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Chemistry of polynuclear allenyl complexes: the μ-$\eta^1:\eta^2$-allenyl diruthenium system $Ru_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}\eta^1:\eta^2\text{-}C(Ph){=}C{=}CH_2)$. Dimetallocycles via C–C, C–N and C–S bond forming reactions and the X-ray structure of $Ru_2(CO)_6(\mu\text{-}PPh_2)[\mu\text{-}\eta^1:\eta^1\text{-}PhC{=}C\{C(EtS)N(H)^tBu\}CH_2]$

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Abstract

The μ-$\eta^1:\eta^2$-allenyl complex $Ru_2(CO)_6(\mu\text{-}\eta^1:\eta^2\text{-}C(Ph){=}C{=}CH_2)(\mu\text{-}PPh_2)$ (1), which has a structure with $C_\alpha(Ph)$ coordinated to one ruthenium atom and the $C_\beta{=}C_\gamma$ double bond attached to the second metal atom, undergoes regiospecific attack at C_β by $^tBuN{\equiv}C$ to afford quantitative yields of an adduct $Ru_2(CO)_6[\mu\text{-}\eta^1:\eta^1\text{-}PhC{=}C(CN^tBu)CH_2](\mu\text{-}PPh_2)$ (3), which has been characterized by microanalysis, IR and NMR spectroscopy. Complex **3** is converted into $Ru_2(CO)_6(\mu\text{-}PPh_2)[\mu\text{-}\eta^1:\eta^1\text{-}PhC{=}C\{C(EtNH)N(H)^tBu\}CH_2]$ (4) and $Ru_2(CO)_6(\mu\text{-}PPh_2)[\mu\text{-}\eta^1:\eta^1\text{-}PhC{=}C\{C(EtS)N(H)^tBu\}CH_2]$ (5) by the addition of $EtNH_2$ or EtSH respectively across the $C{\equiv}N$ bond of the 'carbon coordinated' isonitrile. The X-ray structure of **5** has been determined. Crystal data: $C_{34}H_{32}NO_6PRu_2S \cdot 0.5CH_2Cl_2$, monoclinic, space group $P2_1/n$, $a = 11.486(5)$, $b = 14.956(5)$, $c = 21.465(8)$ Å, $\beta = 101.82(2)°$, $Z = 4$, $R = 0.032$, $R_w = 0.041$. The nature of the amidinium and thioamidinium centres in **4** and **5** and the formation of the C–C, C–N and C–S bonds in **1** to form **3**, **4** and **5** are discussed.

Key words: Ruthenium; Allene; Metallacycle; Crystal structure; Bridging ligand

1. Introduction

Although the reactivity of C_1 and C_2 hydrocarbyl ligands bridging two or more metal centres has been extensively explored over the past two decades [1], the chemistry of polynuclear transition metal complexes containing C_3 ligands such as μ-allenyls (propadienyls) [2] or μ-allenylidenes (propadienylidenes) has received much less attention. These C_3 hydrocarbyls, like allene ($CH_2{=}C{=}CH_2$), have cumulated double bonds and are of interest because they offer a variety of bonding modes, multiple sites of attack and the potential for electronic communication along the unsaturated chain. Allenyl ligands ($R^1C{=}C{=}CR^2R^3$) are isomeric with the well known and synthetically useful allyls $\{R^1CC(R^2)C(R^3)\}$. Finally, the parent allenyl group ($HC{=}C{=}CH_2$) is formally constituted from three C_1 fragments, carbide

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(C), methylidyne (CH) and methylene (CH_2), all of which have been extensively investigated as ligands in organometallic chemistry and intermediates in catalysis.

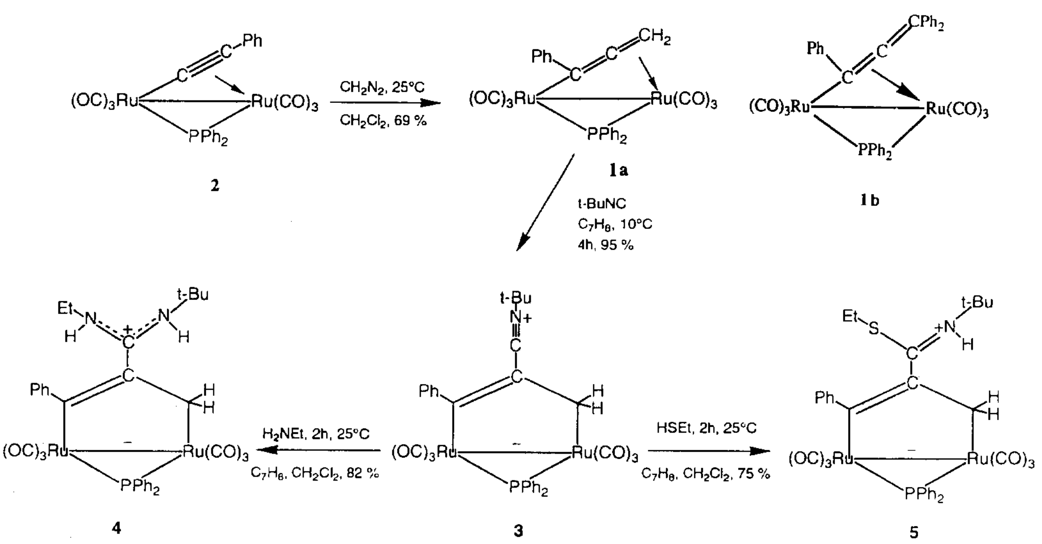
Our initial investigations of polynuclear allenyl complexes centred on the preparation of a series of binuclear allenyl complexes $Ru_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}\eta^1:\eta^2\text{-}PhC{=}C{=}CR_2)$ (**1**) (R = H, **1a**; R = Ph, **1b**; R = Me, **1c**) via addition of CR_2 (from CR_2N_2) to C_α of the acetylide ligand in $Ru_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}\eta^1:\eta^2\text{-}C{\equiv}CPh)$ **2** [3]. The triphenylallenyl complex **1b** has a $\mu\text{-}\eta^1:\eta^2$-allenyl ligand bound to one ruthenium atom via C_α and to the second metal atom via an η^2-interaction with the $C_\alpha{=}C_\beta$ double bond, C_γ being uncoordinated. In a recent communication, we briefly described the generation of five membered dimetallacyclopentanes and cyclopentenes via regiospecific attack at C_β of **1a** by neutral phosphorus, nitrogen and carbon nucleophiles [4]. These reactions provide a simple, attractive and high yield route to classes of dimetallacycles previously represented by only a few examples.

Although we originally assumed that **1a** had a structure similar to that proven by X-ray crystallography for **1b**, the accumulation of ^{13}C NMR data for a range of other allenyl complexes and the observation of an unusually high field shift for C_γ in **1a** [5], led us to carry out an X-ray determination [4b] which revealed the isomeric structure with $C_\beta{=}C_\gamma$ attached to Ru(2) as illustrated in Scheme 1.

The carbon atom C_β of **1a** is unusually activated towards nucleophilic attack and in this paper we describe the addition of the carbon nucleophile $^tBuN{\equiv}C$ at C_β in a process which generates directly a carbon–carbon bond to give $Ru_2(CO)_6(\mu\text{-}PPh_2)[\mu\text{-}\eta^1:\eta^1\text{-}PhC{=}C(CN^tBu)CH_2]$ (**3**). The sensitivity of the $\mu\text{-}\eta^1:\eta^2$-allenyl ligand to nucleophiles resembles the reactivity of the $\mu\text{-}\eta^1:\eta^2$-acetylides $M_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}\eta^1:\eta^2\text{-}C{\equiv}CPh)$ (M = Fe, Ru, Os) whose chemistry has been well exploited [6]. Reaction of the isonitrile adduct **3** with H_2NEt and HSEt leads to functionalization of the carbon bound isonitrile multiple bond leading to amidinium- or thioamidinium-dimetallacyclopentene complexes $Ru_2(CO)_6(\mu\text{-}PPh_2)[\mu\text{-}\eta^1:\eta^1\text{-}PhC{=}C\{C(EtNH)(NH^tBu)\}CH_2]$ (**4**) and $Ru_2(CO)_6(\mu\text{-}PPh_2)[\mu\text{-}\eta^1:\eta^1\text{-}PhC{=}C\{C(EtS)N(H)^tBu\}CH_2]$ (**5**). The synthetic route to **3** and the reactions leading to **4** and **5** are shown in Scheme 1. The structure of **5** determined by X-ray diffraction is described and compared to that of **4**. There are structural similarities between the amidinium and thioamidinium substituents in **4** and **5** and those generated via nucleophilic attack on the diosmium acetylide $Os_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}\eta^1:\eta^2\text{-}C{\equiv}CPh)$ [7].

2. Results and discussion

The binuclear allenyl complex $Ru_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}\eta^1:\eta^2\text{-}PhC{=}C{=}CH_2)$ (**1a**) reacts with t-butyl isocyanide at 5–10°C in toluene affording quantitative yields of the adduct $Ru_2(CO)_6(\mu\text{-}PPh_2)[\mu\text{-}\eta^1:\eta^1\text{-}PhC{=}C(CN^tBu)CH_2]$ (**3**). Monitoring of this reaction by $^{31}P\{^1H\}$ NMR at 10°C showed the disappearance of the resonance at 141 ppm due to **1a** and the growth of a single product peak at 180.7 ppm confirmed to be



Scheme 1.

due to **3** by NMR measurements of a crystalline sample. **3** is therefore formed from **1a** in a single step process without detectable intermediates.

The zwitterionic dimetallacyclopentene structure of **3** was assigned on the following basis: (i) an IR ν(CO) spectrum with five medium-strong bands in the range 2056–1943 cm^{-1}, 22–39 cm^{-1} lower than in the parent allenyl complex **1a** and indicative of greater electronic charge delocalization onto the $Ru(CO)_3$ fragments; (ii) three distinct ^{13}C NMR resonances for C_α, C_β and C_γ of the Ru_2C_3 metallacycle (*vide infra*) and six separate ^{13}CO resonances; (iii) a ^{31}P NMR chemical shift consistent with a μ-PPh_2 group across a strong Ru–Ru bond [8]; (iv) stoichiometric conversion of **3** to **4** with $EtNH_2$ and **5** with EtSH, both of which have been characterized by X-ray diffraction.

The most significant features of the synthesis of **3** from **1a** are the specificity for nucleophilic attack at C_β of the μ-$\eta^1:\eta^2$-allenyl group and the preference over displacement of a carbonyl group, for addition at an unsaturated carbon atom. Indeed, competing CO displacement reactions can be effectively eliminated by operating at 10°C. The driving force for the conversion of **1a** to **3** is the formation of a strong C_β-C(CN^{t}Bu) bond, and the insolubility of the dipolar adducts in hydrocarbon solvents.

At first sight, the results of this study appeared surprising. Based on previous work, we anticipated nucleophilic addition to **1** at the γ-carbon atom producing zwitterionic μ-alkyne adducts $Ru_2(CO)_6(\mu$-$PPh_2)\{\mu$-$\eta^1:\eta^1$-PhC=C=CH$_2$(Nu)\} in accordance with the reactivities reported for $HOs_3(CO)_9(\mu_3$-$\eta^1:\eta^2:\eta^2$-H_2C=C=CMe) [9] and the cationic dimer $[(C_5H_4Me)_2Mo_2(CO)_4(\mu$-$\eta^2:\eta^3$-HC=C=CH$_2)]^+$ [10] both of which gave γ-adducts. However, $Ru_3(CO)_8(\mu$-$PPh_2)(\mu$-$\eta^1:\eta^2:\eta^2$-CH$_2$=C=C^{i}Pr) reacts with phosphites at a metal centre [11] suggesting that the behaviour of allenyl bridged bi- and polynuclear systems towards nucleophiles may be sensitive to steric and/or electronic effects induced by the substituents on the organic fragment, the CO-ligands, the metal and the attacking reagent. Many μ_2-$\eta^2:\eta^3$ and μ_3-$\eta^1:\eta^2:\eta^3$-allenyl compounds appear to be unreactive towards nucleophiles under mild conditions [1a,12].

Recent results on mononuclear allenyl complexes lend some support to the hypothesis of preferential nucleophilic attack at C_β. Thus, *trans*-Pt(CH=C=CH$_2$)(Br)(PPh$_3$)$_2$ reacts with amines NHRR′ at C_β affording η^3-azatrimethylenemethane $[Pt(PPh_3)_2\{CH_2C(NRR')CH_2\}]^+$ complexes and with hydrazine to give the platinum pyrazoline compound $[Pt(PPh_3)_2\{CH_2C(Me)NNH_2\}]^+$ [2d]. For $(\eta^5$-$C_5H_5)W(CO)_3$CH=C=CH$_2$, excess methylamine produces the azatungstacyclobutane $(\eta^5$-$C_5H_5)W(CO)_2$CH(CONHMe)CHMe(NHMe) via addition at C_β and at a carbonyl carbon atom [13]. Casey and Yi [2b] have demonstrated that the η^3-propargyl ligand in cationic $[(\eta^5$-$C_5Me_5)Re(CO)(\eta^3$-CH$_2$C≡CH)$]^+$ undergoes nucleophilic attack at C_β by phosphines, acetylide anions and malonate anions to form rhenacyclobutene derivatives. Unfortunately, there is as yet no unifying model to account for all these experimental observations.

Treatment of **3** with excess $EtNH_2$ dried over anhydrous $MgSO_4$ gave, after crystallization, the yellow adduct $Ru_2(CO)_6(\mu$-$PPh_2)[\mu$-$\eta^1:\eta^1$-PhC=C\{C(EtNH)N(H)^{t}Bu\}CH$_2$] (**4**) (82.5%). A similar reaction of **3** with EtSH afforded 77.5% of $Ru_2(CO)_6(\mu$-$PPh_2)[\mu$-$\eta^1:\eta^1$-PhC=C\{C(EtS)N(H)^{t}Bu\}CH$_2$] (**5**). The structure of **4** [3] and **5** have been confirmed by X-ray diffraction to be the amidinium and thioamidinium dimetallacyclopentenes illustrated in Scheme 1.

Spectroscopically **4** and **5** have ν(CO) IR spectra similar to that of **3** but with ν(CO) frequencies 6–12 cm^{-1} lower in frequency and ^{31}P NMR shifts ($\delta(^{31}P)$ **4** and **5** 182.5 ppm) downfield of **1** indicating longer Ru–Ru bonds and larger Ru–P–Ru angles [8] than in **1**, in accordance with the X-ray data.

The room temperature $^{13}C\{^1H\}$ NMR spectra of **4** and **5** show static structures on the NMR timescale with six different ^{13}CO resonances assigned to CO

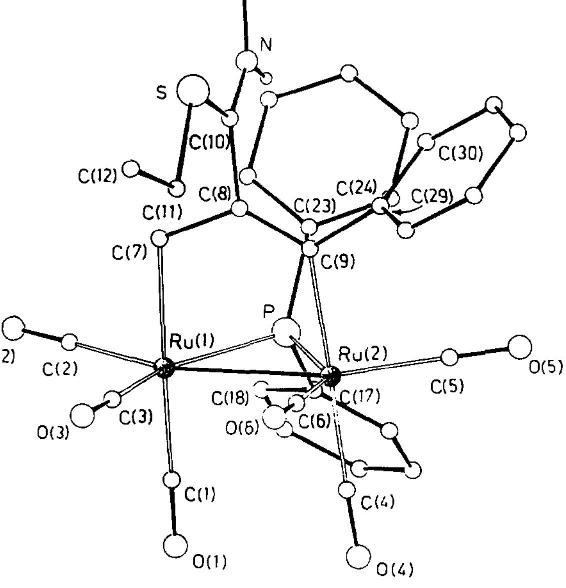
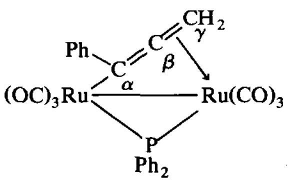


Fig. 1. View of the molecular structure of $Ru_2(CO)_6(\mu$-$PPh_2)[\mu$-$\eta^1:\eta^1$-PhC=C\{C(EtS)N(H)^{t}Bu\}CH$_2$] (**5**) together with the atomic numbering scheme.

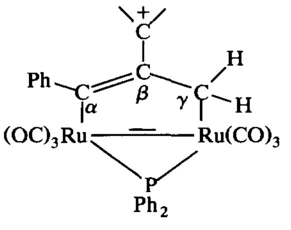
groups *trans* to the μ-PPh$_2$ bridge (*e.g.*, **4** $\delta = 211.2$(d), 211.0(d); $^2J_{P-C} = 54.0$, 57.0 Hz), *trans* to the Ru–Ru bond (**4** $\delta = 200.3$(s), 198.2(s)) and *cis* to the μ-PPh$_2$ bridge (**4** $\delta = 198.6$(d), 197.9(d), $^2J_{P-C} = 9.1$, 8.7 Hz) on the basis of an analysis of the dependence of $^2J_{P-C}$ on the magnitude of the geminal C–M–P bond angle [14]. The ^{13}C NMR resonances of C_α ($\delta = 164.5$(d), $^2J_{P-C} = 10.0$ Hz), C_β ($\delta = 155.8$(s)) and C_γ ($\delta = 8.8$(d), $^2J_{P-C} = 8.7$ Hz) and C_{NCN} ($\delta = 169.3$(s)) in **4** were assigned from ^{1}H coupled spectra, quadrupolar broadening and comparison with related dipolar complexes [4].

Table 1 compares ^{13}C NMR shifts and J_{P-C} coupling constants for the parent complex **1a**, the ^{t}BuN≡C adduct **3** and the amidinium and thioamidinium zwitterions **4** and **5**. In **1a**, C_γ, the CH_2 carbon, ($\delta = 29.4$ ppm) is highly shielded as a result of coordination to Ru(2). Upon formation of zwitterions **3–5**, this methylene carbon atom becomes the sp^3 carbon of the Ru$_2$C$_3$ metallacycle and is readily identified as a high field doublet at 5.0–11.3 ppm with a $^2J_{P-C}$ coupling of ≈ 9 Hz. The central carbon C_β of **1a** is dramatically deshielded upon formation of the metallacycle presumably because of the proximity of the positive charge on the adjacent carbon of the added nucleophile. Carbon atom C_α in **1a** regains its sp^2 character in the conversion of **1a** to the metallacycles **3–5**. In two instances (**3** and **4**), C_α exhibits coupling to the phosphido bridge. The sp^2 carbon atoms C_{NCN} or C_{NCS} of the amidinium or thioamidinium groups are, as expected, deshielded by the formal charge on these groups.

TABLE 1. A comparison of ^{13}C{^{1}H} NMR resonances and ^{13}C–^{31}P coupling constants for **1a** and the zwitterions (coupling in Hz)



1a



3–5

Complex	δ (J) ^{a}			
	C_α	C_β	C_γ	$C_{NCN(S)}$
1a	137.8	99.4	0.29	–
3	112.9 (18.9)	184.2	5.0 (8.5)	–
4	164.5 (10.0)	155.8	8.8 (8.7)	169.3
5	125.6	199.6	11.3 (8.9)	155.3

[a] (^{13}C) ppm; J(^{13}C–^{31}P) (Hz)

TABLE 2. Important bond distances (Å) and angles (°) with esd's in parentheses for complex **5**

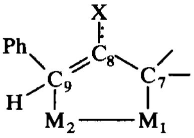
Ru(1)–Ru(2)	2.841(1)	O(2)–C(2)	1.134(7)
Ru(1)–P	2.320(1)	O(3)–C(3)	1.128(8)
Ru(1)–C(1)	1.922(5)	O(4)–C(4)	1.137(6)
Ru(1)–C(2)	1.889(6)	O(5)–C(5)	1.136(7)
Ru(1)–C(3)	1.923(6)	O(6)–C(6)	1.138(8)
Ru(1)–C(7)	2.199(5)	N–C(10)	1.293(7)
Ru(2)–P	2.324(1)	N–C(13)	1.508(6)
Ru(2)–C(4)	1.920(5)	C(7)–C(8)	1.509(6)
Ru(2)–C(5)	1.905(6)	C(8)–C(9)	1.323(6)
Ru(2)–C(6)	1.910(6)	C(8)–C(10)	1.499(6)
Ru(2)–C(9)	2.159(4)	C(9)–C(29)	1.497(6)
S–C(10)	1.718(5)	C(11)–C(12)	1.493(9)
S–C(11)	1.807(7)	C(13)–C(14)	1.519(8)
P–C(17)	1.824(5)	C(13)–C(15)	1.531(8)
P–C(23)	1.828(5)	C(13)–C(16)	1.508(8)
O(1)–C(1)	1.141(7)		
C(3)–Ru(1)–C(7)	86.6(2)	Ru(2)–P–C(23)	120.5(2)
C(2)–Ru(1)–C(7)	87.8(2)	Ru(2)–P–C(17)	120.9(2)
C(2)–Ru(1)–C(3)	102.0(2)	Ru(1)–P–C(23)	124.4(2)
C(1)–Ru(1)–C(3)	95.2(3)	Ru(1)–P–C(17)	119.0(2)
C(1)–Ru(1)–C(2)	92.6(2)	C(17)–P–C(23)	98.1(2)
P–Ru(1)–C(7)	87.4(1)	C(10)–N–C(13)	131.8(4)
P–Ru(1)–C(3)	147.4(2)	Ru(1)–C(1)–O(1)	179.6(5)
P–Ru(1)–C(2)	109.8(2)	Ru(1)–C(2)–O(2)	178.1(6)
P–Ru(1)–C(1)	90.7(2)	Ru(1)–C(3)–O(3)	177.7(6)
Ru(2)–Ru(1)–C(7)	87.2(1)	Ru(2)–C(4)–O(4)	177.7(5)
Ru(2)–Ru(1)–C(3)	95.3(2)	Ru(2)–C(5)–O(5)	178.7(5)
Ru(2)–Ru(1)–C(2)	161.6(2)	Ru(2)–C(6)–O(6)	177.9(5)
Ru(2)–Ru(1)–C(1)	91.8(2)	Ru(1)–C(7)–C(8)	115.5(3)
Ru(2)–Ru(1)–P	52.4(1)	C(7)–C(8)–C(10)	110.8(4)
Ru(1)–Ru(2)–C(9)	85.3(1)	C(7)–C(8)–C(9)	128.9(4)
Ru(1)–Ru(2)–C(6)	93.1(2)	C(9)–C(8)–C(10)	120.4(4)
Ru(1)–Ru(2)–C(5)	157.8(2)	Ru(2)–C(9)–C(8)	123.1(4)
Ru(1)–Ru(2)–C(4)	93.7(2)	C(8)–C(9)–C(29)	120.0(4)
Ru(1)–Ru(2)–P	52.2(1)	Ru(2)–C(9)–C(29)	116.9(3)
C(6)–Ru(2)–C(9)	84.5(2)	N–C(10)–C(8)	118.2(4)
C(5)–Ru(2)–C(9)	89.6(2)	S–C(10)–C(8)	121.4(4)
C(5)–Ru(2)–C(6)	107.9(2)	S–C(10)–N	120.4(4)
C(4)–Ru(2)–C(6)	95.0(3)	S–C(11)–C(12)	107.0(5)
C(4)–Ru(2)–C(5)	91.6(2)	N–C(13)–C(16)	109.3(4)
P–Ru(2)–C(9)	86.1(1)	N–C(13)–C(15)	109.8(4)
P–Ru(2)–C(6)	144.8(2)	N–C(13)–C(14)	105.3(4)
P–Ru(2)–C(5)	105.9(2)	C(15)–C(13)–C(16)	112.5(5)
P–Ru(2)–C(4)	93.8(2)	C(14)–C(13)–C(16)	110.1(4)
C(10)–S–C(11)	105.2(3)	C(14)–C(13)–C(15)	109.6(4)
Ru(1)–P–Ru(2)	75.4(1)		

2.1. Description of the structure of $Ru_2(CO)_6(\mu$-$PPh_2)$-$[\mu$-$\eta^1:\eta^1$-$PhC{=}C\{C(EtS)N(H)^tBu\}CH_2]$ *(5)*

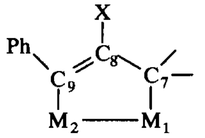
The structure of complex **5** is depicted in Fig. 1 together with the atomic numbering system. Selected bond distances and angles are given in Table 2. In **5**, the two ruthenium atoms, linked by a short Ru–Ru bond of 2.841(1) Å, are symmetrically bridged by a phosphido group [Ru(1)–P = 2.320(1) Å, Ru(2)–P = 2.324(1) Å, Ru(1)–P–Ru(2) = 75.4(1)°]. Three terminal carbonyl groups are bound to each Ru atom.

TABLE 3. Comparison of relevant distances and angles in dimetallacycles for complexes **6**, **7**, **4**, **5**, **8** and **9**

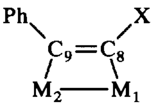
Distances (Å) and angles (°)	**6** [4a]	**7** [4a]	**4**	**5**	**8** [7b]	**9** [7c]
M_1–M_2	2.872(1)	2.851(1)	2.869(1)	2.841(1)	2.829(1)	2.813(3)
M_2–C_9	2.239(8)	2.204(3)	2.197(3)	2.159(4)	2.15(1)	2.15(2)
M_1–C_8	–	–	–	–	2.162(9)	2.17(2)
M_1–C_7	2.255(8)	2.169(3)	2.154(3)	2.199(5)	–	–
C_9–C_8	1.447(12)	1.510(5)	1.505(5)	1.323(6)	1.37(1)	1.28(2)
C_8–C_7	1.441(13)	1.336(4)	1.342(4)	1.509(6)	–	–
C_9–C_8–C_7	120.0(8)	127.7(3)	128.6(3)	128.9(4)	–	–
C_8–C_9–M_2	106.1(6)	115.9(2)	116.1(2)	123.1(4)	108.3(7)	107.1(1)
C_8–C_7–M_1	101.1(5)	121.9(2)	123.2(2)	115.5(3)	–	–
C_8–C_9–M_1	–	–	–	–	111.3(7)	114(1)
M_2–M_1–C_8	–	–	–	–	69.2(3)	67.3(5)
M_1–M_2–C_9	84.6(2)	86.1(1)	85.9(1)	85.3(1)	71.2(3)	71.1(5)
M_2–M_1–C_7	85.6(2)	85.9(1)	86.1(1)	87.2(1)	–	–
C_8–X	1.314(11)	1.808(3)	1.501(4)	1.499(6)	1.47(2)	1.48(3)
C_9–C_8–X	118.6(8)	121.2(2)	118.7(3)	120.4(4)	125.1(9)	129(2)
C_7–C_8–X	121.4(9)	111.1(2)	112.6(2)	110.8(4)	–	–



$M_1 = M_2 = Ru$
X = NEtH [a] **6**



$M_1 = M_2 = Ru$
X = PCy_2H **7**
X = C(EtNH)(NH^tBu) **4**
X = C(EtS)(NH^tBu) **5**



$M_1 = M_2 = Os$
X = C(^tBuNH)(NEt_2) **8**
X = C(^nBuS)(NH^tBu) **9**

[a] In this complex, hydrogen shift has occurred at C_9[CHPh] and the C_8–C_9 is a single bond.

A substituted propenyl ligand [C(7)–C(8)–C(9)] is bound to Ru(1) and Ru(2) via σ-bonds to the terminal C(7) and C(9) atoms [Ru(1)–C(7) = 2.199(5) and Ru(2)–C(9) 2.159(4) Å], forming a planar diruthenacyclopentene ring. The C(8)–C(9) and C(7)–C(8) bond distances, 1.323(6) and 1.509(6) Å, respectively, are in agreement with localized double and single bonds. The phosphido bridge is almost orthogonal to the five-membered ring, the dihedral angle being 88.6(1)°. In the thioamidinium substituent, the values of the C(10)–S and C(10)–N bond distances, 1.718(5) and 1.293(7) Å, respectively, suggest that multiple bonding is essentially localized in the C–N bond. The C(8)–C(10) bond distance of 1.499(6) Å is typical of a single bond between two sp^2 hybridized carbon atoms. The SC(10)NC(8) moiety is planar and approximately perpendicular to the mean plane passing through the C(7)C(8)C(9)C(10) atoms (the dihedral angle is 88.9(2)°).

Several examples of dimetallacyclic five (M_2C_3) and four (M_2C_2) membered ring systems have recently been structurally characterized [15]. In Table 3, the most significant structural features of the diruthenacyclopentene ring of **5** are compared with those of **4**, the amine and phosphine adducts of **1a**, namely $Ru_2(CO)_6(\mu\text{-}PPh_2)[\mu\text{-}\eta^1:\eta^1\text{-}PhHC\text{-}C(EtNH)CH_2]$ (**6**) and $Ru_2(CO)_6(\mu\text{-}PPh_2)[\mu\text{-}\eta^1:\eta^1\text{-}PhC{=}C(PCy_2H)CH_2]$ (**7**) [4], and with the two diosmacyclobutene rings found in the complexes $Os_2(CO)_6(\mu\text{-}PPh_2)[\mu\text{-}\eta^1:\eta^1\text{-}PhC{=}C\{C(^tBuNH)(NEt_2)\}]$ (**8**) [7b] and $Os_2(CO)_6(\mu\text{-}PPh_2)[\mu\text{-}\eta^1:\eta^1\text{-}PhC{=}C\{C(^nBuS)(NH^tBu)\}]$ (**9**) [7c]. With the exception of **6** where addition of an N–H bond across the allenyl ligand forms a saturated metallocycle with C(7)–C(8) and C(8)–C(9) bonds of comparable length (1.441(13) and 1.447(12) Å), the complexes **4**, **5** and **7** exhibit quite similar structural characteristics. The amidinium and thioamidinium substituents in **4** and **8** as well as the thioamidinium groups in **5** and **9** are closely comparable. This strongly suggests that the electronic influence of the nucleophile or the substituent derived therefrom, on the hydrocarbyl fragment is relatively the same for allenyl and acetylide complexes.

3. Conclusions

We have shown that the transformation of the acetylide **2** to the allenyl ligand in **1a** and the subsequent conversion of **1a** to **3**, **4** and **5** occurs via two successive C–C bond forming steps (at C_α of **2** by "CH_2" and C_β of **1a** by $^tBuN{\equiv}C$) and C–N or C–S bond formation via nucleophilic addition to the carbon bound isonitrile. Such reactions although less well documented than other coupling or insertion reactions of multi-site bound C_1 ligands such as μ-CH_2, μ-CH and μ-C with unsaturated substrates may offer an attractive strategy for C–C and C–X (X = heteroatom) bond generation on clusters. The acetylide itself in **2** undergoes a similar sequence of C–C and C–N or C–S bond syntheses via an isonitrile adduct. Although a rationale for the regiospecificity of nucleophilic attack at C_β in **1a** is not evident from either of the μ_2-$\eta^1:\eta^2$ structures (Scheme 1) since C_β is attached to Ru(2) in both instances, EHMO calculations [16] show that these reactions are favoured by both orbital and charge considerations.

4. Experimental details

All manipulations were carried out in a double manifold using standard Schlenk techniques. Toluene was dried and distilled over $Na^+Ph_2CO^-$ under nitrogen, prior to use. Purification of products was by simple crystallization procedures.

IR spectra were measured on a Nicolet DMS 500 FT instrument using sodium chloride cells of 0.5 mm path length. NMR spectra were recorded on Bruker AM-250 (^1H, 250 MHz; $^{13}C\{^1H\}$ 62.8 MHz; $^{31}P\{^1H\}$ 101.2 MHz) or AC-200 (^1H, 200 MHz; $^{13}C\{^1H\}$ 50.1 MHz; $^{31}P\{^1H\}$ 81.01 MHz) instruments. Chemical shifts are referenced to TMS and 85% H_3PO_4.

4.1. Synthesis of $Ru_2(CO)_6(\mu\text{-}PPh_2)[\mu\text{-}\eta^1:\eta^1\text{-}PhC{=}C(CN^tBu)CH_2]$ (3)

$Ru_2(CO)_6(\mu\text{-}PPh_2)(\mu\text{-}\eta^1:\eta^2\text{-}PhC{=}C{=}CH_2)$ (**1**) (0.18 g, 0.27 mmol) was dissolved in toluene (20 ml); the solution was cooled in an ice/water bath. Two equivalents of ^tBuNC were added (0.061 ml, 0.54 mmol); the temperature was kept between 5 and 10°C. After 0.5 h, a pale yellow precipitate was evident; the reaction was monitored by IR spectroscopy and was halted when complete consumption of the starting material was indicated (approximately 4 h). The solvent and excess ^tBuNC were removed *in vacuo*. The precipitate was washed with hexane and dried *in vacuo*, yielding $Ru_2(CO)_6(\mu\text{-}PPh_2)[\mu\text{-}\eta^1:\eta^1\text{-}PhC{=}C(CN^tBu)CH_2]$ (**3**) (0.19 g, 0.25 mmol, 93.4%). Anal. Calcd. for $C_{32}H_{26}NO_6PRu_2 \cdot 0.33\ C_7H_8$: C, 52.57; H, 3.68. Found: C, 52.82, H, 3.98%. IR (ν(CO), $CHCl_3$): 2056vs, 2020vs, 1989m, 1966m, 1943w cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 81.0 MHz, 298 K); δ 179.2 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 50.3 MHz, 298 K); δ 208.6 (d, CO, $^2J(PC) = 54.4$ Hz), 208.5 (d, CO, $^2J(PC) = 52.6$ Hz), 198.9 (s, CO), 198.3 (d, CO, $^2J(PC) = 9.7$ Hz), 196.7 (d, CO, $^2J(PC) = 9.2$ Hz), 196.6 (s, CO), 184.2 (s, C_β), 157.5–121.7 (m, *C*Ph and *C*N), 112.9 (d, C_α, $^2J(PC) = 18.9$ Hz), 60.1 (s, ^tBuC), 28.8 (s, $^tBu\text{-}CH_3$), 5.0 (d, C_γ, $^2J(PC) = 8.5$ Hz). ^1H NMR ($CDCl_3$, 200.1 MHz, 298 K); δ 7.83–7.04 (m, Ph–*H*), 1.54 (s, $C_\gamma H_2$), 0.99 (s, $^tBuCH_3$).

4.2. Synthesis of $Ru_2(CO)_6(\mu\text{-}PPh_2)[\mu\text{-}\eta^1:\eta^1\text{-}PhC{=}C\{C(EtNH)NH^tBu\}CH_2]$ (4)

$Ru_2(CO)_6(\mu\text{-}PPh_2)[\mu\text{-}\eta^1:\eta^1\text{-}PhC{=}C(CN^tBu)CH_2]$ (**3**) (0.30 g, 0.40 mmol) was dissolved in a mixture of toluene (20 ml) and dichloromethane (10 ml); a hexane extract of a solution consisting of 4 ml hexane and 3 ml 70% aqueous $EtNH_2$ dried over anhydrous $MgSO_4$ was added. After 2 h, when monitoring of the CO bands in the IR spectrum revealed the complete consumption of the starting material, solvent and excess amine were removed *in vacuo*. Dissolution of the residue in a mixture of dichloromethane (5 ml), ethanol (1 ml) and hexane (1 ml), followed by refrigeration at 2°C, resulted in the formation of pale yellow crystals of $Ru_2(CO)_6(\mu\text{-}PPh_2)[\mu\text{-}\eta^1:\eta^1\text{-}PhC{=}C\{C(EtNH)NH^tBu\}CH_2]$ (**4**). The supernatant was removed, the crystals were washed with cold hexane and then dried *in vacuo* (0.26 g, 0.33 mmol, 82.5%). Anal. Calcd. for $C_{34}H_{33}N_2O_6PRu_2$: C, 51.13; H, 4.16; N, 3.51. Found: C, 51.06; H, 4.05; N, 3.44%. IR (ν(CO), $CHCl_3$): 2049vs, 2011vs, 1979s, 1956m, 1931m cm^{-1}. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 81.0 MHz, 298 K): δ 182.5 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 50.3 MHz, 298 K): 211.2 (d, CO, $^2J(PC) = 54.0$ Hz), 211.0 (d, CO, $^2J(PC) = 57.0$ Hz), 200.3 (s, CO), 198.6 (d, CO, $^2J(PC) = 9.1$ Hz), 198.2 (s, CO), 197.9 (d, CO, $^2J(PC) = 8.7$ Hz), 169.3 (s, N–*C*–N), 164.5 (d, C_α, $^2J(PC) = 10.0$ Hz), 155.8 (s, C_β), 146.0–124.2 (m, Ph*C*), 52.8 (s, ^tBuC), 40.9 (s; CH_2CH_3), 28.6 (s, $^tBuCH_3$), 15.1 (s, CH_2CH_3), 8.8 (d, C_γ, $^2J(PC) = 8.7$ Hz). ^1H NMR ($CDCl_2$, 200.1 MHz, 298 K): δ 8.02–6.85 (m, Ph*H*), 4.74 (br, s, *H*NEt), 3.54(br s, HN^tBu), 3.32 (ddq, NCH_2, $^3J(HCH_3) = 7.2$ Hz, $^3J(HNH) = 7.2$ Hz, $^2J(HH) = 12.6$ Hz), 3.10 (ddq, NCH_2, $^3J(HCH_3) = 7.2$ Hz, $^3J(HNH) = 7.2$ Hz, $^2J(HH) = 12.6$ Hz), 1.33 (dd, $C_\gamma H_2$, $^3J(PH) = 4.6$ Hz, $^2J(HH) = 16.5$ Hz), 1.09 (t, NCH_2CH_3, $^3J(HH) = 7.2$ Hz), 0.96 (dd, $C_\gamma H_2$, $^3J(PH) = 5.0$ Hz, $^2J(HH) = 16.5$ Hz), 0.81 (s, $^tBuCH_3$).

4.3. Synthesis of $Ru_2(CO)_6(\mu\text{-}PPh_2)[\mu\text{-}\eta^1:\eta^1\text{-}PhC{=}C\{C(EtS)N(H)^tBu\}CH_2]$ (5)

Complex **5** was synthesized via a procedure identical to that employed for the generation of $Ru_2(CO)_6(\mu\text{-}PPh_2)[\mu\text{-}\eta^1:\eta^1\text{-}PhC{=}C\{C(EtNH)NH^tBu\}CH_2]$, using EtSH in place of $EtNH_2$. From 0.30 g $Ru_2(CO)_6(\mu\text{-}PPh_2)[\mu\text{-}\eta^1:\eta^1\text{-}PhC{=}C(CN^tBu)CH_2]$ **3** there was obtained 0.25 g of the thioamidinium complex (0.31 mmol,

TABLE 4. Crystallographic data for $Ru_2(CO)_6(\mu\text{-}PPh_2)[\mu\text{-}\eta^1:\eta^1\text{-}PhC{=}C\{C(EtS)(NH^tBu)\}CH_2]$ (5)

Formula	$C_{34}H_{32}NO_6PRu_2S \cdot 1/2CH_2Cl_2$
FW	858.27
Crystal system	monoclinic
Space group	$P2_1/n$
a, Å	11.486(5)
b, Å	14.956(5)
c, Å	21.465(8)
β, deg	101.82(2)
V, Å^3	3609(3)
Z	4
μ(Mo Kα), cm^{-1}	10.37
d_{calc}, g cm^{-3}	1.580
R	0.0322
R_w	0.0412

77.5%) **5**. Anal. Calcd. for $C_{34}H_{32}NO_6PRu_2S \cdot 0.5CH_2Cl_2$: C, 48.28; H, 3.86; N, 1.63, P, 3.61, S. 3.74, Found: C, 48.87; H, 4.10; N, 1.69; P, 3.66; S, 3.73%. IR (ν(CO), $CHCl_3$): 2051vs, 2013vs, 1980s, 1959m, 1935w cm^{-1}. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 81.0 MHz, 298 K): δ 182.5 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 50.3 MHz, 298 K): δ 211.3 (d, CO, $^2J(PC) = 53.6$ Hz), 210.7 (d, CO, $^2J(PC) = 57.8$ Hz), 199.8 (s, CO), 199.6 (s, C_β), 198.4 (d, CO, $^2J(PC) = 9.4$ Hz), 197.8 (s, CO), 197.7 (d, CO, $^2J(PC) = 9.2$ Hz), 155.3 (s, NCS), 145.8–124.5 (m, Ph*C*), 126.6 (s, C_α), 58.7 (s, ^{t}Bu*C*), 31.8 (s, $\mathit{C}H_2CH_3$), 27.4 (s, ^{t}Bu$\mathit{C}H_3$), 13.6 (s, $CH_2\mathit{C}H_3$), 11.3 (d, $C_\gamma H_2$, $^2J(PC) = 8.9$ Hz). ^1H NMR (CD_2Cl_2, 200.1 MHz, 298 K): δ 8.27–6.94 (m, Ph*H*), 5.38 (br, s, *H*N^{t}Bu), 3.17 (m, $C\mathit{H}_2CH_3$), 3.00 (m, $C\mathit{H}_2CH_3$), 1.37 (m, $C_\gamma \mathit{H}_2$), 1.32 (t, $CH_2C\mathit{H}_3$, $^3J(HH) = 7.5$ Hz), 0.93 (s, ^{t}Bu$C\mathit{H}_3$).

4.4. X-ray data collection, structure determination and refinement for $Ru_2(CO)_6(\mu\text{-}PPh_2)[\mu\text{-}\eta^1:\eta^1\text{-}PhC{=}C\{C(EtS)(NH^tBu)\}CH_2]$ (5)

A single crystal *ca.* 0.15 × 0.20 × 0.25 mm was selected and used for data collection. The crystallographic data are summarized in Table 4. Unit cell parameters were determined from the θ values of 30 carefully centred reflections, having $10 < \theta < 16°$. Data were collected at room temperature on a Siemens AED diffractometer, using niobium-filtered Mo Kα radiation (λ = 0.71073 Å) and the $\theta/2\theta$ scan type. The reflections were collected with a variable scan speed of 3–12° min^{-1} and a scan width from $(\theta\text{-}0.60)°$ to $(\theta + 0.60 + 0.346\tan\theta)°$. Of 7932 unique reflections, with θ in the range 3–27°, 4463 with $I > 2\sigma(I)$ were used for the analysis. One standard reflection was monitored every 50 measurements; no significant decay was noticed over the time of data collection. The individual profiles were analyzed following Lehmann and Larsen [17]. Intensities were corrected for Lorentz and polarization effects. No correction for absorption was applied. (μ(Mo Kα) = 10.37 cm^{-1}).

The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares first with isotropic thermal parameters and then with

TABLE 5. Atomic coordinates (× 10^4) and isotropic thermal parameters (Å^2 × 10^4) with esd's in parentheses for the non-hydrogen atoms of **5a**

	x	y	z	U
Ru(1)	815(1)	1790(1)	2473(1)	349(1) [a]
Ru(2)	750(1)	−49(1)	2137(1)	320(1) [a]
S	−3003(1)	1498(1)	403(1)	644(6) [a]
P	99(1)	608(1)	2986(1)	320(4) [a]
O(1)	3282(4)	1588(3)	3332(2)	768(18) [a]
O(2)	379(5)	3540(3)	3092(2)	845(21) [a]
O(3)	1705(4)	2427(3)	1304(2)	833(20) [a]
O(4)	3248(4)	−445(3)	2901(2)	712(17) [a]
O(5)	96(5)	−2017(3)	2170(2)	837(21) [a]
O(6)	1537(4)	326(4)	890(2)	813(20) [a]
N	−3601(4)	1117(3)	1487(2)	375(13) [a]
C(1)	2362(5)	1663(4)	3015(3)	487(19) [a]
C(2)	523(5)	2880(4)	2858(3)	496(19) [a]
C(3)	1399(5)	2194(4)	1744(3)	520(20) [a]
C(4)	2318(5)	−282(4)	2625(3)	464(18) [a]
C(5)	333(5)	−1281(4)	2151(3)	487(19) [a]
C(6)	1261(5)	175(4)	1359(3)	500(19) [a]
C(7)	−978(4)	1900(3)	1874(2)	404(16) [a]
C(8)	−1492(4)	1044(3)	1561(2)	353(15) [a]
C(9)	−1001(4)	241(3)	1586(2)	325(14) [a]
C(10)	−2733(4)	1191(3)	1191(2)	377(15) [a]
C(11)	−1559(5)	1527(5)	192(3)	686(25) [a]
C(12)	−1726(7)	1942(5)	−453(3)	922(33) [a]
C(13)	−4926(4)	1234(3)	1268(2)	413(16) [a]
C(14)	−5452(5)	998(4)	1841(3)	540(20) [a]
C(15)	−5393(5)	584(4)	723(3)	597(21) [a]
C(16)	−5193(5)	2196(4)	1082(3)	585(22) [a]
C(17)	813(4)	351(3)	3806(2)	404(16) [a]
C(18)	835(5)	988(4)	4275(3)	594(22) [a]
C(19)	1311(7)	786(6)	4909(3)	802(30) [a]
C(20)	1765(6)	−35(6)	5072(3)	807(29) [a]
C(21)	1774(7)	−664(5)	4607(3)	787(28) [a]
C(22)	1295(6)	−473(4)	3979(3)	596(22) [a]
C(23)	−1448(4)	487(3)	3066(2)	351(15) [a]
C(24)	−1964(5)	−352(4)	3061(2)	484(19) [a]
C(25)	−3101(6)	−450(5)	3167(3)	628(24) [a]
C(26)	−3732(5)	268(5)	3290(3)	655(24) [a]
C(27)	−3248(5)	1103(5)	3307(3)	600(22) [a]
C(28)	−2116(5)	1221(4)	3190(2)	458(18) [a]
C(29)	−1661(4)	−516(3)	1215(2)	361(15) [a]
C(30)	−2655(5)	−904(3)	1389(2)	424(17) [a]
C(31)	−3230(5)	−1626(3)	1056(3)	543(20) [a]
C(32)	−2822(5)	−1985(4)	558(3)	577(21) [a]
C(33)	−1853(6)	−1615(4)	374(3)	609(22) [a]
C(34)	−1290(5)	−888(4)	695(2)	490(18) [a]
Cl(1)	4967(7)	951(5)	5397(4)	1689(26)
Cl(2)	5095(9)	−796(7)	5144(5)	2209(39)
C(35)	4701(30)	116(19)	4666(11)	1755(120)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

anisotropic thermal parameters for all non-hydrogen atoms, excepting those of the solvent molecule. All hydrogen atoms of the complex (excluding the solvent molecule), with the exception of the H(N) hydrogen atom which was clearly located in the final ΔF map and refined, were placed at their geometrically calculated positions (C–H = 1.00 Å) and refined "riding" on the corresponding carbon atoms. The final cycles of refinement were carried out on the basis of 431 variables; after the last cycle, no parameters shifted by more than 0.42 esd. The largest remaining peak in the final difference map was equivalent to about 0.66 e/Å^3. In the final cycle of refinement a weighting scheme, $\omega = K[\sigma^2(F_o) + gF_o{}^2]^{-1}$ was used; at convergence the K and g values were 0.4916 and 0.0034, respectively. The analytical scattering factors, corrected for the real and imaginary parts of anomalous dispersion, were taken from ref. 18. All calculations were carried out on the Cray X-MP/48 computer of the "Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale" (CINECA, Casalecchio Bologna) and on the Gould Powernode 6040 of the "Centro di Studio per la Strutturistica Diffrattometrica" del C.N.R., Parma, using the SHELX-76 and SHELXS-86 systems of crystallographic computer programs [19]. The final atomic coordinates for the non-hydrogen atoms are given in Table 5. The atomic coordinates of the hydrogen atoms are given in Table S1 and the thermal parameters in Table S2 and have been deposited with the Cambridge Crystallographic Data Centre.

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References and notes

1 (a) M.I. Bruce, *Chem. Rev., 91* (1991) 197; (b) M.I. Bruce and A.G. Swincer, *Adv. Organomet. Chem., 22* (1983) 59; (c) W.A. Herrmann, *Adv. Organomet. Chem., 20* (1982) 159; (d) R. Nast, *Coord. Chem. Rev., 47* (1982) 89; (e) J. Holton, M.F. Lappert, R. Pearce and P.I.W. Yarrow, *Chem. Rev., 83* (1983) 135; (f) E. Sappa, A. Tiripicchio and P. Braunstein, *Chem. Rev., 83* (1983) 203; (g) J.E. Hahn, *Prog. Inorg. Chem., 31* (1984) 205; (h) E. Sappa, A. Tiripicchio and P. Braunstein, *Coord. Chem. Rev., 65* (1985) 219; (i) C.P. Casey and J.D. Audett, *Chem. Rev., 86* (1986) 339; (j) R.D. Adams, *Chem. Rev., 89* (1989) 1703.

2 For a selection of recent references on the chemistry of mono and polynuclear allenyl complexes see: (a) A. Wojcicki, *J. Cluster Sci., 4* (1993) 59; (b) P.W. Blosser, J.C. Galluci and A. Wojcicki, *J. Am. Chem. Soc., 115* (1993) 2994; (c) G.H. Young, R.R. Willis, A. Wojcicki, M. Calligaris and P. Faleschini, *Organometallics, 11* (1992) 154; (d) J.T. Cheng, T.M. Huang, M.C. Cheng, Y.C. Lin and Y. Wang, *Organometallics, 11* (1992) 1761; (e) M.C. Cheng, R.S. Keng, Y.C. Lin, Y. Wang, M.C. Cheng, G.H. Lee, *J. Chem. Soc., Chem. Commun.*, (1990) 1138; (f) C.P. Casey and C.S. Yi, *J. Am. Chem. Soc., 114* (1992) 6597; (g) C.P. Casey, T.L. Underiner, P.C. Vosejpka, J.A. Gavney Jr. and P. Kiprof, *J. Am. Chem. Soc., 114* (1992) 10826; (h) M.A. Collins, S.G. Feng, P.A. White and J.L. Templeton, *J. Am. Chem. Soc., 114* (1992) 3771; (i) J. Pu, F.S. Peng, A.M. Arif and J.A. Gladysz, *Organometallics, 11* (1992) 3232; (j) F.J. Feher, M. Green and R.A. Rodrigues, *J. Chem., Soc. Chem. Commun.*, (1987) 1206; (k) A. Meyer, D.J. McCabe and M.D. Curtis, *Organometallics, 6* (1987) 1491; (l) M.E. Welker, *Chem. Rev., 92* (1992) 97; (m) V.V. Krivykh, E.S. Taits, P.V. Petrovski, Yu T. Struchkov and A.I. Yanovskii, *Mendeleev Commun.*, (1991) 103.

3 (a) D. Nucciarone, PhD Dissertation, University of Waterloo, Ontario, Canada, 1986; (b) D. Nucciarone, N.J. Taylor and A.J. Carty, *Organometallics, 5* (1986) 1179.

4 (a) S.M. Breckenridge, N.J. Taylor and A.J. Carty, *Organometallics, 10* (1991) 837; (b) S.M. Breckenridge, J. Corrigan, S. Doherty, P. Pixner, N.J. Taylor and A.J. Carty, unpublished results.

5 A.A. Cherkas, S.M. Breckenridge and A.J. Carty, *Polyhedron, 11* (1992) 1075.

6 (a) Y.S. Wong, H.N. Paik, P.C. Chieh and A.J. Carty, *J. Chem. Soc., Chem. Commun.*, (1975) 309; (b) A.A. Cherkas, L.H. Randall, N.J. Taylor, G.N. Mott, J.E. Yule, J.L. Guinamant and A.J. Carty, *Organometallics, 9* (1990) 1677; (c) A.J. Carty, N.J. Taylor, H.N. Paik, W. Smith and J.G. Yule, *J. Chem. Soc., Chem. Commun.*, (1976) 41; (d) A.J. Carty, G.N. Mott, N.J. Taylor and J.E. Yule, *J. Am. Chem. Soc., 100* (1978) 3051; (e) A.J. Carty, G.N. Mott, N.J. Taylor, G. Ferguson, M.A. Khan and P.J. Roberts, *J. Organomet. Chem., 149* (1978) 345; (f) A.J. Carty, N.J. Taylor, W.F. Smith, M.F. Lappert and P.L. Pye, *J. Chem. Soc., Chem. Commun.*, (1978) 1017; (g) G.N. Mott and A.J. Carty, *Inorg. Chem., 22* (1983) 2726; (h) A.A. Cherkas, G.N. Mott, R. Granby, S.A. McLaughlin, J.E. Yule, N.J. Taylor and A.J. Carty, *Organometallics, 7* (1988) 1115; (i) A.A. Cherkas, PhD Dissertation, University of Waterloo, Ontario, Canada, 1989.

7 (a) A.J. Carty, G.N. Mott and N.J. Taylor, *J. Organomet. Chem., 212* (1981) C54; (b) A.A. Cherkas, N. Hadj-Bagheri, A.J. Carty, E. Sappa, M.A. Pellinghelli and A. Tiripicchio, *Organometallics, 9* (1990) 1887; (c) A.A. Cherkas, A.J. Carty, E. Sappa, M.A. Pellinghelli and A. Tiripicchio, *Inorg. Chem., 26* (1987) 3201.

8 (a) A.J. Carty, *Adv. Chem. Ser., 196* (1982) 163; (b) S.A. MacLaughlin, D. Nucciarone and A.J. Carty, in J.G. Verkade and L.D. Quinn (eds.), *Phosphorus-31 NMR Spectroscopy in Spectrochemical Analysis: Organic Compounds and Metal Complexes*, Ch. 16, VCH Publishers, New York, 1987.

9 K. Henrick, M. McPartlin, A.J. Deeming, S. Hasso and P. Manning, *J. Chem. Soc., Dalton Trans.*, (1982) 899.

10 A. Meyer, D.J. McCabe and M.D. Curtis, *Organometallics, 6* (1987) 1491.

11 D. Nucciarone, N.J. Taylor and A.J. Carty, *Organometallics, 7* (1988) 127.

12 (a) G.H. Young, M.V. Raphael, A. Wojcicki, M. Calligaris, G. Nardin and N. Bresciani-Pahor, *Organometallics, 10* (1991) 1934; (b) A. Wojcicki and C.E. Shuchart, *Coord. Chem. Rev., 105* (1990) 35.

13 T.W. Tseng, I.Y. Wu, Y.C. Lin, C.T. Chen, M.C. Chen, Y.J. Tsai, M.C. Chen and Y. Wang, *Organometallics, 10* (1991) 43.

14 L.H. Randall, A.A. Cherkas and A.J. Carty, *Organometallics, 8* (1989) 568.

15 (a) A.F. Dyke, S.A.R. Knox, P.J. Naish and G.E. Taylor, *J. Chem. Soc., Chem. Commun.*, (1980) 409; (b) A.F. Dyke, S.A.R. Knox, P.J. Naish and G.E. Taylor, *J. Chem. Soc., Dalton Trans.*, (1982) 1297; (c) K.H. Theopold and R.G. Bergman, *Organometallics, 1* (1982) 1571; (d) R.S. Dickson, B.M. Gatehouse, M.D. Nesbit and G.N. Pain, *J. Organomet. Chem., 215* (1981) 97; (e) M.R. Burke, J. Takats, F.W. Grevels and J.G.A. Reuvers, *J. Am. Chem. Soc., 105* (1983) 4092; (f) J. Takats, *Polyhedron, 7* (1988) 931; (g) N.M. Doherty, M.J. Fildes, N.J. Forrow, S.A.R. Knox, K.A. Macpherson and A.G. Orpen, *J. Chem. Soc., Chem. Commun.*, (1986) 1355. See also: (h) D. Seyferth, J.B. Hoke and D.R. Wheeler, *J. Organomet. Chem., 341* (1988) 421; (i) A.J. Carty, G.N. Mott and N.J. Taylor, *J. Organomet. Chem., 182* (1979) C69; (j) K.M. Motyl, J.R. Norton, C.K. Schauer and O.P. Anderson, *J. Am. Chem. Soc., 104* (1982) 7325; (k) M.J. Burn, G.Y. Kiel, F. Seils, J. Takats and J. Washington, *J. Am. Chem. Soc., 111* (1989) 6850.

16 S.M. Breckenridge, *PhD Dissertation*, University of Waterloo, Ontario, Canada, 1992.

17 M.S. Lehmann and F.K. Larsen, *Acta Crystallogr., Sect. A, 30* (1974) 580.

18 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, UK, 1974; Vol IV.

19 G.M. Sheldrick, SHELX-76 Program for crystal structure determination, University of Cambridge, UK, 1976; SHELXS-86 Program for the solution of crystal structures, University of Göttingen, Germany, 1986.