh$_3$ **4b** or dppe **4c**) have been obtained by reaction of [I(py)$_2$][BF_4] (py = pyridine) with **2b** and **2c**, respectively. Reaction of **2a**–**2d** with $SnPh_3Cl$ yielded the ethynediyl bridging bimetallic complexes [(η^5-C_5H_5)(dppm)Fe–C≡C–SnPh$_3$] **5a** and [(η^5-C_9H_7)L_2Ru–C≡C–SnPh$_3$] [L_2 = 2PPh$_3$ **5b**, dppe **5c** or (PPh_3)(PMe_3) **5d**]. Similar heterobimetallic complexes [(η^5-C_5H_5)(dppm)Fe–C≡C–Au(PPh_3)] **6a** and [(η^5-C_9H_7)L_2Ru–C≡C–Au(PPh_3)] **6b**–**6d** have been obtained by treatment of ethynyl complexes **1a**–**1d** with [AuCl(PPh_3)] and Tl(acac) (acac = acetylacetonate) in dichloromethane. Complexes **6a** and **6b** can alternatively be obtained by reaction of **5a** and **5b** with [AuCl(PPh_3)] in the presence of [$PdCl_2$(MeCN)$_2$]. The crystal structure of **5a** has been determined by X-ray diffraction methods. It shows a typical three-legged piano-stool geometry. The iron atom is bonded to the cyclopentadienyl ring, the two phosphorus atoms of a chelating dppm ligand, with a narrow bite angle [74.90(5)°] and the terminal carbon of the triphenyltin acetylide group. The ethynyl bridge is bound to the iron and tin forming an C≡C–Sn angle of 162.8(4)° and an almost linear Fe–C≡C arrangement [178.0(3)°].

Metal alkynyl complexes are currently of great interest[1] since they can be used as valuable synthons for constructing species with longer organic chains. Over the last few years we have been engaged in this chemistry and have reported the synthesis of iron[2a,b] and ruthenium[2c,d] alkynyl complexes including the ethynyl derivatives [Fe(C≡CH)(η^5-C_5H_5)(dppm)] **1a** (dppm = $Ph_2PCH_2PPh_2$) and [Ru(C≡CH)(η^5-C_9H_7)L_2] [L_2 = 2PPh$_3$ **1b** or $Ph_2PCH_2CH_2PPh_2$ (dppe) **1c**] obtained from the corresponding vinylidene complexes *via* deprotonation with KOBu^t.[2a,c]

Ethynyl complexes show an acidic character and can be deprotonated to generate anionic species which have been used as precursors of bimetallic complexes containing the ethynediyl group as a bridging ligand. Following this methodology Gladysz and co-workers[3a] have described the generation of the lithium derivatives [Re(C≡CLi)(η^5-C_5R_5)(NO)(PPh_3)] (R = H or Me) which have proved to be good nucleophiles and excellent precursors of bridging dicarbide bimetallic species of the type Re–C≡C–Si,[3b,c] Re–C≡C–Sn,[3b,c] Re–C≡C–Pd,[3b] Re–C≡C–Rh[3b] and of heterobimetallic complexes containing bridging alkynyl Fischer carbene moieties Re–C≡C–C(OMe)=M (M = Mn, W or Fe).[3d]

In this work we report on the generation of the lithium derivatives [M(C≡CLi)(η^5-ring)L_2] **2a**–**2d** obtained by deprotonation reactions of the known[2a,c] ethynyl complexes **1a**–**1c** and the novel (here described) [Ru(C≡CH)(η^5-C_9H_7)(PPh_3)(PMe_3)] **1d** which have been used as precursors of a wide variety of alkynyl and vinylidene complexes. Heterobimetallic complexes containing the ethynediyl group as bridging ligand have also been synthesized (see Scheme 1). Furthermore, the novel vinylidene complex [Ru(=C=CH$_2$)(η^5-C_9H_7)(PPh_3)(PMe_3)][PF_6], which is used as precursor for the synthesis of **1d**, is also described.

The resulting bimetallic complexes with a dicarbide C_2 bridging system belong to a rapidly expanding class of new materials containing C_x linkages with optical and electronic properties[4] of interest in non-linear optics and liquid-crystal materials.[5] Related organometallic complexes with unsaturated hydrocarbon moieties acting as bridges between metal atoms have also undergone a rapid development in the last decade.[6]

Results and Discussion

The synthesis and transformations of the novel lithium alkynyl derivatives are summarized in Scheme 1. Treatment of solutions of the ethynyl complexes **1a**–**1d** with LiBu^t in thf or diethyl ether at −78 °C generates the lithiated species **2a**–**2d**. The reaction

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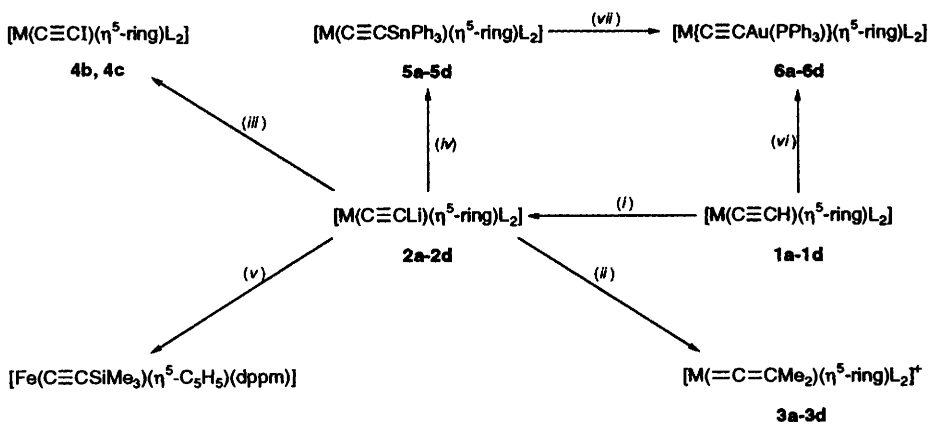
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.



Scheme 1 M = Fe **a** or Ru **b–d**; ring = η^5-C_5H_5 **a** or η^5-C_9H_7 **b–d**; L_2 = dppm **a**, $2PPh_3$ **b**, dppe **c** or $(PPh_3)(PMe_3)$ **d**. (*i*) + $LiBu^t$ [tetrahydrofuran (thf) or diethyl ether at −78 °C, 15 min]; (*ii*) + $MeOSO_2CF_3$ (−78 °C, 15 min); (*iii*) + $[I(py)_2][BF_4]$ (py = pyridine) (−78 °C, 15 min); (*iv*) + $SnPh_3Cl$ (−78 °C, 20 min); (*v*) + $SiMe_3Cl$ (−78 °C, 20 min); (*vi*) + Tl(acac) (acac = acetylacetonate) + $[AuCl(PPh_3)]$ [dichloromethane at room temperature (r.t.), 1.5 h]; (*vii*) for **6a** and **6b**, + $[AuCl(PPh_3)]$ + $[PdCl_2(MeCN)_2]$ (thf at r.t., 1 h)

only results in deprotonation of the ethynyl group in contrast to the behaviour of the rhenium complex $[Re(C{\equiv}CH)(\eta^5$-$C_5H_5)(PPh_3)(NO)]$ for which ring-deprotonation processes also take place.[3a,c] The species **2a–2d** are generated at −78 °C but rapidly decompose as the temperature increases. Thus, the ruthenium–lithium derivatives are unstable above −20 °C and the analogous iron complexes are even less stable so that the reactivity studies must be carried out below −50 °C.

Although these species have not been isolated their nature can be inferred from their reactivity. Thus, treatment of the diethyl ether solutions containing **2a–2d** with $MeOSO_2CF_3$ at −78 °C leads to the formation of the novel cationic vinylidene complexes $[Fe(=C=CMe_2)(\eta^5$-$C_5H_5)(dppm)]^+$ **3a** and $[Ru(=C=CMe_2)(\eta^5$-$C_9H_7)(PPh_3)(PMe_3)]^+$ **3d** (isolated as the triflate salts in 60–70% yield) and the known ruthenium complexes **3b** and **3c**.*[,2c] The reactions probably proceed through the formation of the propynyl complexes which, however, could not be isolated even when the electrophile was added in stoichiometric amount. Proton and ^{13}C NMR spectra are in accordance with the presence of the $=C=CMe_2$ moiety, showing the proton methyl resonance at δ 0.98 and 1.74 for **3a** and **3d**, respectively, and the typical low-field signal of C_α of the vinylidene group as a triplet at δ 364.17 [^2J(CP) 32.5] and as a doublet of doublets at δ 348.45 [^2J(CP) 18.1, 14.5 Hz] for **3a** and **3d** respectively. Similarly, **2a** reacts with $SiMe_3Cl$ to give the known complex $[Fe(C{\equiv}CSiMe_3)(\eta^5$-$C_5H_5)(dppm)]$.[2a]

Treatment of solutions of the lithium derivatives **2a–2d** with stoichiometric amounts of $[I(py)_2][BF_4]$ in thf at −78 °C leads to the formation of the iodoalkynyl derivatives **4a–4d**. Infrared spectra of the solutions show an absorption in the range 2010–1996 cm^{-1} identified as the characteristic ν(C≡C). However, after working up the reaction mixture, only complexes **4b** and **4c** could be isolated with analytical purity. Their ^{13}C NMR spectra exhibit (see Experimental section) the expected signals for the alkynyl moiety.

The most general method for preparing bimetallic species with ethynediyl bridges M–C≡C–M′ consists of the reactions of lithium ethynyl complexes with metal halide derivatives. Therefore, we investigated the synthetic utility of the lithium derivatives **2a–2d** as precursors for the preparations of bimetallic complexes by reactions with $SnPh_3Cl$ and $[AuCl(PPh_3)]$. When $SnPh_3Cl$ is added to the solutions in thf of the lithium derivatives at −78 °C an immediate reaction occurs. After working up, pink **5a** or yellow **5b–5d** air-stable solids can be isolated in 50–65% yield (Scheme 1). Although unsatisfactory analyses were obtained for the latter complexes even after recrystallization (due to the presence of residual amounts of $SnPh_3Cl$) the spectroscopic properties and the X-ray structural determination of **5a** (see below) allow their characterization. In contrast, no reaction is observed when the lithium derivatives are treated with $[AuCl(PPh_3)]$. However, when a mixture of equimolar amounts of the ethynyl complexes **1a–1d** $[AuCl(PPh_3)]$ and Tl(acac) was allowed to react in dichloromethane at room temperature for 1.5 h the desired heterobimetallic complexes **6a–6d** are formed and isolated as air-stable yellowish solids in 60–70% yield.

Alternatively, complexes **6a** and **6b** can be also prepared from the palladium-catalysed Stille's coupling of the tin derivatives **5a** and **5b** with $[AuCl(PPh_3)]$. In order to prove the generality of this synthetic methodology[7] we have explored the reactivity with other metallic halides such as $[Fe(\eta^5$-$C_5H_5)Cl(CO)_2]$ and $[Mo(\eta^5$-$C_5H_5)Cl(CO)_3]$. However, the reactions lead to reductive coupling of the halides, generating the corresponding carbonyl dimer and other unidentified products.

The IR spectroscopic data and NMR spectra (^1H and ^{31}P-$\{^1H\}$) of the bimetallic complexes are in accordance with the proposed formula. Moreover, the molecular structure of **5a** has been confirmed by an X-ray determination (see below). Infrared spectra show the expected ν(C≡C) absorptions which appear in the range 1976–1961 and 1966–1933 cm^{-1} for **5a–5d** and **6a–6d**, respectively. Proton and ^{13}C NMR spectra at room temperature exhibit aromatic, methylene (CH_2P), cyclopentadienyl and indenyl signals of the ligands (see Experimental section). The ^{13}C-$\{^1H\}$ NMR spectra also exhibit the characteristic low-field resonances for the carbon nucleus of the ethynediyl group, M–C≡ and ≡C–M′. Significantly, for **6a–6d** the signal of the carbon bonded to iron or ruthenium appears as a triplet at δ 220–227 [^2J(CP) 19 Hz] while that of the carbon bonded to gold is obscured by the aromatic signals.

Indenyl carbon resonances have been assigned (see Experimental section) and the chemical shifts are in accordance with the η^5 co-ordination. The values of the parameter Δδ ($C^{3a,7a}$), which is used as a reference of the η^5-indenyl ring distortion[8] (see Experimental section for definition), have been calculated. For the alkynyl complexes, the values are in the range from *ca.* −19.5 to −24 ppm consistent with a moderate distortion of the ring. However, the indenyl ring in the vinylidene complexes appears to be more distorted as is shown by the corresponding Δδ values {−15.78 for $[Ru(=C=CH_2)(\eta^5$-$C_9H_7)(PPh_3)(PMe_3)][PF_6]$ and −16.58 for **3d**}. These data are in accordance with calculated data for other alkynyl and vinylidene indenyl complexes.[2c]

Crystal Structure of $[Fe(C{\equiv}CSnPh_3)(\eta^5$-$C_5H_5)(dppm)]$ **5a**.—The structure of the complex is depicted in Fig. 1 together with the atomic numbering scheme. Selected bond distances

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* The present methodology leads to much higher yields (65%).

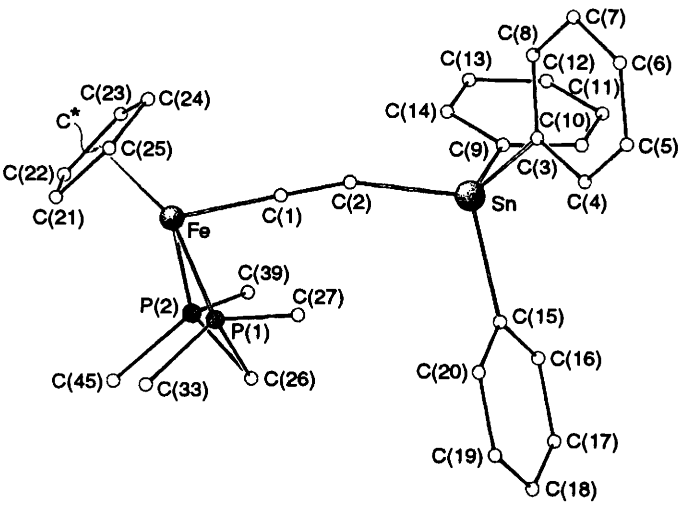


Fig. 1 Molecular structure of the complex [Fe($C\equiv CSnPh_3$)(η^5-C_5H_5)(dppm)] **5a**. For clarity, aryl groups of the triphenylphosphine ligands are omitted (C* = centroid of the cyclopentadienyl ring)

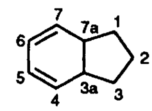
Table 1 Selected bond lengths (Å) and angles (°) in complex **5a**

Fe–C*	1.70(4)	Sn–C(2)	2.063(4)
C(1)–C(2)	1.217(5)	Fe–C(1)	1.903(4)
Sn–C(3)	2.048(4)	Sn–C(9)	2.144(4)
Sn–C(15)	2.152(4)	Fe–P(1)	2.167(1)
Fe–P(2)	2.174(1)	Fe–C(21)	2.081(4)
Fe–C(22)	2.089(5)	Fe–C(23)	2.067(5)
Fe–C(24)	2.075(5)	Fe–C(25)	2.095(4)
C(3)–Sn–C(2)	110.5(2)	C(9)–Sn–C(2)	110.5(2)
C(15)–Sn–C(2)	109.9(2)	C(1)–C(2)–Sn	162.8(4)
C(1)–Fe–P(1)	86.2(1)	C(1)–Fe–P(2)	82.9(1)
C(2)–C(1)–Fe	178.0(3)	P(2)–Fe–P(1)	74.90(5)
P(2)–C(26)–P(1)	91.2(2)	C*–Fe–C(1)	124.0(1)
C*–Fe–P(1)	134.0(1)	C*–Fe–P(2)	134.0(1)

and angles are listed in Table 1 and fractional atomic coordinates in Table 2. The complex consists of discrete monomeric molecules in which the cyclopentadienyl ring is η^5 bonded to the iron atom with a distance between the metal atom and the centroid (C*) of 1.70(4) Å. The molecule shows the typical structure of cyclopentadienyl complexes in the pseudo-octahedral three-legged piano-stool geometry. The values of the interligand angles P(1)–Fe–P(2), C(1)–Fe–P(1), C(1)–Fe–P(2) are 74.90(5), 86.2(1) and 82.9(1)°, respectively, whereas those between the centroid and the legs are C*–Fe–P(1) 134.0(1), C*–Fe–P(2) 134.0(1) and C*–Fe–C(1) 124.0(1) as expected for a pseudo-octahedron. The iron atom is bonded to the two phosphorus atoms of a bis(diphenylphosphino)methane molecule acting as a chelate ligand forming a strained four-membered ring with a narrow bite angle [P(1)–Fe–P(2) 74.90(5)°] which is similar to that found for the analogous complex [Fe($C\equiv CPh$)(η^5-C_5H_5)(dppm)] [74.6(2)° average].[2a] The ethynyl bridge is bound to Fe and Sn with Fe–C(1) and Sn–C(2) distances of 1.903(4) and of 2.063(4) Å, respectively. The C(1)–C(2) distance [1.217(5) Å] is typical for a triple carbon–carbon bond and the angle Fe–C(1)–C(2) [178.0(3)°] shows the expected linearity of the metal alkynyl bonding. Nevertheless, the angle C(1)–C(2)–Sn 162.8(4)° deviates significantly from linearity, as is also observed for a number of bridging ethynyl heterobimetallic complexes, *e.g.* Re–$C\equiv C$–Pd (Re–$C\equiv C$ 173.2, $C\equiv C$–Pd 169.5 °)[3b] and Ru–$C\equiv C$–Zr [Ru–$C\equiv C$ 169.9(3), $C\equiv C$–Zr 174(2)°].[9]

Experimental

The reactions were carried out under dry nitrogen using Schlenk techniques. All solvents were dried by standard methods and distilled under nitrogen before use. The complexes [Fe($C\equiv CH$)(η^5-C_5H_5)(dppm)] **1a**,[2a] [Ru($C\equiv CH$)(η^5-C_9H_7)L_2][2c] (L = PPh_3 **1b**, L_2 = dppe **1c**), [AuCl(PPh_3)][10a] and [I$(py)_2$][BF_4][10b] were prepared by literature methods; Tl(acac) was prepared from Tl_2CO_3.[11] The reactants LiBu^t, $MeOSO_2CF_3$, KOBu^t, $SnPh_3Cl$, NH_4PF_6 and $HC\equiv CSiMe_3$ were used as received from Aldrich Chemical Co. and Lancaster Chemical Co.



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Infrared spectra were recorded on a Perkin-Elmer 1720-XFT spectrometer, mass spectra (FAB) using a VG-Autospec spectrometer, operating in the positive mode; 3-nitrobenzyl alcohol was used as the matrix. The conductivities were measured at room temperature, in *ca.* 10^{-3} mol dm^{-3} acetone solutions, with a Jenway PCM3 conductimeter. The C, H and N analyses were carried out with a Perkin-Elmer 240-B microanalyzer. The NMR spectra were recorded on a Bruker AC300 instrument at 300 (^1H), 121.5 (^{31}P) or 75.4 MHz (^{13}C) using $SiMe_4$ or 85% H_3PO_4 as standards. The atom labelling for the indenyl group used for ^1H and ^{13}C-{^1H} NMR spectroscopic data is as shown in **A**. The parameter $\Delta\delta(C^{3a,7a})$ is defined as the difference between $\delta(C^{3a,7a})$ for the indenyl complex and $\delta(C^{3a,7a})$ for indenyl sodium.

Preparation of the Complexes.—[Ru(=C=CH_2)(η^5-C_9H_7)(PPh_3)(PMe_3)][PF_6]. A mixture of [RuCl(η^5-C_9H_7)(PPh_3)(PMe_3)][12] (1 mmol), $HC\equiv CSiMe_3$ (0.7 cm^3, 5 mmol) and NH_4PF_6 (0.326 g, 2 mmol) in dichloromethane (40 cm^3) was refluxed during 6 h. The resulting suspension was then partially concentrated and filtered over stirred diethyl ether (100 cm^3). The resulting yellow solid was washed with diethyl ether (3 × 20 cm^3) and vacuum-dried. Yield 80%: $\tilde{\nu}_{max}$/cm^{-1} (KBr) 839 (PF_6^-) (Found: C, 53.6; H, 4.4. $C_{32}H_{33}F_6P_3Ru$ requires C, 53.0; H, 4.6%); conductivity (acetone, 20 °C) 135 Ω^{-1} cm^2 mol^{-1}; $\delta_P(CDCl_3)$ 1.66 [d, $^2J(PP')$ 29.6, PMe_3] and 48.35 [d, $^2J(PP')$ 29.6 Hz, PPh_3]; $\delta_H[(CD_3)_2CO]$ 1.40 [9 H, d, $^2J(HP)$ 10.6 Hz, PMe_3], 4.14 (2 H, m, =CH_2), 6.05 and 6.08 (1 H each, br, H^1 and H^3), 6.17 (1 H, br, H^2), 6.34 and 7.23 (1 H each, m, indenyl) and 7.36–7.81 (17 H, m, PPh_3, indenyl); $\delta_C(CDCl_3)$ 18.80 [d, $J(CP)$ 34.6, PMe_3], 78.00 and 80.90 [d, $^2J(CP)$ 6.8, C^1 and C^3], 94.33 (=C_β), 99.33 (C^2), 114.22 and 115.65 (C^{3a} and C^{7a}), 122.32 and 124.13 (indenyl), 128.53–133.89 (PPh_3, indenyl) and 342.41 [dd, $^2J(CP)$ 17.8, 15.2 Hz, Ru=C_α]; $\Delta\delta(C^{3a,7a}) = -15.78$ (average); *m/z* 581 (M^+), 555 ($M^+ - C_2H_2$) and 479 ($M^+ - C_2H_2 - PMe_3$).

[Ru($C\equiv CH$)(η^5-C_9H_7)(PPh_3)(PMe_3)] **1d**. A solution of [Ru(=C=CH_2)(η^5-C_9H_7)(PPh_3)(PMe_3)][PF_6] (1 mmol) in thf (10 cm^3) was treated with KOBu^t (0.123 g, 1.1 mmol) and the mixture stirred at room temperature for 10 min. The solution was then evaporated to dryness and the residue extracted with diethyl ether. Evaporation of the diethyl ether gave **1d** as a yellow solid. Yield 60%; $\tilde{\nu}_{max}$/cm^{-1} (KBr) 1936 ($C\equiv C$) (Found: C, 66.2; H, 5.6. $C_{32}H_{32}P_2Ru$ requires C, 66.3; H, 5.5%); $\delta_P(CDCl_3)$ 9.63 [d, $^2J(PP')$ 33.1, PMe_3] and 55.75 [d, $^2J(PP')$ 33.1 Hz, PPh_3]; $\delta_H(CDCl_3)$ 1.05 [9 H, d, $^2J(HP)$ 9.3 Hz, PMe_3], 1.60 (1 H, m, $\equiv$C–H), 4.74 and 4.84 (1 H each, br, H^1 and H^3), 5.41 (1 H, br, H^2), 6.30, 6.83, 6.96 and 7.06 (1 H each, m, H^{4-7}) and 7.20–7.40 (15 H, m, PPh_3); $\delta_C(CDCl_3)$ 19.80 [d, $J(CP)$ 30.0, PMe_3], 70.75 and 70.95 [d, $J(CP)$ 6.0, C^1 and C^3], 93.42 and 94.60 (C^2 and C_β), 107.94 and 108.85 (C^{3a} and C^{7a}), 108.10 [dd, $J(CP)$ 26.4 and 21.3 Hz, C_α], 122.27, 124.06, 124.74 and 125.32 (C^{4-7}) and 127.61–139.35 (PPh_3); $\Delta\delta(C^{3a,7a}) = -22.53$ (average).

Lithiated species [M($C\equiv CLi$)(η^5-ring)L_2] **2a–2d**. *General procedure.* Complexes **2a–2d** were obtained by treating a

Table 2 Fractional atomic coordinates with estimated standard deviations (e.s.d.s) in parentheses for the non-hydrogen atoms of complex **5a**

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Sn	0.162 67(3)	0.162 58(1)	0.206 37(1)	C(24)	−0.251 7(6)	0.091 2(3)	0.381 9(3)
Fe	−0.171 27(5)	0.018 18(3)	0.320 53(3)	C(25)	−0.236 9(4)	0.033 3(3)	0.419 7(2)
P(1)	−0.009 40(9)	−0.046 36(5)	0.335 89(5)	C(26)	0.012 4(4)	−0.063 0(2)	0.243 8(2)
P(2)	−0.147 30(9)	−0.032 59(5)	0.222 96(5)	C(27)	0.142 2(3)	−0.017 9(2)	0.371 3(2)
C(1)	−0.058 8(4)	0.081 8(2)	0.282 5(2)	C(28)	0.155 8(4)	0.047 7(2)	0.395 7(2)
C(2)	0.012 5(4)	0.121 5(2)	0.256 3(2)	C(29)	0.271 9(4)	0.070 4(2)	0.420 1(2)
C(3)	0.277 9(4)	0.220 0(2)	0.276 5(2)	C(30)	0.372 3(4)	0.027 6(3)	0.420 7(2)
C(4)	0.399 4(4)	0.201 9(2)	0.292 4(2)	C(31)	0.360 1(4)	−0.037 7(2)	0.396 6(2)
C(5)	0.472 5(4)	0.238 3(3)	0.338 8(3)	C(32)	0.244 7(4)	−0.060 8(2)	0.371 8(2)
C(6)	0.423 4(4)	0.293 6(3)	0.370 7(2)	C(33)	−0.024 2(3)	−0.127 6(2)	0.379 3(2)
C(7)	0.302 1(5)	0.313 4(3)	0.355 0(3)	C(34)	−0.028 7(4)	−0.126 9(2)	0.450 5(2)
C(8)	0.231 0(4)	0.277 2(3)	0.308 5(3)	C(35)	−0.043 5(5)	−0.185 9(3)	0.487 7(3)
C(9)	0.099 5(4)	0.226 3(2)	0.123 8(2)	C(36)	−0.053 2(5)	−0.245 8(3)	0.454 7(3)
C(10)	0.185 2(5)	0.261 3(2)	0.084 3(2)	C(37)	−0.049 5(6)	−0.248 7(3)	0.385 0(3)
C(11)	0.144 7(6)	0.301 5(3)	0.030 3(3)	C(38)	−0.035 0(5)	−0.189 6(2)	0.346 7(3)
C(12)	0.020 0(7)	0.308 5(3)	0.015 1(3)	C(39)	−0.148 4(4)	0.016 3(2)	0.144 2(2)
C(13)	−0.065 0(6)	0.274 7(3)	0.054 0(3)	C(40)	−0.045 3(5)	0.027 2(3)	0.104 5(2)
C(14)	−0.026 2(4)	0.233 9(2)	0.107 6(2)	C(41)	−0.055 8(7)	0.067 7(4)	0.046 0(3)
C(15)	0.276 8(4)	0.083 2(2)	0.165 8(2)	C(42)	−0.167 9(9)	0.095 9(3)	0.028 3(3)
C(16)	0.304 1(5)	0.080 7(3)	0.096 1(2)	C(43)	−0.270 8(7)	0.084 7(3)	0.066 8(3)
C(17)	0.373 3(5)	0.028 2(3)	0.070 1(3)	C(44)	−0.260 9(5)	0.046 3(2)	0.124 5(3)
C(18)	0.415 2(5)	−0.022 8(3)	0.112 1(4)	C(45)	−0.235 3(3)	−0.108 1(2)	0.195 2(2)
C(19)	0.390 0(5)	−0.021 7(3)	0.180 4(3)	C(46)	−0.244 4(4)	−0.127 6(2)	0.127 4(2)
C(20)	0.321 0(4)	0.031 1(2)	0.207 4(2)	C(47)	−0.309 6(5)	−0.185 7(2)	0.108 0(3)
C(21)	−0.305 1(4)	−0.018 3(3)	0.386 9(2)	C(48)	−0.364 8(4)	−0.224 5(3)	0.156 6(3)
C(22)	−0.361 5(4)	0.010 8(4)	0.328 9(3)	C(49)	−0.357 2(5)	−0.206 2(3)	0.224 0(3)
C(23)	−0.329 1(6)	0.078 2(4)	0.325 2(3)	C(50)	−0.293 6(4)	−0.148 0(2)	0.243 5(2)

solution of the corresponding **1a**–**1d** (0.5 mmol) in diethyl ether or thf (50 cm^3) at −78 °C with LiBu^t (0.3 cm^3, 1.7 mol dm^{-3} in hexane) and stirring during 15 min. These solutions were used for further reactions.

[M(=C=CMe$_2$)(η^5-ring)L$_2$][CF$_3$SO$_3$] **3a**–**3d**. *General procedure*. To a solution of complexes **2a**–**2d** (0.5 mmol) in diethyl ether (50 cm^3) at −78 °C was added MeOSO$_2$CF$_3$ (0.17 cm^3, 1.5 mmol). After 30 min a light precipitate appeared, the cooling bath was removed and the mixture stirred for 1 h. The solution was then decanted and the resulting solid washed with diethyl ether (3 × 20 cm^3) and dried under vacuum to give **3a**–**3d** as brownish solids. Complex **3a**: yield 60%; $\tilde{\nu}_{max}$/cm^{-1} (KBr) 1266s (br), 1225s and 1156s (CF$_3$SO$_3$) (Found: C, 58.4; H, 4.7. $C_{34}H_{33}F_3FeO_3P_2S$ requires C, 58.6; H, 4.8%); conductivity (acetone, 20 °C) 130 Ω^{-1} cm^2 mol^{-1}; δ_P(CD$_2$Cl$_2$) 27.24; δ_H (CD$_2$Cl$_2$) 0.98 (6 H, s, 2CH$_3$), 4.44 (1 H, m, PCH_aH$_b$P), 4.64 (1 H, m, PCH$_a$$H_b$P), 5.25 (5 H, s, C$_5H_5$) and 7.25–7.51 (20 H, m, PPh$_2$); δ_C(CD$_2$Cl$_2$) 11.43 (2CH$_3$), 40.66 [t, *J*(CP) 26.0, PCH$_2$P], 86.08 (C$_5$H$_5$), 129.15–136.25 (PPh$_2$) and 364.17 [t, ^2J(CP) 32.5 Hz, Fe=C$_\alpha$]. Complexes **3b** and **3c**: yield 65%; identified by comparison with reported data.[2c] Complex **3d**: yield 70%; $\tilde{\nu}_{max}$/cm^{-1} (KBr) 1270s (br), 1227s and 1190s (CF$_3$SO$_3$) (Found: C, 56.3; H, 5.0. $C_{35}H_{37}F_3O_3P_2$ RuS requires C, 55.5; H, 4.9%); conductivity (acetone, 20 °C) 136.5 Ω^{-1} cm^2 mol^{-1}; δ_P[(CD$_3$)$_2$CO] 4.40 [d, ^2J(PP′) 29.5, PMe$_3$] and 48.89 [d, ^2J(PP′) 29.5 Hz, PPh$_3$]; δ_H[(CD$_3$)$_2$CO] 1.30 [9 H, d, ^2J(HP) 10.3 Hz, PMe$_3$], 1.74 (6 H, s, 2CH$_3$), 5.87, 5.94 and 6.04 (1 H each, m, H$^{1-3}$), 6.51 (1 H, m, indenyl) and 7.29–7.80 (18 H, m, PPh$_3$, indenyl); δ_C(CD$_2$Cl$_2$) 11.65 (2CH$_3$), 20.45 [d, *J*(CP) 34.3, PMe$_3$], 78.70 [d, ^2J(CP) 5.9 Hz] and 80.87 [d, ^2J(CP) 5.9 Hz] (C^1 and C^3), 98.63 (C^2), 113.79 and 114.45 (C^{3a} and C^{7a}), 114.17 (=C$_\beta$), 122.91 and 124.04 (indenyl), 129.06–134.58 (PPh$_3$, indenyl) and 348.45 [dd, ^2J(CP) 18.1, ^2J(CP′) 14.5 Hz, Ru=C$_\alpha$]; $\Delta\delta$(C^{3a,7a}) = −16.58 (average).

[Ru(C≡CI)(η^5-C$_9$H$_7$)L$_2$] (L$_2$ = 2PPh$_3$ **4b** *or* dppe **4c**). *General procedure*. To a solution of complex **2b** or **2c** (0.5 mmol) in thf (10 cm^3) at −78 °C was added [I(py)$_2$][BF$_4$] (0.186 g, 0.5 mmol). The mixture was stirred at −78 °C for 20 min and then the solvent was evaporated to dryness under vacuum. The solid residue was extracted with diethyl ether from which complexes **4b** and **4c** were obtained as yellow solids after evaporation of the solvent. Complex **4b**: yield 55%; $\tilde{\nu}_{max}$/cm^{-1} (KBr) 1996 (C≡C) (Found: C, 62.7; H, 4.5. $C_{47}H_{37}IP_2Ru$ requires C, 63.3; H, 4.2%); δ_p(C$_6$D$_6$) 51.33; δ_H(C$_6$D$_6$) 4.90 [2 H, d, *J*(HH) 2.2, H^{1,3}], 5.78 [1 H, t, *J*(HH) 2.2 Hz, H^2], 6.56 and 6.88 (2 H each, m, H^{4,7} and H^{5,6}) and 7.15–7.63 (30 H, m, PPh$_3$); δ_C(C$_6$D$_6$) 75.42 (C^{1,3}), 96.03 (C^2), 109.89 (C^{3a,7a}), 123.93 and 124.18 (C^{4,7} and C^{5,6}) and 124.82–135.97 (PPh$_3$, C$_\beta$ and C$_\alpha$); $\Delta\delta$ (C^{3a,7a}) = −20.81; *m*/*z* 893 (M^+ + 1), 767 [(M^+ + 1) − I], 741 [(M^+ + 1) − C$_2$I] and 479 [(M^+ + 1) − C$_2$I − PPh$_3$]. Complex **4c**: yield 50%; $\tilde{\nu}_{max}$/cm^{-1} (KBr) 2004 (C≡C) (Found: C, 57.8; H, 3.8. $C_{37}H_{31}IP_2Ru$ requires C, 58.05; H, 4.1%); δ_p(C$_6$D$_6$) 82.22; δ_H(C$_6$D$_6$) 1.75 [2 H, m, P(CH_aH$_b$)$_2$P], 2.30 [2 H, m, P(CH$_a$$H_b$)$_2$P], 4.85 [2 H, d, *J*(HH) 2.7, H^{1,3}], 5.07 [1 H, t, *J*(HH) 2.7 Hz, H^2], 6.60 and 6.80 (2 H each, m, H^{4,7} and H^{5,6}) and 6.88–7.50 (20 H, m, PPh$_2$).

[M(C≡CSnPh$_3$)(η^5-ring)L$_2$] **5a**–**5d**. *General procedure*. To a solution of complexes **2a**–**2d** (0.5 mmol) in thf (15 cm^3) at −78 °C was added SnPh$_3$Cl (0.578 g, 1.5 mmol). The mixture was stirred at −78 °C during 20 min and then the solvent was removed under vacuum. The residue was extracted with diethyl ether and the solvent evaporated to dryness to give a solid which was dissolved in hexane. Cooling this solution overnight at −20 °C gave complexes **5a**–**5d** as crystalline powders. Complex **5a**: yield 50%; pink; $\tilde{\nu}_{max}$/cm^{-1} (KBr) 1962 (C≡C) (Found: C, 67.5; H, 4.5. $C_{50}H_{42}FeP_2Sn$ requires C, 68.3; H, 4.8%); δ_p(C$_6$D$_6$) 44.90; δ_H(C$_6$D$_6$) 4.17 (2 H, m, PCH$_2$P), 4.75 (5 H, s, C$_5$H$_5$) and 7.40–7.95 (35 H, m, PPh$_2$, SnPh$_3$); δ_C(C$_6$D$_6$) 44.65 [t, *J*(CP) 21.1 Hz, PCH$_2$P], 77.93 (C$_5$H$_5$), 85.01 (≡CSn) and 128.22–142.27 (PPh$_2$, SnPh$_3$, Fe–C≡); *m*/*z* 531 [(M^+ + 1) − SnPh$_3$], 507 [(M^+ + 1) − C$_2$SnPh$_3$] and 440 [(M^+ + 1) − C$_2$SnPh$_3$ − C$_5$H$_5$]. Complex **5b**: yield 65%; yellow; $\tilde{\nu}_{max}$/cm^{-1} (KBr) 1976 (C≡C); δ_p(C$_6$D$_6$) 52.10; δ_H(C$_6$D$_6$) 4.74 [2 H, d, *J*(HH) 2.2, H^{1,3}], 5.55 [1 H, t, *J*(HH) 2.2 Hz, H^2], 6.33 and 6.70 (2 H each, m, H^{4,7} and H^{5,6}) and 6.81–7.90 (45 H, m, PPh$_3$, SnPh$_3$); δ_C(C$_6$D$_6$) 75.92 (C^{1,3}), 96.95 (C^2), 107.08 (≡CSn), 110.44 (C^{3a,7a}), 123.86 and 126.73 (C^{4,7} and C^{5,6}) and 128.02–142.18 (PPh$_3$, SnPh$_3$, Ru–C≡); $\Delta\delta$(C^{3a,7a}) = −20.26; *m*/*z* 767

$[(M^+ + 1) - SnPh_3]$, 743 $[(M^+ + 1) - C_2SnPh_3]$ and 479 $[(M^+ + 1) - C_2SnPh_3 - PPh_3]$. Complex **5c**: yield 65%; yellow; $\tilde{\nu}_{max}/cm^{-1}$ (KBr) 1976 ($C\equiv C$); $\delta_p(C_6D_6)$ 89.16; $\delta_H(C_6D_6)$ 2.31 [2 H, m, $P(CH_aH_b)_2P$], 2.65 [2 H, m, $P(CH_aH_b)_2P$], 5.01 (2 H, m, $H^{1,3}$), 5.15 (1 H, m, H^2) and 7.00–7.86 (39 H, m, PPh_3, $SnPh_3$, indenyl); $\delta_C(C_6D_6)$ 28.36 [m, $P(CH_2)_2P$], 70.44 ($C^{1,3}$), 93.10 (C^2), 108.33 ($C^{3a,7a}$), 124.02 and 124.51 ($C^{4,7}$ and $C^{5,6}$) and 127.53–141.45 (PPh_2, $SnPh_3$, $RuC\equiv$, $\equiv CSn$); $\Delta\delta(C^{3a,7a}) = -22.37$. Complex **5d**: yield 60%; yellow; $\tilde{\nu}_{max}/cm^{-1}$ (KBr) 1961 ($C\equiv C$); $\delta_p(C_6D_6)$ 9.85 [d, $^2J(PP')$ 33.4, PMe_3] and 56.68 [d, $^2J(PP')$ 33.4 Hz, PPh_3]; $\delta_H(C_6D_6)$ 0.95 [d, 9 H, $^2J(HP)$ 9.4 Hz, PMe_3], 4.70 and 4.95 (1 H each, br, H^1 and H^3), 5.47 (1 H, br, H^2), 6.43 (1 H, m, indenyl) and 6.50–7.85 (33 H, m, PPh_3, $SnPh_3$, indenyl); $\delta_C(C_6D_6)$ 18.20 [d, $J(CP)$ 30.6 Hz, PMe_3], 69.46 and 70.48 (C^1 and C^3), 98.98 (C^2), 94.10 ($\equiv CSn$), 106.48 and 107.97 (C^{3a} and C^{7a}), 120.56 and 122.40 (indenyl) and 126.13–136.40 (PPh_3, $SnPh_3$, indenyl, $RuCu\equiv$); $\Delta\delta(C^{3a,7a}) = -23.47$ (average); m/z 581 $[(M^+ + 1) - SnPh_3]$ and 479 $[(M^+ + 1) - C_2SnPh_3 - PMe_3]$.

$[Fe(C\equiv CSiMe_3)(\eta^5\text{-}C_5H_5)(dppm)]$. To a solution of complex **2a** (0.5 mmol) in thf (15 cm^3) at −78 °C was added $SiMe_3Cl$ (0.163 g, 1.5 mmol) and the mixture stirred at −78 °C during 20 min. After removing the solvent under vacuum the residue was extracted with diethyl ether and the solvent evaporated to dryness. The resulting powder was identified as the known complex $[Fe(C\equiv CSiMe_3)(\eta^5\text{-}C_5H_5)(dppm)]$ by comparison of the IR and NMR spectra with those reported.[2a]

$[M\{C\equiv CAu(PPh_3)\}(\eta^5\text{-ring})L_2]$ **6a–6d**. *Method (a): general procedure.* A mixture of complexes **1a–1d** (0.5 mmol), Tl(acac) (0.154 g, 0.5 mmol) and $[AuCl(PPh_3)]$ (0.247 g, 0.5 mmol) in dichloromethane was stirred at room temperature for 1.5 h. The resulting suspension was then filtered and the solvent evaporated to dryness under vacuum to give complexes **6a–6d** as yellow-brown solids. Complex **6a**: yield 60%; $\tilde{\nu}_{max}/cm^{-1}$ (KBr) 1966 ($C\equiv C$) (Found: C, 61.5; H, 4.5. $C_{32}H_{33}F_6FeP_3$ requires C, 60.75; H, 4.3%); $\delta_p(CD_2Cl_2)$ 36.11 (s br, $AuPPh_3$) and 41.98 (s, PPh_2); $\delta_H(CD_2Cl_2)$ 4.30 (1 H, m, PCH_aH_bP), 4.50 (1 H, m, PCH_aH_bP), 4.60 (5 H, s, C_5H_5) and 6.55–8.30 (35 H, m, PPh_2 and $AuPPh_3$); $\delta_C(CD_2Cl_2)$ 38.00 [t, $J(CP)$ 22.0 Hz, PCH_2P], 82.00 (C_5H_5) and 128.80–133.00 (PPh_2, PPh_3, $FeC\equiv$, $\equiv CAu$). Complex **6b**: yield 70%; $\tilde{\nu}_{max}/cm^{-1}$ (KBr) 1933 ($C\equiv C$) (Found: C, 62.9; H, 4.35. $C_{65}H_{52}AuP_3Ru$ requires C, 63.8; H, 4.25%); $\delta_P(CD_2Cl_2)$ 35.15 (br, $AuPPh_3$) and 47.70 (PPh_3); $\delta_H(CD_2Cl_2)$ 4.86 (2 H, m, $H^{1,3}$), 5.54 (1H, m, H^2), 5.85 and 6.82 (2 H each, m, $H^{4,7}$ and $H^{5,6}$) and 7.01–7.48 (45 H, m, PPh_3, $AuPPh_3$); $\delta_C(CD_2Cl_2)$ 77.49 ($C^{1,3}$), 97.62 (C^2), 111.61 ($C^{3a,7a}$), 123.70 and 127.22 ($C^{4,7}$ and $C^{5,6}$), 127.33–138.70 (PPh_3, $\equiv CAu$, $AuPPh_3$) and 226.39 [t, $^2J(CP)$ 19.4 Hz, $RuC\equiv$]; $\Delta\delta(C^{3a,7a}) = -19.54$. Complex **6c**: yield 65%; $\tilde{\nu}_{max}/cm^{-1}$ (KBr) 1935 ($C\equiv C$) (Found: C, 59.1; H, 4.3. $C_{53}H_{42}AuP_3Ru$ requires C, 60.1; H, 4.8%); $\delta_P(CD_2Cl_2)$ 35.32 (br, $AuPPh_3$) and 85.11 (PPh_2); $\delta_H(CD_2Cl_2)$ 2.30 [2 H, m, $P(CH_aH_b)_2P$], 2.70 [2 H, m, $P(CH_aH_b)_2P$], 5.15 [2 H, d, $J(HH)$ 2.5 Hz, $H^{1,3}$], 5.35 (1 H, m, overlapped with CH_2Cl_2 signal, H^2) and 7.01–7.48 (39 H, m, PPh_3, $AuPPh_3$, indenyl); $\delta_C(CD_2Cl_2)$ 27.90 [m, $P(CH_2)_2P$], 72.97 ($C^{1,3}$), 94.52 (C^2), 108.58 ($C^{3a,7a}$), 124.31 and 125.36 ($C^{4,7}$ and $C^{5,6}$), 128.06–134.55 (PPh_2, $\equiv CAu$, $AuPPh_3$) and 220.80 [t, $^2J(CP)$ 19.7 Hz, $RuC\equiv$]; $\Delta\delta(C^{3a,7a}) = -22.12$. Complex **6d**: yield 65% (Found: C, 56.1; H, 4.5. $C_{50}H_{46}AuP_3Ru$ requires C, 57.9; H, 4.5%); $\delta_P(CD_2Cl_2)$ 7.73 [d, $^2J(PP')$ 30.0, PMe_3], 36.18 (br, $AuPPh_3$) and 54.79 [d, $^2J(PP')$ 30.0 Hz, PPh_3]; $\delta_H(CD_2Cl_2)$ 1.07 [9 H, d, $^2J(HP)$ 9.6 Hz, PMe_3], 4.92, 5.07 and 5.47 (1 H each, m, H^{1-3}), 6.10 (1 H, m, indenyl) and 7.01–7.54 (33 H, m, PPh_3, $AuPPh_3$, indenyl); $\delta_C(CD_2Cl_2)$ 19.00 [d, $J(CP)$ 30.0, PMe_3], 73.06 and 75.36 [d, $J(CP)$ 6.0 Hz, C^1 and C^3], 97.55 (C^2), 109.09 and 111.86 (C^{3a} and C^{7a}), 122.07, 124.97, 125.68 and 127.44 (C^{4-7}), 127.65–139.61 (PPh_3, $\equiv CAu$) and 227.70 (m, $RuC\equiv$); $\Delta\delta(C^{3a,7a}) = -20.12$ (average).

Method (*b*). A suspension of complex **5a** or **5b** (0.05 mmol) and $[AuCl(PPh_3)]$ (25 mg, 0.05 mmol) in thf (10 cm^3) was treated with $[PdCl_2(MeCN)_2]$ (1.2 mg, 10%) at room temperature. The yellow solution turned orange after stirring at room temperature for 1 h. The solution was then evaporated to dryness and the residue extracted with dichloromethane to give a solution from which complex **6a** or **6b** was obtained by evaporation of the solvent. Yields: 45%.

X-Ray Diffraction Analysis of $[Fe(C\equiv CSnPh_3)(\eta^5\text{-}C_5H_5)(dppm)]$ **5a**.—A red crystal of dimensions 0.26 × 0.13 × 0.13 mm crystallized from hexane was used for the X-ray analysis.

Crystal data. $C_{50}H_{42}FeP_2Sn$, $M = 879.4$, monoclinic, space group $P2_1/n$, $a = 10.693(2)$, $b = 19.794(3)$, $c = 19.520(2)$ Å, $\beta = 91.24(2)°$, $U = 4130(1)$ Å^3, $Z = 4$, $D_c = 1.41$ g cm^{-3}, $\mu = 10.66$ cm^{-1}, $F(000) = 1792$, $T = 200$ K.[13]

Data collection and processing. Enraf-Nonius CAD4 diffractometer, ω–2θ scan technique, Mo-Kα radiation (λ = 0.710 73 Å). Of 7975 reflections measured ($0 < \theta < 25°$), 4387 were used in refinement.

Structure analysis and refinement. The structure was solved by Patterson methods. Full-matrix least-squares refinement was made with SHELX 76.[14] An empirical absorption correction was applied.[15] All non-hydrogen atoms in the molecule were anisotropically refined. Hydrogen atoms were located by difference synthesis. Final conventional $R = 0.027$ for 4387 observed reflections with $F_o > 3\sigma(F_o)$ and $R' = 0.026$ where $w = 1.0/[\sigma^2(F_o^2) + 0.0001F_o^2]$. Total number of parameters 614. Residual electronic density less than 0.28 e Å^{-3}. Geometric calculations were made with PARST,[16] diagrams were drawn with the EUCLID package.[17]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Acknowledgements

Financial support by the Spanish Dirección General de Investigación Científica y Técnica (Project PB90-385) and Universidad de Oviedo (Project DF-93-222-74) is acknowledged. We thank the European Erasmus Programme, the Fundación para la Investigación Científica y Técnica de Asturias (FICYT) and the Spanish Ministerio de Educación y Ciencia for grants to I. G. (University of Rennes, France), B. M. M.-V. and A. G.-R, respectively.

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Received 13*th December* 1994; *Paper* 4/07586B