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ScienceDirect
Journal of Organometallic Chemistry 693 (2008) 1759–1770
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Chromium, iron, ruthenium and gold complexes of 3,3-(biphenyl-2,2′-diyl)-1-diphenylphosphino-1-phenylallene: A versatile ligand

Emilie V. Banide [a], John P. Grealis [a], Helge Müller-Bunz [a], Yannick Ortin [a], Michael Casey [a], Claudio Mendicute-Fierro [b], M. Cristina Lagunas [b,*], Michael J. McGlinchey [a,*]

[a] School of Chemistry and Chemical Biology, University College Dublin, Belfield, Dublin 4, Ireland
[b] School of Chemistry and Chemical Engineering, Queen's University Belfast, Belfast BT9 5AG, U.K.

Received 4 November 2007; received in revised form 5 January 2008; accepted 6 January 2008
Available online 7 February 2008

Abstract

Successive treatment of 9-(phenylethynyl)fluoren-9-ol (**1a**), with HBr, butyllithium and chlorodiphenylphosphine furnishes 3,3-(biphenyl-2,2′-diyl)-1-diphenylphosphino-1-phenylallene (**5**). Moreover, reaction of **1a** directly with chlorodiphenylphosphine yields the corresponding allenylphosphine oxide (**6**). The allenylphosphine (**5**), and $Fe_2(CO)_9$ initially form the phosphine–$Fe(CO)_4$ complex, **11**, which is very thermally sensitive and readily loses a carbonyl ligand. In the resulting phosphine–$Fe(CO)_3$ system, **12**, the additional site at iron is coordinated by the allene double bond adjacent to phosphorus; the $Fe(CO)_3$ tripod in **12** exhibits restricted rotation on the NMR timescale even at room temperature. The corresponding chromium complex, (**5**)-$Cr(CO)_5$ (**9**), has also been prepared. The gold complexes (**5**)-AuCl (**13**), and [(**5**)-Au(THT)]$^+$ X^-, where (THT) is tetrahydrothiophene, and X = PF_6 (**14a**), or ClO_4 (**14b**), are analogous to the known triphenylphosphine–gold complexes. In contrast, in the (arene)(allenylphosphine)$RuCl_2$ system the allene double bond adjacent to phosphorus displaces a chloride, and the resulting cationic species undergoes nucleophilic attack by water yielding ultimately a five-membered Ru–P–C═C–O ruthenacycle (**17**). Thus, the allenylphosphine (**5**), reacts initially as a conventional mono-phosphine but, when the metal centre has a readily displaceable ligand such as a carbonyl or halide, the allene double bond adjacent to the phosphorus can also function as a donor. X-ray crystal structures are reported for **5**, **6**, **11**, **12**, **13**, **14a**, **14b** and **17**.

Keywords: Allenyl-phosphines; Iron carbonyls; Ruthenium chloride; Gold

1. Introduction

In continuation of our studies on the syntheses and dimerizations of fluorenylidene-derived allenes to form bis-alkylidenecyclobutanes, and ultimately tetracenes [1–3], we wished to incorporate substituents containing other main group elements, in particular phosphorus, silicon and halogens. Since many tetracenes are known to be electroluminescent [4], it was hoped that the introduction of a wider range of functional groups into the precursor allenes would allow greater control of their luminescent and other photophysical or electro-conductive properties. We here report the synthesis and characterization of 3,3-(biphenyl-2,2′-diyl)-1-bromo-1-phenylallene (**2a**), and its conversion to the novel ligand 3,3-(biphenyl-2,2′-diyl)-1-diphenylphosphino-1-phenylallene (**5**); the corresponding phosphine oxide (**6**), has also been prepared. Furthermore, the reactions of the allenylphosphine (**5**) with chromium and iron carbonyls, and also with gold and ruthenium chlorides, are described.

* Corresponding authors. Tel.: +353 1 716 2880; fax: +353 1 716 1178.
E-mail addresses: c.lagunas@qub.ac.uk (M. Cristina Lagunas), michael.mcglinchey@ucd.ie (M.J. McGlinchey).

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doi:10.1016/j.jorganchem.2008.01.046

2. Results and discussion

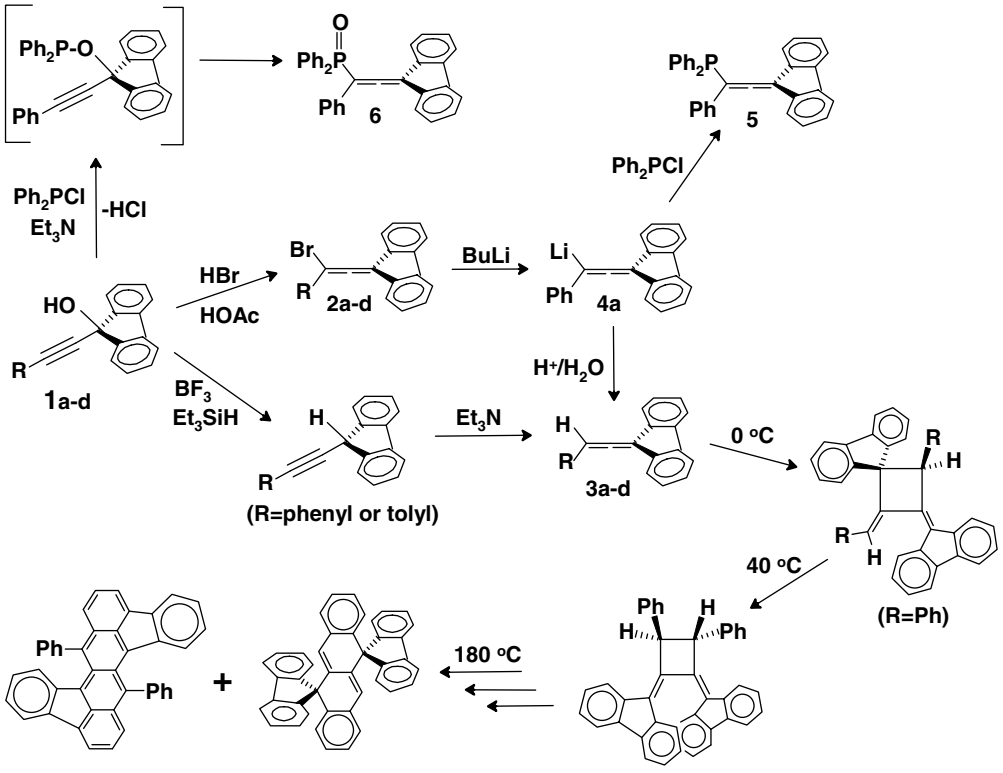
The reaction of fluorenone with lithio-alkynes yields, after hydrolysis, the corresponding 9-alkynyl-fluoren-9-ols, where R = phenyl (**1a**), *p*-tolyl (**1b**), *p*-methoxyphenyl (**1c**), or trimethylsilyl (**1d**). A general method for the conversion of an alkynol into the corresponding alkyne involves treatment with BF_3 and triethylsilane [5]. Presumably, the reaction proceeds via coordination of the hydroxyl group to boron, transfer of fluoride from boron to silicon, and delivery of a hydride from silicon to carbon, possibly in a six-membered transition state. As shown in Scheme 1, subsequent reaction with triethylamine brings about efficient isomerization from alkynes to allenes [6], dimerization via a series of 1,2-dialkenylidene-cyclobutanes and, finally, formation of two families of tetracenes [3].

However, this procedure for the conversion of alkynols into alkynes fails when the R group possesses a substituent with a lone pair to which the BF_3 can coordinate, e.g. the methoxy group in **1c**; likewise, this route is inapplicable for **1d** since the trimethylsilyl substituent is susceptible to attack by fluoride. Consequently, we chose to treat the alkynols, **1a**–**d**, with HBr to generate bromoallenes, **2a**–**d**; conversion to the corresponding Grignard or organolithium reagent and subsequent hydrolysis yielded the required allenes, **3a**–**d**, directly. The formation and dimerization of a range of silyl- and halo-allenes has been described elsewhere [7]. However, the ready accessibility of 3,3-(biphenyl-2,2′-diyl)-1-lithio-1-phenylallene (**4a**) prompted the investigation of its reaction with a chlorophosphine with a view to obtaining a novel ligand possessing several potential coordination sites.

When the bromoallene (**2a**) was treated successively with *n*-butyllithium and chlorodiphenylphosphine, the novel ligand 3,3-(biphenyl-2,2′-diyl)-1-diphenylphosphino-1-phenylallene (**5**), was isolated in 84% yield after chromatographic separation; this allene does not dimerize. Interestingly, when initially isolated as an oil, the product **5** is purple, but after recrystallization from dichloromethane/pentane it was obtained as pale yellow X-ray quality crystals. The structure (Fig. 1) reveals that the allene double bonds in **5** are not significantly different [C(9)=C(10) 1.312(3) Å; C(10)=C(11) 1.309(3) Å], and the allenyl-carbon–phosphorus distance is 1.853(3) Å. This contrasts with the situation in the precursor bromoallene (**2a**), in which the C(9)=C(10) bond [1.321(3) Å] is significantly longer than the C(10)=C(11) bond [1.292(3) Å] [7].

Previously synthesized phosphinoallenes include $H_2C{=}C{=}CH{-}P(Ar)X$, where X = Cl or NEt_2 [8], $H_2C{=}C(Me){-}P(Ar)R$, where R = H, Cl, Me, TMS [9], and $PhCH{=}C{=}C(Ph){-}PPh_2$ [10]. The phosphonium-allene $[Ph_2C{=}C{=}CH\text{-}P(cyclohexyl)_3]^+$ [11], the bis(phosphonium)allenes $[Ph_3P{-}CR{=}C{=}CR{-}PPh_3]^{2+}$, where $R = NMe_2$ or H [12,13], and a diphosphaisobenzene [14], have also been reported.

By analogy to previously reported syntheses of phosphinoyl allenes [15], we have also prepared the phosphine-oxide analogue of **5**, i.e. 3,3-(biphenyl-2,2′-diyl)-1-diphenyl-



Scheme 1. Syntheses and dimerizations of (biphenyl-2,2′-diyl)-allenes.

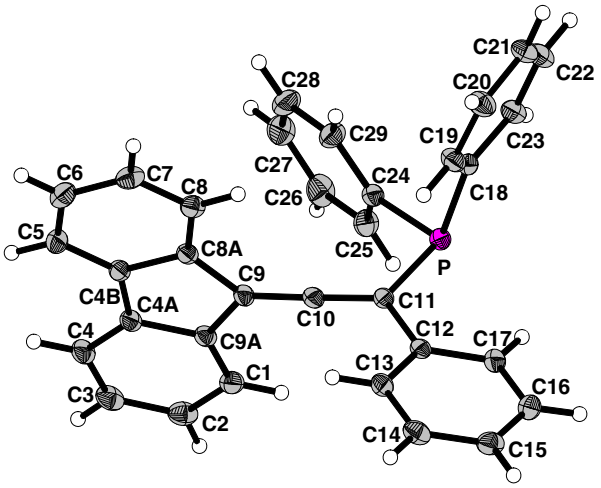


Fig. 1. X-ray crystal structure of 3,3-(biphenyl-2,2′-diyl)-1-diphenylphosphino-1-phenylallene (**5**). Thermal ellipsoids are drawn at the 15% probability level.

phosphinoyl-1-phenylallene (**6**). The reaction of 9-phenylethynyl-9*H*-fluoren-9-ol (**1a**), with chlorodiphenylphosphine proceeded with elimination of hydrogen chloride, whereupon spontaneous migration of the phosphinoyl moiety led directly to **6**, whose structure is shown in Fig. 2. As in the allenylphosphine (**5**), the allene double bonds in **6** are not significantly different [C(9)═C(10) 1.313(3) Å; C(10)═C(11) 1.311(3) Å], but the allenyl-carbon–phosphorus distance is 1.8249(10) Å, significantly shorter than in **5**. A search of the Cambridge Crystallographic Database revealed that structurally characterized allenylphosphine oxides are rather rare. In $H_2C{=}C{=}C(Ph)P(=O)Ph_2$, the $H_2C{=}C$ double bond [1.316(5) Å] is longer than in the C═C–P linkage [1.290(5) Å] [16], whereas when the allenyl-bonded phenyl bears a tricarbonylchromium group, as in $Me_2C{=}C{=}C[Ph–Cr(CO)_3]P(=O)Ph_2$, the situation is reversed [$Me_2C{=}C$ 1.291(4) Å; C═C–P 1.318 (3) Å] [17]. In other systems, the two double bonds are of similar length [18,19].

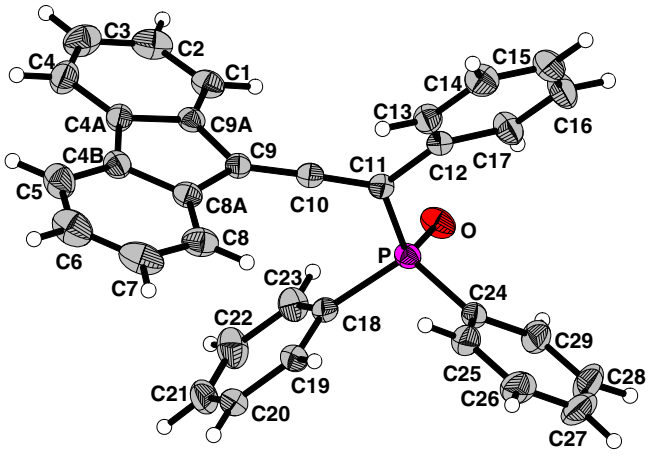
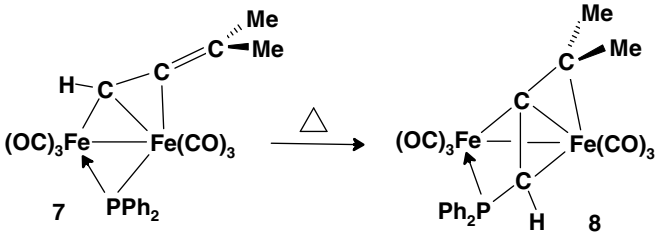


Fig. 2. X-ray crystal structure of 3,3-(biphenyl-2,2′-diyl)-1-diphenylphosphinoyl-1-phenylallene (**6**). Thermal ellipsoids are drawn at the 25% probability level.

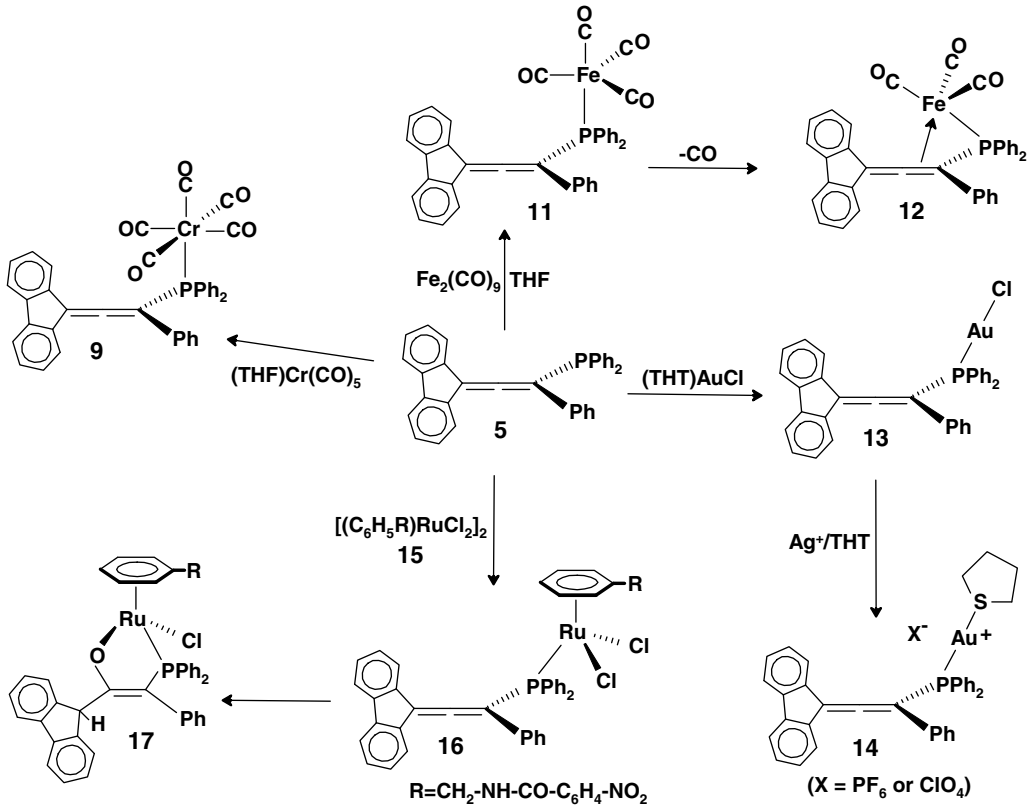
Only a small number of organometallic derivatives of allenylphosphines are known [11], and we are aware of only a single example where a metal is coordinated directly to the phosphorus [20]. In that case, a μ-η^1:η^2-allenyl di-iron complex, **7**, that possesses a bridging phosphido fragment, rearranges (see Scheme 2) into the μ-η^1:η^3–allenylphosphine complex **8**, in which both the allenyl linkage and the phosphorus act as donors to iron.

Since allenylphosphine-organometallics with metal–phosphine linkages appear not to have been extensively explored, we chose to investigate the reactions of **5** with a range of different precursors, as indicated in Scheme 3. Initially, 3,3-(biphenyl-2,2′-diyl)-1-diphenylphosphino-1-phenylallene (**5**), was allowed to react with $(THF)Cr(CO)_5$ and yielded the expected $(allenylphosphine)Cr(CO)_5$ (**9**), whose spectroscopic data corresponded well with those previously reported for $(Ph_3P)Cr(CO)_5$ (**10**) [21,22]. Thus, ^{13}CO NMR resonances for **9** (**10**) are found at 221.2, $J_{C–P} = 5.7$ Hz (221.7, $J_{C–P} = 6$ Hz) ppm [1 CO], and at 216.4, $J_{C–P} = 12.8$ Hz (216.9, $J_{C–P} = 13$ Hz) ppm [4 CO's], the ^{31}P NMR peak occurs at 63.0 (55.3) ppm, and ν_{CO} absorptions appear at 2063, 1982 and 1942 (2065, 1980 and 1940) cm^{-1}. These data indicate clearly the formation of the $(allenylphosphine)Cr(CO)_5$ (**9**). Thermolysis, or treatment with trimethylamine-*N*-oxide, did not lead to loss of a carbonyl ligand.

Thus, the allenylphosphine (**5**), apparently behaves toward $(THF)Cr(CO)_5$ as does triphenylphosphine. Conversely, with iron carbonyl a different type of reactivity manifests itself. When 3,3-(biphenyl-2,2′-diyl)-1-diphenylphosphino-1-phenylallene was allowed to react with $Fe_2(CO)_9$ in tetrahydrofuran at room temperature it formed initially the yellow tetracarbonyliron complex **11**, the structure of which appears as Fig. 3. As with the long-known $(Ph_3P)Fe(CO)_4$, the allenylphosphine complex **11** adopts a trigonal bipyramidal geometry in which the phosphine is axial. The allene double bonds C(9)═C(10) and C(10)═C(11), 1.312(3) and 1.303(3) Å, respectively, are not significantly different, and the C(11)–P and P–Fe linkages [1.844(3) and 2.2458(7) Å, respectively] closely parallel those found in $(Ph_3P)Fe(CO)_4$ [23]. The allene moiety is almost linear [C(9)–C(10)–C(11) is 178.4°], and the



Scheme 2. Rearrangement of a μ-η^1:η^2-allenyl complex into a μ-η^1:η^3-allenylphosphine.



Scheme 3. Reactions of 3,3-(biphenyl-2,2′-diyl)-1-diphenylphosphino-1-phenylallene (**5**).

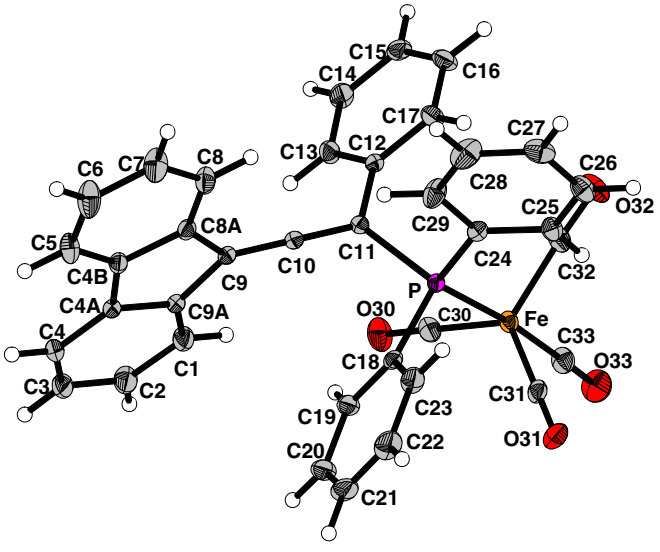


Fig. 3. X-ray crystal structure of the allenylphosphine–$Fe(CO)_4$ complex, **11**. Thermal ellipsoids are drawn at the 25% probability level.

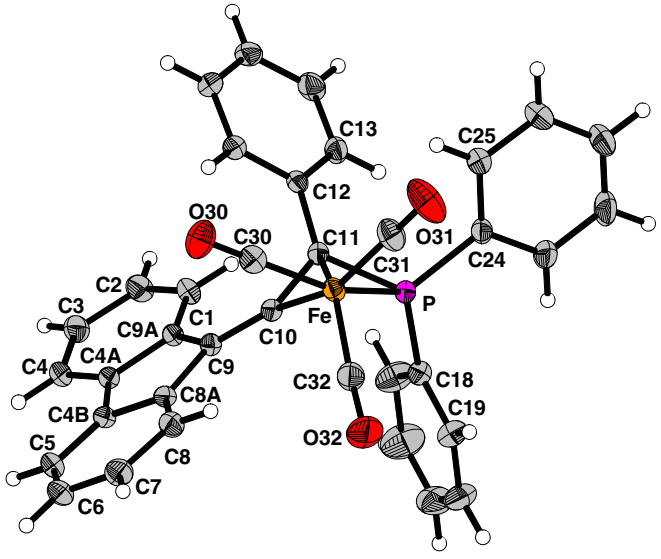


Fig. 4. X-ray crystal structure of the allenylphosphine–$Fe(CO)_3$ complex, **12**. Thermal ellipsoids are drawn at the 25% probability level.

C(10)–C(11)–P and C(11)–P–Fe angles are 119.9° and 115.2°, respectively.

However, the $Fe(CO)_4$ complex, **11**, is thermally very sensitive and, even during the removal of solvent on a rotary evaporator, readily loses carbon monoxide to produce red crystals of the corresponding $Fe(CO)_3$ system, **12**, in which the vacant site on iron is now occupied by the adjacent double bond of the allene. As shown in Fig. 4, the tricarbonyliron tripod in **12** is bonded in a pseudo-allylic manner to two carbons and the phosphorus. The allenyl moiety is no longer linear [C(9)–C(10)–C(11) is 138.6°], and the bonds C(9)═C(10) and C(10)═C(11) are 1.357(3) and 1.425(3) Å, respectively; the deviation of the allene moiety from linearity is near the extreme of the

known range (~134–160°) for metal-bonded allenes, which average ~150° [24]. The Fe–C(10) and Fe–C(11) distances are markedly different [1.971(3) and 2.185(2) Å, respectively], the Fe–P [2.185(16) Å] and P–C(11) [1.771(15) Å] bonds have shortened compared to those in **11**, and, evidently, the C(10)–C(11)–P and C(11)–P–Fe angles (102.5° and 63.8°, respectively) have decreased as the iron leans toward the C(10)=C(11) double bond. Finally, the three carbonyl ligands adopt positions so as to place the iron in an octahedral environment.

The ^{13}C NMR spectrum of the (allenylphosphine)$Fe(CO)_4$ complex **11** in the metal carbonyl region shows only a single resonance, doublet split by phosphorus, thus paralleling the fluxional behaviour previously found in $(Ph_3P)Fe(CO)_4$ [25]. In contrast, the tricarbonyliron complex, **12**, exhibits three ^{13}CO resonances (each exhibiting a different coupling constant to phosphorus) even at room temperature, and it is only as the temperature is raised to ~40 °C that line broadening becomes very evident. However, the ^{1}H and ^{13}C resonances attributable to the two non-equivalent benzo rings of the fluorenylidene moiety remain unchanged, as do those of the diastereotopic phenyl groups on phosphorus, indicating that, although rotation of the $Fe(CO)_3$ tripod is an observable process, the metal retains its attachment to one face of the allene double bond, and racemization of the molecule does not occur on the NMR time-scale. We are unaware of any previous reports of η^3-bonded monometallic allenylphosphines of this type (although Doherty's [20] di-iron species **8** is somewhat related); however, we note the relevance of Mathey's observation of the equilibrium between η^3- and η^1-(phospha-allyl)[Fe(CO)Cp]$W(CO)_5$ complexes [26].

The allenylphosphine (**5**) also reacted with metal halides and, once again, quite diverse behaviour was observed with different metals. The reaction of **5** with (THT)AuCl (THT = tetrahydrothiophene) parallels the behaviour of triphenylphosphine. The initial reaction displaces the weakly-bonded THT ligand to produce the (allenylphosphine)AuCl complex, **13**, shown in Fig. 5. As with the tetracarbonyliron analogue, **11**, the C(9)=C(10) and C(10)=C(11) bond lengths [1.305(5) and 1.312(5) Å, respectively] are not significantly different; moreover, both the allenyl and P–Au–Cl linkages are almost linear (175.0° and 178.8°, respectively). When **13** was treated *in situ* with a silver(I) salt to remove the chloride, the product reacted with remaining THT to yield the [(allenylphosphine)gold(THT)]$^+$ cation, **14**, that was crystallographically characterized as both the PF_6^- and ClO_4^- salts, **14a** and **14b**, respectively. The metric parameters for the two salts are very similar, and Fig. 6 depicts the cation in the hexafluorophosphate case. Removal of THT before the addition of the silver(I) salt to **13** resulted in extensive decomposition to metallic gold. The elemental analysis of **14a** is consistent with the proposed formula, but its ^{31}P NMR spectrum in $CDCl_3$ solution shows, in addition to the PF_6 anion (septuplet at −142.9 ppm), two singlets at 45.4 and 37.3 ppm in a *ca.* 1:5 ratio, indicating the presence of more than one species in solution. The signal at 37.3 ppm is broad at room temperature but sharp at −60 °C. In addition, the THT ligand appears in the room temperature ^{1}H NMR spectrum of **14a** as two broad singlets centered at 3.41 and 2.11 ppm. At −60 °C, however, four broad singlets corresponding to two sets of THT signals at *ca.* 1:10 ratio can be observed at 3.71 and 2.38 ppm, and 3.46 and 2.10 ppm, respectively. This behaviour may be attributed to the formation in solution of the symmetric cations [(allenylphosphine)$_2$Au]$^+$ and [Au(THT)$_2$]$^+$, in equilibrium with the mixed species **14**. The broadening of the signals indicates ligand exchange on the NMR time

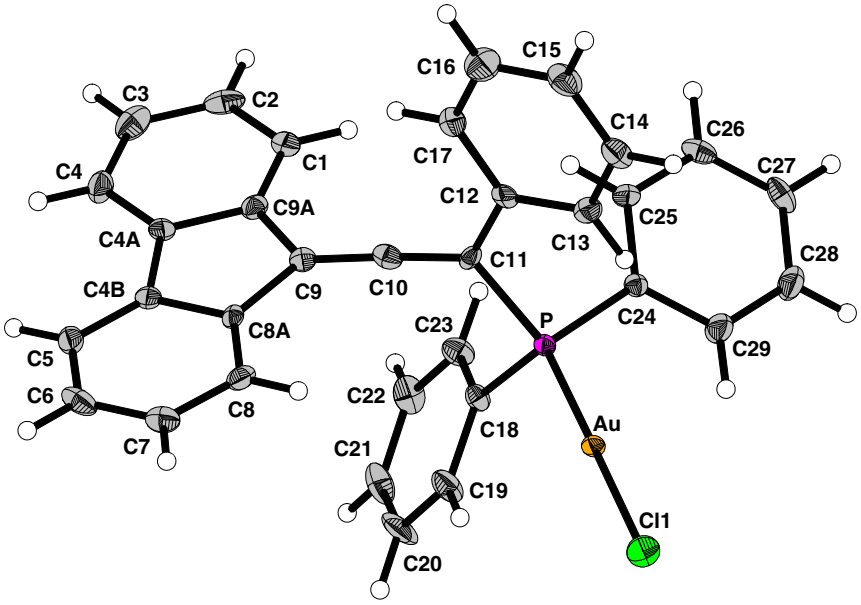


Fig. 5. X-ray crystal structure of the allenylphosphine–gold chloride complex, **13**. Thermal ellipsoids are drawn at the 70% probability level.

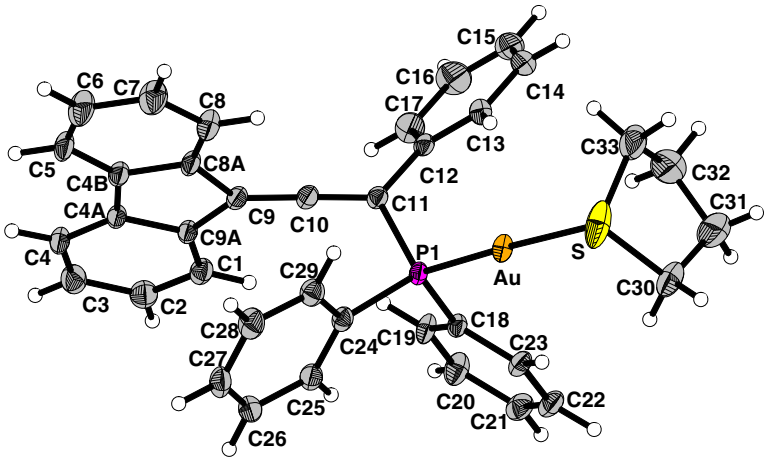


Fig. 6. X-ray crystal structure of the allenylphosphine–gold-tetrahydrothiophene cation, **14a**. Thermal ellipsoids are drawn at the 50% probability level.

scale. The ^{1}H and ^{31}P NMR spectra of **14b** were obtained only at room temperature but showed similar features to those of **14a**. Despite THT being a weakly coordinating ligand, it can yield stable Au(I) species, although only a few of them have been characterized by X-ray crystallography [27,28]. The Au–S and Au–P distances in **14a** [2.3321(13) and 2.2579(10) Å, respectively] are comparable to those observed in $[Au(THT)(PPh_2C_6H_4NH_2-2)]^+$ [2.321(2) and 2.261(2) Å] [28]. The P–Au–S angle is almost linear in the latter [179.19(7)°] [28] but deviates slightly from linearity in **14a** [174.32(4)°]. The allenyl C=C bond lengths [1.316(6) Å and 1.307(5) Å] and the C(9)–C(10)–C(11) angle [175.9(4)°] in **14a** are similar to those of **13**.

As part of a bioorganometallic project involving the linking of an organoruthenium moiety to a commercial anticancer drug, the complex $[(p\text{-}O_2N\text{–}C_6H_4\text{–}CO\text{–}NH\text{–}CH_2\text{–}C_6H_5)RuCl_2]_2$ (**15**), was treated with a number of ligands, such as DMSO, phosphines, etc., that cleave the halogen bridges and yield the desired (arene)$RuCl_2L$ systems. These results will be reported elsewhere [29]. However, when **15** was allowed to react with the allenylphosphine (**5**), the anticipated phosphine complex, **16**, was not detected. Instead an unexpected product, **17**, was identified crystallographically as the chelate complex (arene) $\overline{Ru[Ph_2P\text{-}C(Ph)=CR\text{-}O}$, where R is 9-fluorenyl. The structure of **17** (see Fig. 7) reveals the presence of a planar five-membered ruthenacycle in which the metal is linked to a diphenylphosphino group and an oxygen (Ru–P = 2.3060(9), Ru–O = 2.075(2) Å); the former central allene carbon, C(10), is now trigonal planar with a C(9)–C(10)–C(11) angle of 121.6°, and C(9)–C(10) and C(10)–C(11) distances of 1.512(4) Å and 1.364(5) Å, respectively. In the solid state, intermolecular hydrogen bonding between the chlorine and the amide hydrogen is evident (Fig. 8).

The formula of **17** corresponds to initial incorporation of the allenylphosphine, addition of water, and loss of hydrogen chloride. As depicted in Scheme 4, one can readily envisage cleavage of the ruthenium dimer to form **16**, followed by coordination of the allene double bond adjacent to the phosphine with displacement of a chloride ion. The alkene linkage

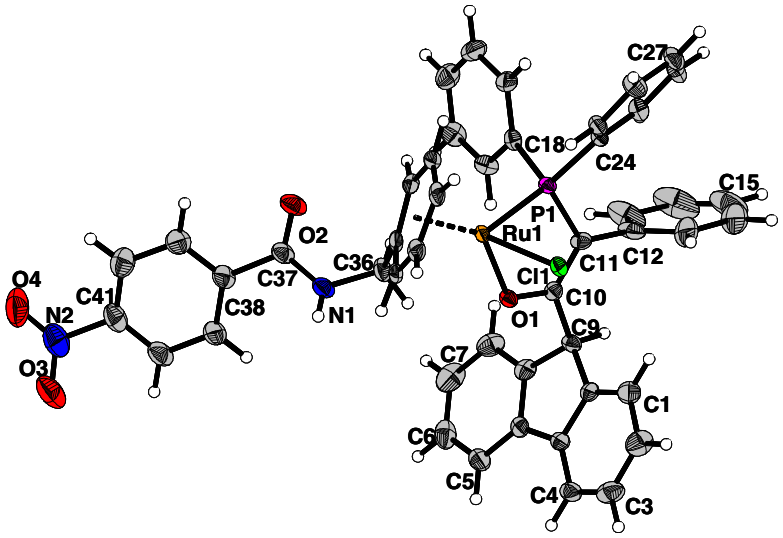


Fig. 7. X-ray structure of the allenylphosphine–ruthenium chelate complex, **17**. Thermal ellipsoids are drawn at the 50% probability level.

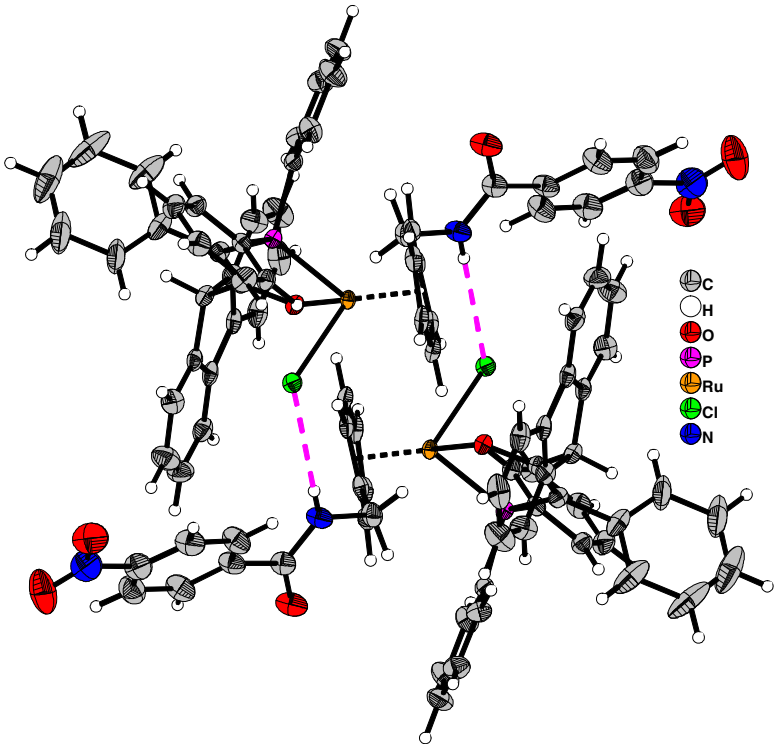
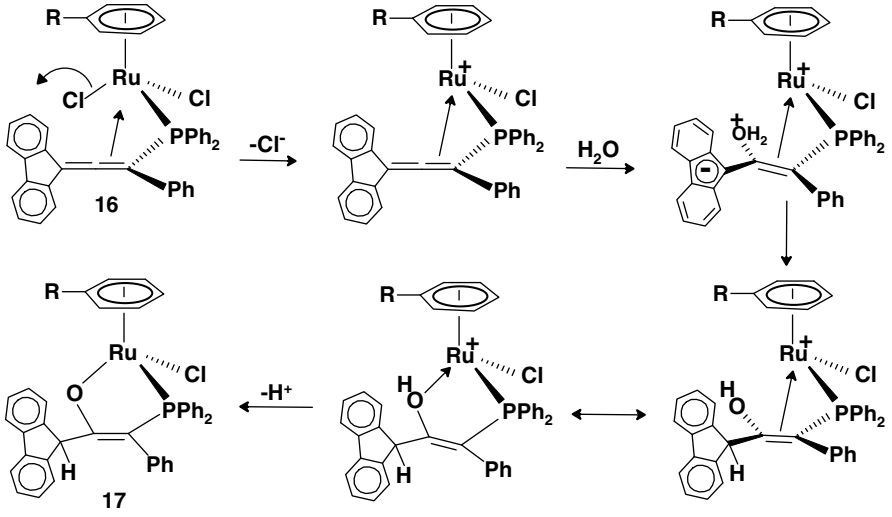


Fig. 8. Intermolecular hydrogen bonding in the Ru chelate complex, **17**.



Scheme 4. Proposed mechanism for the formation of **17**.

coordinated to the ruthenium(II) centre is now susceptible to nucleophilic attack by water; successive proton migration, coordination of oxygen to ruthenium and deprotonation lead directly to the observed product **17**. The most closely related system of which we are aware was reported by Werner [30], whereby treatment of (mesitylene)$RuCl_2(R_2P–CH_2–CO_2Me)$ with $AgPF_6$, and then *t*-BuOK, yielded (mesitylene)(Cl)Ru–PR_2–CH=C(OMe)–O, a chelate complex directly analogous to **17**.

To conclude, the allenylphosphine (**5**), reacts initially as a conventional mono-phosphine but, when the metal centre has a readily displaceable ligand such as a carbonyl or halide, the allene double bond adjacent to the phosphorus can also function as a donor. Moreover, when the alkene moiety is coordinated to a positively charged metal center, it is rendered susceptible to nucleophilic attack. In principle, the fluorenyl fragment could also be a site for metal coordination and work on this aspect is continuing.

3. Experimental

3.1. General methods

All reactions were carried out under an atmosphere of dry nitrogen employing conventional benchtop and glovebag techniques. Merck silica gel 60 (230–400 mesh) was used for flash chromatography. ^{1}H and ^{13}C NMR spectra were recorded on Varian Inova 300 MHz, 400 MHz or 500 MHz spectrometers. Assignments were based on standard 2-dimensional NMR techniques (^{1}H–^{1}H COSY, ^{1}H–^{13}C HSQC and HMBC, NOESY). Infrared spectra were recorded on a Perkin–Elmer Paragon 1000 FT-IR spectrometer and were calibrated with polystyrene. Melting points were determined on an Electrothermal ENG instrument and are uncorrected. Elemental analyses were carried out by the Microanalytical Laboratory at University College Dublin or at the Analytical Services and Environmental Projects (ASEP) Division at Queen's University Belfast. The alkynyl-fluorenols **1a**–**1d** were prepared as described previously [7].

3.2. Preparation of 3,3-(biphenyl-2,2′-diyl)-1-diphenylphosphino-1-phenylallene (5)

To a solution of 3,3-(biphenyl-2,2′-diyl)-1-bromo-1-phenyl-allene (**2a**), (500 mg, 1.45 mmol) in tetrahydrofuran (15 mL), prepared as described previously [7], *n*-BuLi (1.09 mL of a 1.6 M hexane solution, 1.74 mmol) was added dropwise at −78 °C. After 30 min stirring, chlorodiphenylphosphine (340 μL, 1.89 mmol) in dichloromethane (1 mL) was added dropwise. The solution was stirred at −78 °C for 30 min, and at room temperature for 2 h, quenched with water, and extracted with diethyl ether several times. The organic layers were combined, washed with brine, dried over $MgSO_4$, filtered and concentrated to give a yellow oil. Purification of the crude product by chromatography on silica gel using pentane/dichloromethane as eluent gave 3,3-(biphenyl-2,2′-diyl)-1-diphenylphosphino-1-phenyl-allene (**5**), (551 mg, 1.22 mmol; 84%) as a purple solid, m.p. 72–76 °C. Anal. Calc. for $C_{33}H_{23}P0.25CH_2Cl_2$: C, 84.66; H, 5.02. Found: C, 84.36; H, 4.99%. A sample suitable for an X-ray crystal structure determination was obtained by recrystallisation from dichloromethane/pentane. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74 (dt, 2H, $J = 1.5$ Hz, $J = 8.0$ Hz, phenyl *o*-H), 7.66 (dd, 2H, $J = 1.0$ Hz, $J = 8.0$ Hz, H_4, H_5), 7.52–7.47 (m, 4H, phenyl *o*-H), 7.41 (d, 2H, $J = 7.5$ Hz, H_1, H_8), 7.32 (t, 2H, $J = 7.5$ Hz, phenyl *m*-H), 7.29 (td, 2H, $J = 1.0$ Hz, $J = 7.5$ Hz, H_3, H_6), 7.28 (td, 1H, $J = 1.0$ Hz, $J = 7.5$ Hz, phenyl *p*-H), 7.21 (td, 2 H, $J = 1.0$ Hz, $J = 7.5$ Hz, H_2, H_7), 7.14–7.11 (m, 6H, phenyl *m*-H, *p*-H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.8 (C_{10}), 138.28 (C_{4a}, C_{4b}), 137.5 (C_{8a}, C_{9a}), 135.4 (d, $J = 10.8$ Hz, phenyl *ipso*-C), 134.9 (d, $J = 24.9$ Hz, phenyl *ipso*-C), 133.9 (d, $J = 19.6$ Hz, phenyl *ipso*-C), 129.1 (phenyl), 129.0 (phenyl *m*-C), 128.4 (phenyl), 128.3 (phenyl), 128.2 (d, $J = 1.3$ Hz, phenyl *p*-C), 127.9 (d, $J = 10.6$ Hz, phenyl *o*-C), 127.6 (C_3, C_6), 126.8 (C_2, C_7), 122.8 (C_4, C_5), 111.2 (d, $J = 23.6$ Hz, C_{11}), 108.3 (d, $J = 1.9$ Hz, C_9); ^{31}P $\{^{1}H\}$ NMR (121 MHz, $CDCl_3$): δ −6.90; IR (liquid, CH_2Cl_2): 1916 cm^{-1} (C═C═C).

3.3. Preparation of 3,3-(biphenyl-2,2′-diyl)-1-diphenylphosphinoyl-1-phenylallene (6)

Triethylamine (89 μL, 0.64 mmol) was added to a solution of 9-phenylethynyl-9*H*-fluoren-9-ol (**1a**), (150 mg, 0.53 mmol) in pentane (6 mL) and dichloromethane (1 mL) at 0 °C. Chlorodiphenylphosphine (114.9 μL, 0.64 mmol) was then added and, after stirring for 1 h at room temperature, the precipitate was filtered off, washed with water, and dried to give 3,3-(biphenyl-2,2′-diyl)-1-diphenylphosphinoyl-1-phenyl-allene (**6**) (226 mg, 0.48 mmol; 91%) m.p. 193–195 °C as a white powder. Anal. Calc. for $C_{33}H_{23}OP \cdot 0.5H_2O$: C, 83.35; H, 5.09; P, 6.51. Found: C, 83.62; H, 4.90; P, 6.84%. A sample suitable for an X-ray crystal structure determination was obtained by recrystallisation from dichloromethane/pentane. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.83 (d, 2H, $J = 7.0$ Hz, phenyl *o*-H), 7.80 (d, 2H, $J = 7.0$ Hz, phenyl *o*-H), 7.75 (d, 2 H, $J = 7.5$ Hz, phenyl *o*-H), 7.64 (d, 2H, $J = 7.5$ Hz, H_4, H_5), 7.48 (d, 2H, $J = 7.5$ Hz, H_1, H_8), 7.33 (t, 2H, $J = 7.5$ Hz, H_3, H_6), 7.32–7.22 (m, 11H, H_2, H_7, phenyl *m*-H, *p*-H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 209.9 (d, $J = 4.5$ Hz, C_{10}), 138.7 (C_{4a}, C_{4b}), 136.3 (d, $J = 6.1$ Hz, C_{8a}, C_{9a}), 132.5 (phenyl *ipso*-C), 132.1 (d, $J = 29.8$ Hz, phenyl *ipso*-C), 132.0 (d, $J = 3.1$ Hz, phenyl *p*-C), 131.6 (phenyl *o*-C), 131.5 (phenyl *o*-C), 129.0 (phenyl *m*-C), 128.9 (d, $J = 4.8$ Hz, phenyl *o*-C), 128.6 (C_3, C_6), 128.4, 128.3 (phenyl *m*-C), 127.2 (d, $J = 0.8$ Hz, C_2, C_7), 123.2 (d, $J = 1.6$ Hz, C_1, C_8), 120.3 (C_4, C_5), 109.8 (d, $J = 94.4$ Hz, C_{11}), 109.4 (d, $J = 13.0$ Hz, C_9); ^{31}P $\{^{1}H\}$ NMR (121 MHz, $CDCl_3$): δ 30.08. IR ($CHCl_3$) 1921 cm^{-1} (C═C═C).

3.4. Preparation of (3,3-(biphenyl-2,2′-diyl)-1-diphenylphosphino-1-phenylallene)Cr(CO)$_5$ (9)

A solution of $Cr(CO)_6$ (490 mg, 2.2 mmol) in dry tetrahydrofuran (300 mL) was photolysed in a quartz UV reactor for 1 h, and added to a solution of the allenylphosphine, **5**, (1.0 g, 2.2 mmol) in tetrahydrofuran (10 mL). The reaction was stirred overnight under nitrogen, concentrated, and triturated with dichloromethane. The residues were filtered off and the filtrate crystallised to give the (allenylphosphine)$Cr(CO)_5$ complex, **9**, (683 mg, 1.06 mmol; 48%), m.p. 97–99 °C as a yellow powder. Anal. Calc. for $C_{38}H_{23}CrO_5P$: C, 71.03; H, 3.61. Found: C, 70.86; H, 3.74%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85–7.26 (m), 7.72–7.62 (m), 7.57 (d, $J = 7.6$ Hz), 7.42–7.20 (m); ^{13}C NMR (100 MHz, $CDCl_3$): δ 221.2 (d, $J = 5.7$ Hz), 216.4 (d, $J = 12.8$ Hz), 206.8 (d, $J = 1.8$ Hz), 138.9, 136.8 (d, $J = 3.8$ Hz), 134.7 (d, $J = 35.5$ Hz), 133.8 (d, $J = 13.0$ Hz), 133.0 (d, $J = 10.9$ Hz), 130.6 (d,

$J = 2.0$ Hz), 129.5 (d, $J = 3.8$ Hz), 128.8, 128.6, 128.5, 127.4, 123.2, 120.5, 111.3 (d, $J = 23.2$ Hz), 109.2 (d, $J = 8.6$ Hz); ^{31}P $\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 63.0; IR (solid, KBr): 2063 cm^{-1}, 1982 cm^{-1}, 1942 cm^{-1} (CO).

3.5. Preparation of (allenylphosphine)Fe(CO)$_4$ (**11**) and (allenylphosphine)Fe(CO)$_3$ (**12**)

A solution of 3,3-(biphenyl-2,2′-diyl)-1-diphenylphosphino-1-phenylallene (**5**), (290 mg, 0.64 mmol) in THF and diiron nonacarbonyl (585 mg, 1.61 mmol) were stirred for 48 h at room temperature, during which time the $Fe_2(CO)_9$ gradually went into solution. The solvent was removed at low temperature and the crude material was purified by chromatography on silica gel using pentane as eluent. [3,3-(Biphenyl-2,2′-diyl)-1-diphenylphosphino-1-phenyl-allene]Fe(CO)$_4$ (**11**), (215 mg, 0.35 mmol; 54%) was isolated as a temperature-sensitive yellow solid. A sample suitable for an X-ray crystal structure determination was obtained by recrystallisation from diethyl ether/pentane. ^1H NMR (500 MHz, $CDCl_3$): δ 7.79 (d, 2 H, $J = 8.0$ Hz, phenyl *o*-H), 7.76 (d, 2H, $J = 6.5$ Hz, phenyl *o*-H), 7.65 (d, 2H, $J = 7.5$ Hz, H_4, H_5), 7.56 (d, 2H, $J = 7.5$ Hz, H_1, H_8), 7.38 (d, 2H, $J = 8.0$ Hz, phenyl *o*-H), 7.36 (t, 3H, $J = 7.5$ Hz, H_3, H_6, phenyl *p*-H), 7.33–7.27 (m, 10H, H_2, H_7, phenyl *p*-H, phenyl *m*-H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 213.5 (d, $J = 18.8$ Hz, CO), 207.9 (C_{10}), 138.4 (C_{4a}, C_{4b}), 136.5 (d, $J = 5.00$ Hz, C_{8a}, C_{9a}), 133.2 (d, $J = 10.5$ Hz, phenyl *o*-C), 133.0 (d, $J = 11.9$ Hz, phenyl *ipso*-C), 132.7 (d, $J = 48.1$ Hz, phenyl *ipso*-C), 131.2 (d, $J = 2.4$ Hz, phenyl *p*-C), 129.6 (d, $J = 3.6$ Hz, phenyl *o*-C), 128.9 (phenyl *p*-C), 128.6 (phenyl *m*-C), 128.6 (d, $J = 10.5$ Hz, phenyl *m*-C), 128.5 (C_3, C_6), 127.2 (C_2, C_7), 123.1 (C_1, C_8), 120.3 (C_4, C_5), 110.4 (d, $J = 38.0$ Hz, C_{11}), 108.3 (d, $J = 10.0$ Hz, C_9); ^{31}P $\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 79.77; IR (liquid, $CHCl_3$): 2050 cm^{-1}, 1977 cm^{-1}, 1940 cm^{-1} (C═O). A red solid, identified as [3,3-(biphenyl-2,2′-diyl)-1-diphenylphosphino-1-phenylallene]Fe(CO)$_3$ (**12**), (19 mg, 0.03 mmol; 5%), m.p. 203–206 °C, was also isolated, and a sample suitable for an X-ray crystal structure determination was obtained by recrystallisation from dichloromethane/pentane. It was subsequently shown that, upon gentle warming, **11** was converted quantitatively into **12**. ^1H NMR (500 MHz, $CDCl_3$): δ 8.37 (d, 1H, $J = 7.5$ Hz, H_8), 7.78 (d, 1H, $J = 7.5$ Hz, H_5), 7.69 (d, 1H, $J = 7.5$ Hz, H_4), 7.67 (d, 1H, $J = 7.5$ Hz, phenyl-H), 7.65 (d, 1H, $J = 7.5$ Hz, phenyl-H), 7.60–7.56 (m, 1H, phenyl-H), 7.49–7.43 (m, 1H, H_7, phenyl-H), 7.40–7.35 (m, 2H, H_6, phenyl-H), 7.25 (td, 2H, $J = 3.0$ Hz, $J = 7.5$ Hz, phenyl-H), 7.16–7.09 (m, 6H, H_3, phenyl-H), 7.07 (d, 1H, $J = 8.0$ Hz, H_1), 6.96 (td, 1H, $J = 1.0$ Hz,$J = 7.5$ Hz, H_2); ^{13}C NMR (125 MHz, $CDCl_3$): δ 211.7 (d, $^2J_{C-P} = 13.8$ Hz, CO), 210.4 (d, $^2J_{C-P} = 24.0$ Hz, CO), 210.0 (d, $^2J_{C-P} = 27.6$ Hz, CO), 167.3 (d, $J = 5.6$ Hz, C_{10}), 140.0 (d, $J = 3.5$ Hz, C_{8a}), 139.6 (C_{4b}), 136.7 (d, $J = 3.6$ Hz, C_{9a}), 136.7 (d, $J = 2.6$ Hz, phenyl *ipso*-C), 136.1 (C_{4a}), 133.7 (d, $J = 10.8$ Hz), 133.7 (d, $J = 10.8$ Hz), (phenyl *o*-C), 131.9 (d, $J = 3.6$ Hz, phenyl *p*-C), 131.9 (d, $J = 3.6$ Hz, phenyl *p*-C), 129.0 (d, $J = 9.1$ Hz, phenyl *m*-C), 129.0, 128.9 (d, $J = 3.6$ Hz), 128.6, 126.7 (phenyl C), 126.2 (C_7), 125.8 (C_2), 125.8 (C_6), 125.6 (d, $J = 53.6$ Hz, phenyl *ipso*-C), 125.3 (d, $J = 13.3$ Hz, C_9), 124.8 (C_3), 124.0 (d, $J = 57.8$ Hz, phenyl *ipso*-C), 122.1 (C_1), 121.4 (C_8), 119.4 (C_5), 119.0 (C_4), 38.4 (d, $J = 23.5$ Hz, C_{11}); ^{31}P $\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 12.48; IR (liquid, CH_2Cl_2): 2040 cm^{-1}, 1979 cm^{-1} (C═O). Anal. Calc. for $C_{36}H_{23}FeO_3P0.25CH_2Cl_2$: C, 71.19; H, 3.87; Fe, 9.13. Found: C, 71.37; H, 3.93; Fe, 8.67%.

3.6. Preparation of (allenylphosphine)AuCl (**13**)

To [AuCl(THT)] [31] (35.6 mg, 0.11 mmol) dissolved in dichloromethane (15 mL) was added the allenylphosphine, **5**, (50 mg, 0.11 mmol). The solution was stirred for 2 h, after which time the volume of the solution was reduced in vacuo to *ca.* 2 mL. Addition of hexane to the dichloromethane solution yielded an oil that, upon removal of the solvents in vacuo, solidified to give **13** (41 mg, 0.06 mmol; 54%) m.p. 212–213 °C. Anal. Calc. for $C_{33}H_{23}PAuCl0.25CH_2Cl_2$: C, 56.71; H, 3.36. Found: C, 56.47; H, 3.30%. A sample suitable for an X-ray crystal structure determination was obtained by diffusion of hexane into a dichloromethane solution of the product at −20 °C. ^1H NMR (300 MHz, $CDCl_3$): δ 7.75–7.60 (m, 8H, phenyl-H), 7.44–7.19 (m, 15H, phenyl-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 209.6 (C_{10}), 138.7 (C_{4a}, C_{4b}), 135.7 (d, $J = 5.7$ Hz, C_{8a}, C_{9a}), 134.2, 134.0, 132.1, 132.1, 131.6 (d, $J = 11.5$ Hz, phenyl *ipso*-C), 129.2, 129.1, 129.0, 128.9, 128.8, 128.1, 127.9, 127.2, 127.1, 123.1, 120.3, 110.9 (d, $J = 11.5$ Hz, C_9), 106.7 (d, $J = 52.8$ Hz, C_{11}); ^{31}P $\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ 31.3.

3.7. Preparation of [(allenylphosphine)Au(THT)]PF_6 (**14a**)

To [AuCl(THT)] [31] (35.6 mg, 0.11 mmol) dissolved in dichloromethane (15 mL) was added the allenylphosphine, **5**, (50 mg, 0.11 mmol) and the solution was stirred for 30 min after which time $AgPF_6$ (28.1 mg, 0.11 mmol) was added. The solution was stirred for further 30 min, filtered through celite, and the resulting yellow solution was then reduced in vacuo to *ca.* 2 mL. Addition of diethyl ether produced a yellow precipitate (61.6 mg, 0.07 mmol; 68%) m.p. 140–141 °C (turns purple on melting). A sample suitable for X-ray crystallography was obtained by diffusion of hexane into a dichloromethane solution of **14a**. ^1H NMR (300 MHz, $CDCl_3$): δ 7.78–7.60 (m, 6H, phenyl-H), 7.56–7.46 (m, 5H, phenyl-H), 7.44–7.28 (m, 12H, phenyl-H), 3.41 (s, brd, 4H, CH_2S), 2.11 (s, brd, 4H, CH_2); ^{31}P $\{^1H\}$ NMR (121 MHz, $CDCl_3$) δ 45.3 (s), 37.3 (s, brd), −142.9 (septuplet, $J_{PF} = 714$ Hz, PF_6). Anal. Calc. for $C_{37}H_{31}SP_2AuF_60.25CH_2Cl_2$: C, 49.61; H 3.52. Found: C, 49.68; H, 3.56%.

Table 1
Crystallographic data

Compound	**5**	**6**	**11**	**12**	**13**	**14a**	**14b**	**17**
Empirical formula	$C_{33}H_{23}PO_{0.096}$	$C_{33}H_{23}PO$	$C_{37}H_{23}O_4PFe$	$C_{36}H_{23}O_3PFe$	$C_{34}H_{25}PCl_3Au$	$C_{38}H_{33}F_6P_2SCl_2Au$	$C_{38}H_{33}O_4PSCl_3Au$	$C_{49}H_{40}N_2O_4PCl_5Ru$
f_w	450.48	466.48	618.37	590.36	767.83	965.51 contains one molecule of CH_2Cl_2	919.99 contains one molecule of CH_2Cl_2	1030.12 contains two molecules of CH_2Cl_2
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	$P2_1/c$ (#14)	$C2/c$ (#15)	$P\bar{1}$ (#2)	$P\bar{1}$ (#2)	$P2_1/c$ (#14)	$P\bar{1}$ (#2)	$P\bar{1}$ (#2)	$P\bar{1}$ (#2)
a (Å)	16.767(2)	34.947(3)	8.6715(11)	10.159(11)	12.0591(13)	8.8805(10)	9.0214(7)	15.8058(15)
b (Å)	13.1618(17)	9.3112(8)	12.5733(17)	10.767(11)	16.4153(17)	10.9889(12)	10.4304(8)	17.9142(16)
c (Å)	11.3947(15)	15.8040(14)	14.3019(19)	14.288(15)	14.6403(16)	19.250(2)	19.2422(15)	18.4061(17)
α (°)	90	90	94.560(2)	75.101(17)	90	93.885(2)	97.430(2)	79.981(2)
β (°)	95.061(2)	100.035(2)	91.510(2)	89.447(17)	97.219(2)	99.432(2)	98.163(2)	71.888(2)
γ (°)	90	90	97.881(2)	77.311(17)	90	98.917(2)	99.337(2)	68.567(2)
V (Å^3)	2504.8(6)	5063.9(8)	1538.6(4)	1472(3)	2875.1(5)	1822.3(4)	1746.9(2)	4593.1(7)
Z	4	8	2	2	4	2	2	4
Density (calc.) (g cm^{-3})	1.205	1.224	1.335	1.332	1.774	1.760	1.749	1.490
Temp (K)	293(2)	293(2)	293(2)	293(2)	100(2)	100(2)	100(2)	100(2)
Absorption coefficient (mm^{-1})	0.128	0.132	0.581	0.601	5.475	4.387	4.587	0.714
F(000)	952	1952	636	608	1496	948	908	2096
θ Range (°)	50.00	48	52.00	50.00	56.00	60.00	58.00	54.00
Index ranges	$-19 \leqslant h \leqslant 19$, $-15 \leqslant k \leqslant 15$, $-13 \leqslant l \leqslant 13$	$-39 \leqslant h \leqslant 39$, $-10 \leqslant k \leqslant 10$, $-18 \leqslant l \leqslant 17$	$-10 \leqslant h \leqslant 10$, $-15 \leqslant k \leqslant 15$, $-17 \leqslant l \leqslant 17$	$-12 \leqslant h \leqslant 11$, $-10 \leqslant k \leqslant 12$, $-16 \leqslant l \leqslant 16$	$-15 \leqslant h \leqslant 15$, $-21 \leqslant k \leqslant 21$, $-19 \leqslant l \leqslant 19$	$-12 \leqslant h \leqslant 12$, $-15 \leqslant k \leqslant 15$, $-27 \leqslant l \leqslant 27$	$-12 \leqslant h \leqslant 12$, $-14 \leqslant k \leqslant 14$, $-26 \leqslant l \leqslant 26$	$-20 \leqslant h \leqslant 20$, $-22 \leqslant k \leqslant 22$, $-23 \leqslant l \leqslant 23$
Reflections measured	17574	15362	12003	10298	53693	38734	37660	82323
Reflections used (R_{int})	4410 (0.0225)	3698 (0.0265)	5986 (0.0216)	5016 (0.0230)	6931 (0.0699)	10569 (0.0337)	9289 (0.0453)	20036 (0.0537)
Parameters	317	316	388	370	353	451	450	1179
Final R values $I > 2\sigma(I)$]: R_1, wR_2	0.0468, 0.1247	0.0468, 0.1211	0.0451, 0.1108	0.0385, 0.1005	0.0272, 0.0601	0.0403, 0.1034	0.0353, 0.0842	0.0473, 0.1151
R values (all data): R_1, wR_2	0.0558, 0.1316	0.0558, 0.1277	0.0615, 0.1210	0.0439, 0.1047	0.0327, 0.0618	0.0443, 0.1061	0.0408, 0.0867	0.0766, 0.1310
Goodness-of-fit on F^2	1.064	1.030	1.023	1.020	1.083	1.104	1.063	1.045
Largest diffraction peak and hole (e Å^{-3})	0.312, −0.148	0.535, −0.217	0.596, −0.223	0.380, −0.194	1.289, −1.699	4.122 −1.633	1.819, −1.329	0.748, −0.744

3.8. Preparation of [(allenylphosphine)Au(THT)]ClO_4 (**14b**)

To [AuCl(THT)] [31] (35.6 mg, 0.11 mmol) dissolved in dichloromethane (15 mL) was added the allenylphosphine (**5**), (50 mg, 0.11 mmol) and the solution was stirred for 30 min after which time $AgClO_4$ (23.0 mg, 0.11 mmol) was added. The solution was stirred for further 30 min, filtered through celite, and the resulting yellow solution was then reduced in vacuo to *ca.* 2 mL. Addition of diethyl ether produced a white precipitate (56 mg, 0.06 mmol; 61%). A sample suitable for X-ray crystallography was obtained by diffusion of pentane into a dichloromethane solution of **14b**. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.78–7.72 (m, 5H, phenyl-H), 7.64–7.48 (m, 6H, phenyl-H), 7.39–7.26 (m, 12H, phenyl-H), 3.48 (s, brd, 4H, CH_2S), 2.15 (s, brd, 4H, CH_2); ^{31}P {^{1}H} NMR (121 MHz, $CDCl_3$) δ 45.2 (s), 36.8 (s, brd).

3.9. Preparation of (arene)RuCl[Ph_2P–C(Ph)=CR–O] (**17**)

To a solution of dichloro (*N*-benzyl-4-nitro-benzamide)ruthenium(II) dimer (60 mg, 0.07 mmol) [29] dissolved in dry dichloromethane (10 mL) was added the allenylphosphine (**5**), (62 mg, 0.138 mmol), and the solution was heated at reflux overnight. The solution was allowed to cool to room temperature, the solvent removed in vacuo, and the residue chromatographed on a silica column. Elution with dichloromethane containing acetone (5%) gave **17** (83.1 mg, 0.097 mmol; 69%) as an orange solid, m.p. 226–227 °C. Anal. Calc. for $C_{47}H_{36}ClN_2O_4PRu \cdot 0.5CH_2Cl_2$: C, 63.43; H, 4.11; N, 3.08. Found: C, 63.41; H, 4.22; N, 2.77%. A sample suitable for X-ray crystallography was obtained by diffusion of pentane into a dichloromethane solution of **17**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.98 (1H, bd, $J = 14.5$ Hz, H_{36a}), 4.10 (1H, d, $J = 6.0$ Hz, H_{31}), 4.45 (1H, dd, $J = 6$ Hz, 5 Hz, H_{32}), 4.80 (1H, s, H_9), 4.96 (1H, t, $J = 5$ Hz, H_{33}), 4.98 (1H, bd, $J = 14.5$ Hz, H_{36b}), 5.72 (1H, d, $J = 5$ Hz, H_{35}), 5.76 (1H, d, $J = 5$ Hz, H_{34}), 6.99 (1H, t, $J = 7.5$ Hz, H_3), 7.12–7.15 (7H, m, H_2, H_4, H_{13}, H_{17}, H_{14}, H_{16}, H_{15}), 7.21 (1H, t, $J = 7$ Hz, H_6), 7.23–7.30 (3H, m, H_5, H_{19}/H_{23} or H_{20}/H_{22}), 7.31 (1H, t, $J = 7$ Hz, H_7), 7.37–7.42 (3H, m, H_{19}/H_{23} or H_{20}/H_{22}, H_{21}), 7.48 (1H, d, $J = 7.5$ Hz, H_1), 7.53 (1H, d, $J = 7$ Hz, H_8), 7.57–7.60 (5H, m, H_{25}, H_{29}, H_{26}, H_{28}, H_{27}), 7.64 (2H, d, $J = 8.3$ Hz, H_{41}, H_{43}), 8.02 (2H, d, $J = 8.3$ Hz, H_{40}, H_{44}). ^{13}C NMR (125 MHz, $CDCl_3$) δ 41.18 (C_{36}), 53.00 (d, $J = 10$ Hz, C_9), 73.61 (C_{33}), 79.26 (C_{31}), 86.62 (d, $J = 12$ Hz, C_{35}), 88.60 (C_{32}), 97.31 (C_{34}), 97.87 (d, $J = 53$ Hz, C_{11}), 106.93 (C_{30}), 119.43 (C_4), 119.92 (C_5), 123.50 (C_8), 123.90 (C_{41}, C_{43}), 125.21 (C_1), 126.82 (C_7), 126.95 (C_3), 127.07 (C_2), 127.44 (d, $J = 6$ Hz, C_{19}/$_{23}$ or C_{20}/C_{22}), 127.90 (C_6), 127.99 (C_{15}), 128.61 (C_{40}, C_{44}), 128.67 (C_{13}/C_{17} or C_{14}/C_{16}), 128.91 (d, $J = 11$ Hz, C_{25}/C_{29} or C_{26}/C_{28}), 130.45 (C_{27}), 131.05 (C_{21}), 131.61 (d, $J = 11$ Hz, C_{25}/C_{29} or C_{26}/C_{28}), 132.74 (C_{13}/C_{17} or C_{14}/C_{16}), 136.09 (d, $J = 10$ Hz, C_{19}/C_{23} or C_{20}/C_{22}), 137.84 (C_{12}), 139.35 (C_{39}), 139.92 (d, $J = 47$ Hz, C_{18}, C_{24}), 141.09 (C_{4a}), 141.93 (C_{4b}), 145.20 (C_{9a}), 146.25 (C_{8a}), 149.42 (C_{42}), 166.16 (C_{38}), 183.32 (d, $J = 22$ Hz, C_{10}); ^{31}P NMR (162 MHz, $CDCl_3$) δ 61.89.

3.10. X-ray crystal structure determinations

Crystal data for **5**, **6**, **11**, **12**, **13**, **14a**, **14b** and **17** were collected using a Bruker SMART APEX CCD area detector diffractometer, and are listed in Table 1. A full sphere of reciprocal space was scanned by phi-omega scans. Pseudo-empirical absorption correction based on redundant reflections was performed by the program SADABS [32]. The structures were solved by direct methods using SHELXS-97 [33] and refined by full matrix least-squares on F^2 for all data using SHELXL-97 [34]. Hydrogen atoms attached to nitrogen were located in the difference Fourier map and allowed to refine freely with isotropic thermal displacement factors. All other hydrogen atoms were added at calculated positions and refined using a riding model. Their isotropic displacement parameters were fixed to 1.2 times the equivalent isotropic displacement parameters of the carbon atom the H-atom is attached to. Anisotropic temperature factors were used for all non-hydrogen atoms.

Acknowledgement

We thank Science Foundation Ireland and University College Dublin for generous financial support.

Appendix A. Supplementary material

CCDC 647784, 647787, 647786, 647785, 647791, 647789, 647790, 647788 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.01.046.

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