Transition metal alkynyl complexes by transmetallation from Au(C≡CAr)(PPh$_3$) (Ar = C$_6$H$_5$ or C$_6$H$_4$Me-4)†

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Facile acetylide transfer reactions take place between gold(I) complexes Au(C≡CAr)(PPh$_3$) (Ar = C$_6$H$_5$ or C$_6$H$_4$Me-4) and a variety of representative inorganic and organometallic complexes MXL$_n$ (M = metal, X = halide, L$_n$ = supporting ligands) featuring metals from groups 8–11, to afford the corresponding metal–alkynyl complexes M(C≡CR)L$_n$ in modest to good yield. Reaction products have been characterised by spectroscopic methods, and molecular structure determinations are reported for Fe(C≡CC$_6$H$_4$Me-4)(dppe)Cp, Ru(C≡CC$_6$H$_4$Me-4)(dppe)Cp*, Ru(C≡CC$_6$F$_5$)(η^2-O$_2$)(PPh$_3$)Cp*, Ir(C≡CC$_6$H$_4$Me-4)(η^2-O$_2$)(CO)(PPh$_3$)$_2$, Ni(C≡CC$_6$H$_4$Me-4)(PPh$_3$)Cp and *trans*-Pt(C≡CAr)$_2$L$_2$ (Ar = C$_6$H$_5$, L = PPh$_3$; Ar = C$_6$H$_4$Me-4, L = PPh$_3$, PMe$_3$).

Introduction

Transmetallation, defined as the exchange of ligands between two metal centres,[1] is one of the essential reaction steps in numerous organometallic catalytic cycles, illustrated effectively by the development of metal-catalysed procedures for the simple synthesis of C–C, C–N and C–O bonds.[2] On a preparative scale, transmetallation reactions from Sn,[3,4] Hg,[5,6] Cu[7–10] and Ag[11] have long been known. However, new aspects of this chemistry continue to be developed. For example, despite the prevalence of transmetallation reactions involving alkynyl–copper(I) complexes, and the growing awareness of gold catalysis in which the transfer of ligands from gold to other species is involved,[12] transmetallation reactions involving aryl–gold(I) complexes have only recently been carried out on a variety of transition metal complexes by van Koten and co-workers.[13]

Transmetallation reactions involving alkynyl–gold(I) complexes are also scarce. Yam and co-workers have prepared the tetranuclear copper(I)–alkynyl complexes [Cu$_4$(μ$_3$-η^1,η^1,η^2-C≡CAr′)$_3$(PAr$_3$)$_4$]PF$_6$ from the room temperature transmetallation reaction between [Cu(MeCN)$_4$]PF$_6$ and the appropriate alkynyl–gold(I) polymer [Au(C≡CAr′)]$_\infty$ in the presence of phosphines (PAr$_3$).[14] Ferrer and colleagues have observed the ready transfer of 4-pyridylethynyl from [Au(C≡Cpy)$_2$]$^-$ salts to rhenium following reaction with [Re(THF)(CO)$_3$(bpy)]OTf.[15] The Bruce group has recently found that cross-coupling reactions of Au(C≡CR)(PPh$_3$) with halo-carbynes and halo-acetylenes can be promoted by Pd(0)/Cu(I) catalyst.[16,17] These catalytic reactions, which are carried out at room temperature in ethereal solvents, implicate Au(I)–Pd(II) transmetallation processes, and the AuX(PPh$_3$) by-product can be isolated from the reaction mixture and recycled.

Examples of transmetallation involving the readily prepared gold(I) species Au(C≡CR)(PR$_3$)[18] directly in the preparation of metal alkynyl complexes have been limited to NMR scale experiments. Shaw and co-workers used ^{31}P NMR spectroscopy to follow the acetylide group transfer from Au(I) to Ni(II) during the facile reaction of NiCl$_2$(dppm-*P*)$_2$ with Au(C≡CC$_6$H$_5$)(PPh$_3$) (CH$_2$Cl$_2$, *ca* 20 °C), which resulted in the formation of complexes formulated as [Ni(C≡CC$_6$H$_5$)$_2$(μ-dppm)$_2$Au]Cl (dppm = Ph$_2$PCH$_2$PPh$_2$).[19] Cross and Davidson have used ^{31}P NMR spectroscopy to demonstrate that reactions of *cis*-PtCl$_2$(PMePh$_2$)$_2$ with Au(C≡CC$_6$H$_5$)(PPh$_3$) give *cis*- and/or *trans*-Pt(C≡CC$_6$H$_5$)$_2$(PMePh$_2$)$_2$, depending on the conditions used.[20] The same authors reported that reactions of *cis*-PtCl$_2$(CO)(PMePh$_2$) with Au(C≡CR)(PPh$_3$) (R = Me, C$_6$H$_5$) gave *cis*-Pt(C≡CR)$_2$(CO)(PMePh$_2$) as the final product *via cis*- or *trans*-Pt(C≡CR)Cl(CO)(PMePh$_2$).

Our long-standing interest in the preparative chemistry of metal acetylide complexes prompted us to consider the potential application of alkynyl-gold(I) complexes as reagents for the preparation of metal acetylides. Gold(I) phosphine complexes featuring highly conjugated carbon-rich and all-carbon ligands are known,[16,21,22] and are generally easier and safer to handle than their analogous protio, lithio, tin, copper, mercury or Grignard derivatives. Convenient transfer of the carbon ligand from gold to other metals would represent a useful addition to the range of available synthetic methods for the preparation of metal complexes containing carbon-rich and all-carbon ligands.[16,23]

Here, we report transmetallation reactions using the readily available gold complexes Au(C≡CAr)(PPh$_3$) [Ar = C$_6$H$_5$ (**1a**), C$_6$H$_4$Me-4 (**1b**)] and representative inorganic and organometallic compounds MXL$_n$ [M = metal, X = halide, L$_n$ = supporting ligands] featuring metals from groups 8–11 (Scheme 1). The corresponding metal–alkynyl complexes M(C≡CAr)L$_n$ are isolated in their pure form in modest to good yields.

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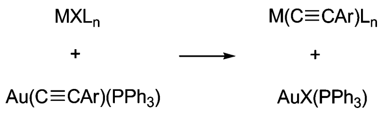


Scheme 1

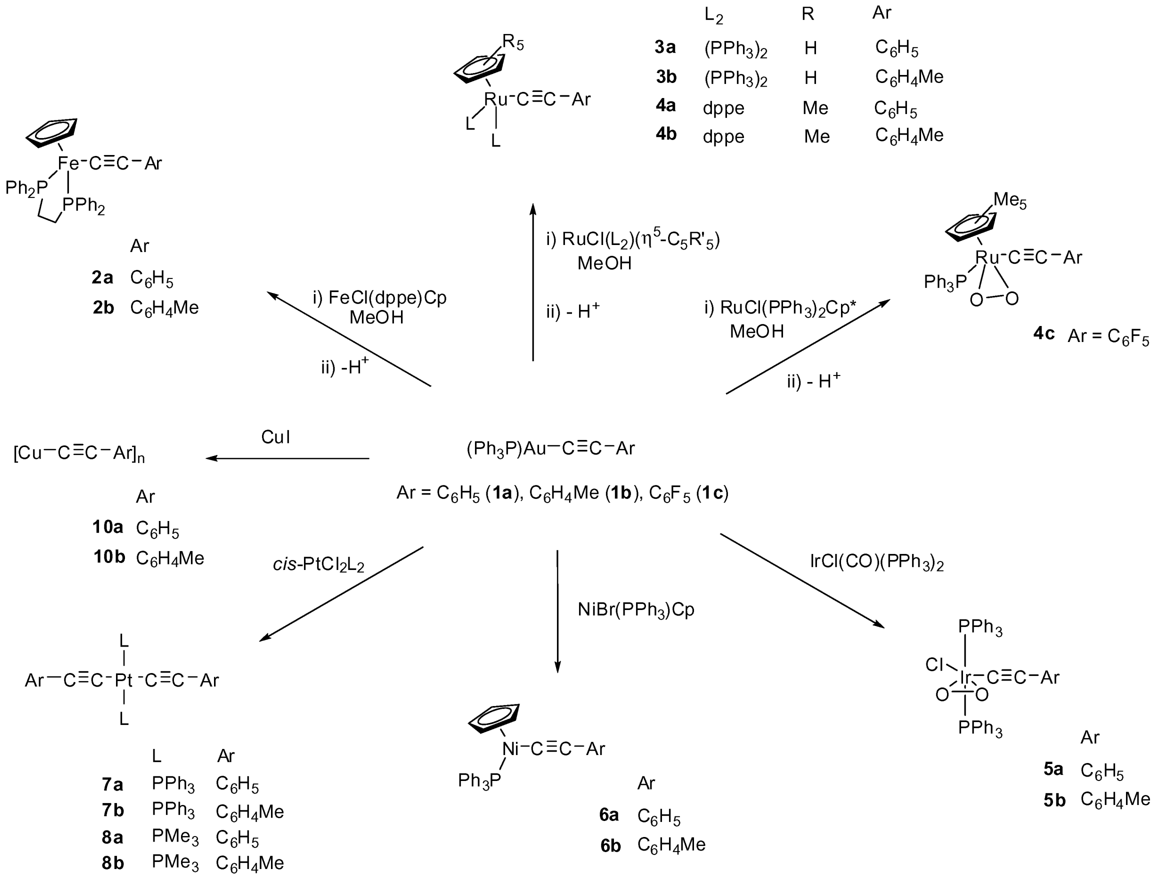
Results and discussion

Syntheses

Group 8 metal–alkynyl complexes M(C≡CR)(L$_2$)Cp′ (M = Fe, Ru, Os; L = PR$_3$; Cp′ = Cp, Cp*) have been prepared on many previous occasions.[24–26] The synthesis of such species usually takes advantage of the ready isomerisation of 1-alkynes to vinylidenes that takes place in the coordination sphere of the group 8 metal centre.[27] The resulting cationic vinylidene complexes [M{C=C(H)R}(L$_2$)Cp′]$^+$ are acidic, and deprotonation occurs readily to give the corresponding acetylide. Whilst the 1-alkyne–vinylidene–alkynyl conversion has proven to be immensely useful in the preparation of metal alkynyl complexes of the type M(C≡CR)(L$_2$)Cp′, it is limited to the use of stable 1-alkynes. Alternative synthetic routes to metal alkynyl and polyynyl complexes from trimethylsilyl-protected alkynes and polyynes based on desilylation/metallation routes have also been developed.[28]

The complexes Fe(C≡CAr)(dppe)Cp [Ar = C$_6$H$_5$ (**2a**) and C$_6$H$_4$Me-4 (**2b**)] were prepared from the reaction between FeCl(dppe)Cp and Au(C≡CAr)(PPh$_3$) [Ar = C$_6$H$_5$ (**1a**), C$_6$H$_4$Me-4 (**1b**)] in the presence of NH$_4$PF$_6$ in refluxing MeOH (see Scheme 2 for a diagrammatic representation of all reactions reported in this work). Although the solvent and salt combination was chosen to promote labilisation of the Fe–Cl bond, the protic conditions also led to formation of the vinylidenes [Fe{=C=C(H)Ar}(dppe)Cp]PF$_6$. Thus, after reaction, the resulting red solution was treated with DBU and purified by extraction into benzene and preparative TLC to give the iron–alkynyl complexes **2a** (43%) or **2b** (53%). In addition, a colourless band containing AuCl(PPh$_3$) was also collected (δ_P 34.2 ppm).[29] In the ^{13}C NMR spectra for **2a** and **2b**, the alkynyl C$_\beta$ carbons were identified as broad peaks at 120.7 and 120.3 ppm, respectively. The alkynyl C$_\alpha$ carbon resonances were very broad (unresolved J_{CP} coupling) peaks at 125.3 and 122.0 for **2a** and **2b**, respectively, with ~150 Hz width at half height. For a series of related Fe(C≡CC$_6$H$_4$X-4)(dppe)Cp* (X = NO$_2$, CN, CF, Br, F, H, Me, ^{t}Bu, OMe, NH$_2$, NMe$_2$) compounds, the C$_\alpha$ and C$_\beta$ resonances were reported as triplets with *ca.* 40 and 3 Hz coupling constants, respectively.[30]

The reactions between **1a** or **1b** and RuCl(PPh$_3$)$_2$Cp, in the presence of NH$_4$PF$_6$ or NaPF$_6$ in refluxing methanol, resulted in the formation of a red solution, also presumed to contain a vinylidene intermediate, the deprotonation of which by DBU resulted in the precipitation of the target compounds Ru(C≡CC$_6$H$_5$)(PPh$_3$)$_2$Cp (**3a**)[24] and Ru(C≡CC$_6$H$_4$Me-4)(PPh$_3$)$_2$Cp (**3b**)[31] as yellow solids in 81 and 73% yields, respectively. As might be reasonably expected,



Scheme 2

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the filtrate recovered from these reactions contained $AuCl(PPh_3)$ (δ_P 34.2 ppm).[29] The compounds $Ru(C{\equiv}CC_6H_5)(dppe)Cp^*$ (**4a**)[25] and $Ru(C{\equiv}CC_6H_4Me\text{-}4)(dppe)Cp^*$ (**4b**)[31] were obtained from similar reactions of **1a** and **1b** with $RuCl(dppe)Cp^*$.

The alkynyl–gold transmetallation reaction appears to be sensitive to the nature of the alkynyl moiety, and a reaction between $RuCl(PPh_3)_2Cp^*$ and $Au(C{\equiv}CC_6F_5)(PPh_3)$ (**1c**) afforded a multitude of products as indicated by separation into several bands upon preparative TLC. One of these bands gave crystals from hexane suitable for a single-crystal X-ray diffraction study (see below) from which the compound was identified as the dioxygen complex $Ru(C{\equiv}CC_6F_5)(\eta\text{-}O_2)(PPh_3)Cp^*$ (**4c**). The analogous hydrocarbon complex $Ru(C{\equiv}CC_6H_5)(\eta\text{-}O_2)(PPh_3)Cp^*$ is known.[32]

Although complete mechanistic details of the transmetallation reaction have not been elucidated, it is important to note that **1a** or **1b** can be recovered unchanged after treatment for 1 h in refluxing methanol containing one equivalent of NH_4PF_6. This observation would appear to discount the possible solvolysis of **1a** or **1b** to give the free alkyne, followed by the usual vinylidene formation, and supports the intermediacy of the gold reagents in the formation of the new metal–carbon bonds.

In the case of group 9 metals, alkynyl complexes such as $Ir(C{\equiv}CR)(CO)(PPh_3)_2$ have been prepared by reactions of Vaska's complex, $IrCl(CO)(PPh_3)_2$, or its NCMe derivative, with lithium acetylides or trialkylstannyl acetylenes,[3,33] and also from copper-catalysed reactions between $IrCl(CO)(PPh_3)_2$ and 1-alkynes carried out in amine solvents or in the presence of NaOMe.[8] The complexes $Ir(C{\equiv}CR)(CO)(PR'_3)_2$ readily take up oxygen to form the η^2-O_2 adducts $Ir(C{\equiv}CR)(\eta^2\text{-}O_2)(CO)(PR'_3)$. For example, the CuI-catalysed reaction between $W(C{\equiv}CC{\equiv}CH)(CO)_3Cp$ and Vaska's complex in $NHEt_2$ gave $\{Cp(CO)_3W\}(\mu\text{-}C{\equiv}CC{\equiv}C)\{Ir(CO)(PPh_3)_2\}$, which on aerobic work-up gave the η^2-O_2 adduct.[34]

In the present work, the complexes $Ir(C{\equiv}CAr)(\eta^2\text{-}O_2)(CO)(PPh_3)_2$ [Ar = C_6H_5 (**5a**),[33,35] C_6H_4Me-4 (**5b**)] were prepared by treating $IrCl(CO)(PPh_3)_2$ with **1a** or **1b** in MeOH at room temperature. The gold by-product $AuCl(PPh_3)$ was removed from the crude product by extraction with acetone. Recrystallisation (chloroform/hexane) of the yellow solid that remained after extraction under aerobic conditions afforded yellow crystals of **5a** (40%) or **5b** (52%). In order to resolve some inconsistencies in literature values relating to the ^{31}P NMR spectra and hence potentially the ν(CO) band positions associated with 16 e acetylide complexes $Ir(C{\equiv}CAr)(CO)(PPh_3)_2$,[36,37] and also to clarify the sequence of reactions leading to the dioxygen adducts $Ir(C{\equiv}CAr)(\eta^2\text{-}O_2)(CO)(PPh_3)_2$ obtained here, the transmetallation/oxidation reaction sequence was followed by ^{31}P NMR and IR spectroscopy. Under anaerobic conditions, reaction solutions of **1a** and Vaska's complex rapidly developed new ^{31}P resonances at 34.2 and 25.2 ppm corresponding to $AuCl(PPh_3)$[29] and $Ir(C{\equiv}CC_6H_5)(CO)(PPh_3)_2$, respectively. The ν(CO) band of the acetylide complex (1962 cm^{-1}) is almost coincident with that of Vaska's complex, although the ν(C≡C) band is distinct (2128 cm^{-1}). Exposure of the reaction solution to air resulted in the rapid disappearance of the δ_P 25.2 ppm peak and the appearance of a peak at 8.3 ppm corresponding to $Ir(C{\equiv}CPh)(\eta^2\text{-}O_2)(CO)(PPh_3)_2$ **5a**, consistent with spectroscopic analysis of the crystallographically characterised sample of **5b**. The IR spectrum of **5a** is characterised by ν(CO) and ν(C≡C) bands at 2005 and 2134 cm^{-1}, respectively.

These spectroscopic data from $Ir(C{\equiv}CC_6H_5)(CO)(PPh_3)_2$ observed *in situ* and authentic samples of **5a** can be compared with those reported for $Ir(C{\equiv}CC_6H_5)(CO)(PPh_3)_2$ ($\delta_P < 10$ ppm, ν(CO) *ca.* 1960 cm^{-1}) by two independent research groups,[38,39] and $Ir\{C{\equiv}CC(CH_2CH_2Ph)_2Me\}(CO)(PPh_3)_2$ (δ_P *ca.* 22 ppm, ν(CO) 1970 cm^{-1}).[40] It appears that the ^{31}P NMR spectra reported previously for $Ir(C{\equiv}CC_6H_5)(CO)(PPh_3)_2$ are actually that of the η^2-O_2 containing species **5a**, although the IR data in the earlier reports are consistent with the proposed 16 e species. It can be concluded that the characteristic ^{31}P resonances for $Ir(C{\equiv}CR)(CO)(PPh_3)_2$ and $Ir(C{\equiv}CR)(\eta^2\text{-}O_2)(CO)(PPh_3)_2$ compounds are found at *ca.* 25 ppm and *ca.* 5 ppm, respectively. These parameters are consistent with those found for other $Ir(R)(CO)(PPh_3)_2$ and $Ir(R)(\eta^2\text{-}O_2)(CO)(PPh_3)_2$ systems.[41]

Group 10 alkynyl complexes have been prepared on numerous occasions, being among the earliest metal–alkynyl complexes characterised.[42] Whilst early synthetic routes took advantage of nucleophilic reactions between alkynyl anions (as lithium salts or Grignard reagents), later developments have given rise to more convenient preparations involving CuI-catalysed reactions between, for example, $MCl_2(PR_3)_2$ and 1-alkynes.[8]

The reaction of **1a** or **1b** with $NiBr(PPh_3)Cp$ in THF resulted in the formation of a green solution, from which $Ni(C{\equiv}CC_6H_5)(PPh_3)Cp$ (**6a**)[42] or the new complex $Ni(C{\equiv}CC_6H_4Me\text{-}4)(PPh_3)Cp$ (**6b**) were obtained in 53 and 42% yields, respectively, after preparative TLC and recrystallisation. In addition, a colourless band from preparative TLC that contained the expected by-product $AuBr(PPh_3)$ was also collected (δ_P 36.3 ppm).[29]

The complexes *trans*-$Pt(C{\equiv}CAr)_2(PPh_3)_2$ [Ar = C_6H_5 (**7a**), C_6H_4Me-4 (**7b**)[8]] were prepared from room temperature reactions between *cis*-$PtCl_2(PPh_3)_2$ and **1a** or **1b** in methanol, which gave the products as pale cream coloured precipitates, whilst $AuCl(PPh_3)$ was recovered from the filtrate.‡ The ^{31}P NMR spectra contain singlet phosphine resonances, each accompanied by platinum satellites, confirming the *trans* geometry in each case. The complexes *trans*-$Pt(C{\equiv}CAr)_2(PMe_3)_2$ [Ar = C_6H_5 (**8a**), C_6H_4Me-4 (**8b**)] were isolated from similar reactions between *cis*-$PtCl_2(PMe_3)_2$ and **1a** or **1b** in methanol, which gave the products as pale green precipitates. Single crystals of **8b** suitable for X-ray diffraction were obtained by recrystallisation ($CHCl_3$/MeOH).

The room temperature reaction of **1a** with a large excess of *cis*-$PtCl_2(PMe_3)_2$ in the presence of NH_4PF_6 in methanol resulted in a myriad of products. The solids obtained after removal of the solvent included *trans*-$PtCl(C{\equiv}CC_6H_5)(PMe_3)_2$ and *trans*-$PtCl(C{\equiv}CC_6H_5)(PMe_3)(PPh_3)$, which were identified by NMR spectrocopy and MS spectrometry. Crystallisation of the solids from MeCN/MeOH gave crystals of a Au(I) salt $[Au(PMe_3)_2]PF_6$ (**9**).[43] Thus, it appears that phosphine exchange, competitive with the acetylide–halide exchange processes noted above, may also take place under certain conditions.

Given the established utility of copper acetylides in the preparation of many transition metal acetylide complexes, we were

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‡ In the process of crystallization of the complex **7b**, crystals of previously unknown chloroform di-solvate of *trans*-$PtCl_2(PPh_3)_2$ were isolated and structurally studied.†

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Table 1 Crystallographic and refinement details†

Complex	**2b**	**4b**	**4c**	**5b**	**6b**	**7a**	**7b**	**8b**
Formula	$C_{40}H_{36}FeP_2\cdot CH_2Cl_2$	$C_{45}H_{46}P_2Ru$	$C_{36}H_{30}F_5O_2PRu\cdot 0.25C_6H_{14}$	$C_{46}H_{37}IrO_3P_2\cdot CHCl_3$	$C_{32}H_{27}NiP$	$C_{52}H_{40}P_2Pt$	$C_{54}H_{44}P_2Pt$	$C_{24}H_{32}P_2Pt$
MW	676.94	749.83	743.2	1011.3	501.22	921.9	949.9	577.5
Crystal system	Triclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P2_1/n$	$Pbca$	$P2_1/n$	$P2_1/c$
T/K	120(2)	120(2)	100(2)	120(2)	120(2)	120(2)	120(2)	120(2)
a/Å	9.5283(2)	15.4106(3)	13.027(4)	9.7735(3)	14.1937	17.9771(3)	13.5550(2)	12.3805(5)
b/Å	18.2097(4)	11.2059(2)	16.959(5)	19.5550(4)	12.6191(4)	9.5527(1)	8.5121(1)	5.7372(2)
c/Å	19.3123(4)	22.1850(4)	17.133(6)	22.3273(6)	14.9549(4)	22.9326(3)	18.0271(3)	17.1229(7)
α/°	93.20(2)	90	111.86(3)	90	90	90	90	90
β/°	93.13(2)	108.33(1)	106.93(3)	99.18(2)	110.05(1)	90	90.30(1)	105.86(1)
γ/°	97.83(2)	90	93.67(2)	90	90	90	90	90
V/Å^3	3307.85(12)	3636.75(12)	3297(2)	4212.6(2)	2516.19(13)	3938.2(1)	2079.97(5)	1169.92(8)
Z	4	4	4	4	4	4	2	2
ρ_c/g cm^{-3}	1.359	1.369	1.497	1.595	1.323	1.555	1.517	1.639
μ(MoKα)/mm^{-1}	0.662	0.551	0.59	3.5	0.853	3.7	3.5	6.1
N_t	71 399	48 050	27 359	37 675	34 844	51 715	25 528	10 382
N (R_{int})	18 098 (0.041)	10 598 (0.045)	11 685 (0.089)	9167 (0.116)	7062 (0.029)	5741 (0.045)	5541 (0.035)	3307 (0.025)
R_1 [$I > 2\sigma(I)$]	0.040	0.033	0.063	0.070	0.029	0.018	0.017	0.018
wR_2 (all data)	0.097	0.093	0.076	0.120	0.079	0.051	0.041	0.041
GOF	1.088	1.063	0.953	1.087	1.017	1.053	1.095	1.098

interested in the interplay between acetylide ligands and Cu(I) and Au(I) centres. The reaction between **1a** or **1b** and CuI in THF afforded striking, bright yellow-coloured precipitates of the copper acetylides $\{Cu(C{\equiv}CAr)\}_n$ [Ar = C_6H_5 (**10a**), C_6H_4Me-4 (**10b**)] in very good yields with AuI(PPh_3) recovered from the filtrate as a cream-coloured solid (δ_P 40.0 ppm).[29]

Molecular structures

The molecular structures of a number of the compounds prepared in this work (**2b**, **4b**, **4c**, **5b**, **6b**, **7a**, **7b** and **8b**) have been determined by single-crystal X-ray diffraction studies. The crystallographic data are summarised in Table 1.

Crystals of Fe(C≡CC_6H_4Me-4)(dppe)Cp (**2b**), obtained from CH_2Cl_2/hexane solutions, contain two independent molecules, which differ by the relative orientation of the phenyl rings on the dppe ligand, together with a molecule of CH_2Cl_2. There are no differences of chemical significance in the two independent molecules, and the geometrical parameters of only one molecule will be used in further discussion here. Although there are many examples of crystallographically characterized arylacetylide complexes of the Fe(dppe)Cp* fragment in both formal Fe(II) and Fe(III) oxidation states,[30,44–48] polymetallic compounds[45,49] and mixed valence examples,[44,50] there are surprisingly few structures of similar compounds containing the Fe(dppe)Cp[51,52] or Fe(dppm)Cp[53] fragments reported to date.

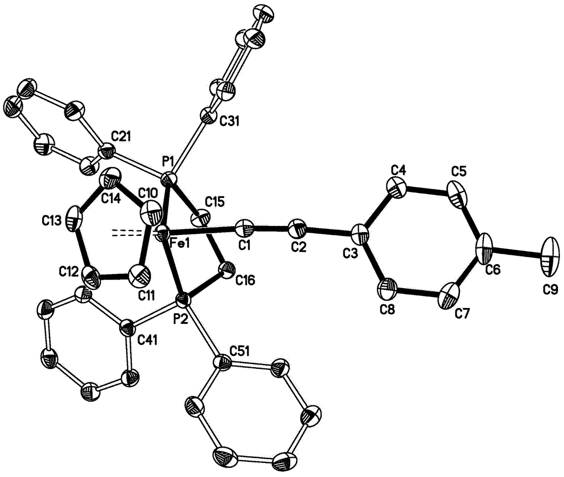

Fig. 1 A plot of one molecule of Fe(C≡CC_6H_4Me-4)(dppe)Cp (**2b**), showing the atom labelling scheme. Hydrogen atoms in this and other figures are removed for clarity. Selected bond lengths (Å) and angles (°): Fe(1)–C(1) 1.907(2); Fe(1)–P(1) 2.1687(6); Fe(1)–P(2) 2.1714(7); C(1)–C(2) 1.220(2); C(2)–C(3) 1.439(2); P(1)–Fe(1)–P(2) 85.95(2); C(1)–Fe(1)–P(1) 90.19(5); C(1)–Fe(1)–P(2) 84.28(5); Fe(1)–C(1)–C(2) 174.93(15); C(1)–C(2)–C(3) 174.84(17).

Complex **2b** (Fig. 1) offers a pseudo-octahedral environment at the metal centre, typical of three-legged piano-stool complexes. The Fe(1)–C(1) [1.907(2) Å], C(1)≡C(2) [1.220(2) Å] and C(2)–C(3) [1.439(2) Å] bond lengths in **2b** are indistinguishable from those found in Fe(C≡CC_6H_4-Me)(dppe)Cp* [Fe–C_α 1.896(3), $C_\alpha{\equiv}C_\beta$ 1.220(4), C_β-C_{ipso} 1.440(4) Å],[47] but somewhat surprisingly the Fe–P bonds in **2b** [2.1687(6) and 2.1714(7) Å], and related compounds,[51] are shorter than in the Cp* analogue [2.1829(8) and 2.1924(7) Å]. Since the more electron-rich, Cp*-substituted metal fragment might be expected to induce more effective Fe–P back-bonding, the relatively elongated Fe–P bonds in Fe(C≡CC_6H_4-Me)(dppe)Cp* might be taken as an indication of steric interactions between the bulky Cp* and dppe ligands. The Fe(1)–C(1)–C(2)–C(3) fragment in **2b** is essentially linear, with small deviations likely to be due to packing effects rather than any profound electronic phenomenon. The plane containing the C(3)–C(8) aromatic ring forms a dihedral angle of 38.6(1)° with the plane of the Cp ring; the significance of the aryl group orientation on the electronic structure of iron aryl acetylide complexes has been discussed elsewhere.[48]

The disposition of the tolyl ring with respect to the metal fragment in the ruthenium complex **4b** (Fig. 2) is similar to that found in **2b**. The Ru(1)–C(1) bond length [2.0205(19) Å] is somewhat longer than in **2b**, reflecting the difference in the covalent

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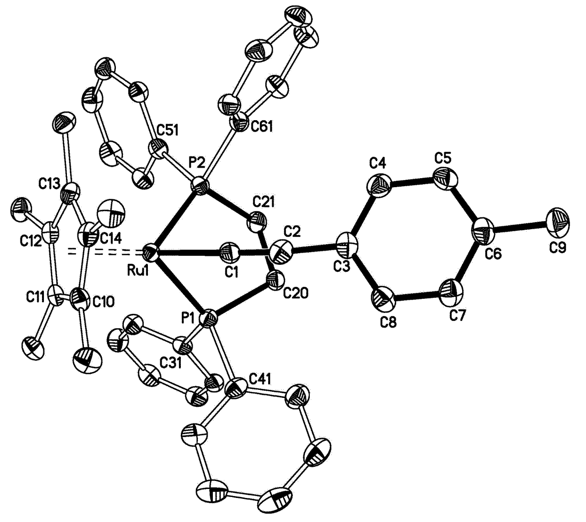

Fig. 2 A plot of one molecule of Ru(C≡CC$_6$H$_4$Me-4)(dppe)Cp* (**4b**), showing the atom labelling scheme. Selected bond lengths (Å) and angles (°): Ru(1)–C(1) 2.0205(19); Ru(1)–P(1) 2.2621(5); Ru(1)–P(2) 2.2622(5); C(1)–C(2) 1.211(3); C(2)–C(3) 1.437(3); P(1)–Ru(1)–P(2) 83.15(2); C(1)–Ru(1)–P(1) 79.22(5); C(1)–Ru(1)–P(2) 85.20(6); Ru(1)–C(1)–C(2) 175.5(2); C(1)–C(2)–C(3) 171.9(2).

radii of the two metals,[54] but within the range noted for similar compounds, including **4a**, noted here and elsewhere.[55] Other metric parameters are unremarkable (Fig. 2).

The molecular structure of Ru(C≡CC$_6$F$_5$)(η^2-O$_2$)(PPh$_3$)Cp* (**4c**) (Fig. 3) is formally related to that of Ru(C≡CC$_6$H$_5$)(η-O$_2$)(PPh$_3$)Cp* by replacement of the C$_6$H$_5$ group on the acetylide ligand by C$_6$F$_5$. Two molecules of the complex **4c**, devoid of crystallographic symmetry, together with one half of a centrosymmetric hexane solvent molecule, comprise the asymmetric unit of the structure. The two independent molecules differ slightly by orientations of one of the phenyl rings and C$_6$F$_5$ group. Structural parameters are similar to those found for many other examples of half-sandwich ruthenium alkynyl complexes characterised here and elsewhere. The dioxygen molecule is unsymmetrically attached to Ru [Ru–O(1;2) 2.042(4), 2.039(4); 1.998(4), 2.019(4) Å], probably as a result of differing *trans* influences of the P and C(1) atoms. The O(1)–O(2) separations are 1.404(4) and 1.400(4) Å. These values are similar to those found in the related non-fluorinated complex Ru(C≡CC$_6$H$_5$)(η^2-O$_2$)(PPh$_3$)Cp*, which has Ru–P 2.327(1), Ru–C(cp) 2.25 (av.), Ru–C(1) 2.022(4), C(1)–C(2) 1.158(5), C(2)–C(21) 1.467(5) and Ru–O 2.032(3), 2.048(3), O–O 1.364(4) Å.[32] In both complexes, the Ru–O distances are longer, and the O–O distances shorter, than those found in related cations, such as [Ru(η^2-O$_2$)(dppm)Cp*]$^+$, which has Ru–O 2.003(9), 2.002(9), O–O 1.37(1) Å.[56]

Although dioxygen adducts of Vaska's complex and derivatives are well known, crystallographically characterised examples are surprisingly rare,[41,57,58] and to the best of our knowledge, the diyndiyl complex {(PPh$_3$)(CO)(η^2-O$_2$)Ir}(μ-C≡CC≡C){W(CO)$_3$Cp} is the only example of a dioxygen adduct of a Vaska-type acetylide derivative that has been structurally characterised to date.[34] However, given the relatively low precision of the diyndiyl structure, **5b** is most conveniently compared with IrCl(η^2-O$_2$)(CO)(PPh$_3$)$_2$[59] and Ir(C≡CC$_6$H$_5$)(CO)(PPh$_3$)$_2$.[39]

The structure of the complex **5b** (Fig. 4) can be described in terms of a five-coordinate, trigonal bipyramid, if the O$_2$ ligand is assumed to occupy a single coordination site, with C(1), C(4) and the midpoint of the O$_2$ ligand defining the equatorial plane [C(1)–Ir(1)–C(4) 94.5(4), C(1)–Ir(1)–O(0) 137, C(4)–Ir(1)–O(0) 128° (O(0) is the midpoint of the O–O bond)]. Alternatively, the structure may be viewed as a highly distorted octahedron[58–60] in keeping with a formal description of the complex in terms of an Ir(III)-peroxo complex. The O–O bond is long [1.492(9) Å] and the Ir–P bonds [Ir(1)–P(1,2) 2.351(2) and 2.350(2) Å] are slightly elongated in comparison with those in the well defined Ir(I) acetylide complex Ir(C≡CC$_6$H$_5$)(CO)(PPh$_3$)$_2$ [2.286(7)–2.313(9) Å

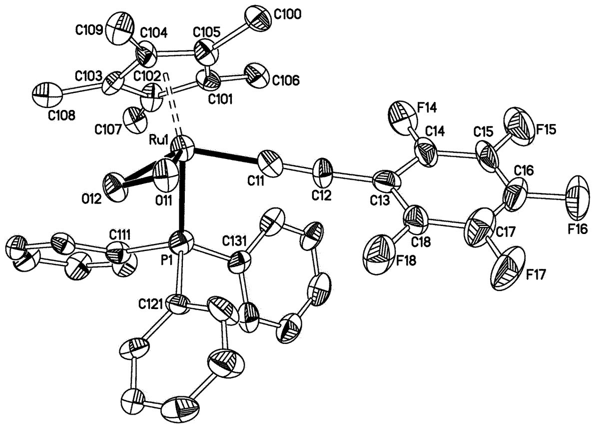

Fig. 3 A projection of one molecule of Ru(C≡CC$_6$F$_5$)(η^2-O$_2$)(PPh$_3$)Cp (**4c**). Selected bond lengths (Å) and angles (°) for two independent molecules: Ru–P(1) 2.328(2), 2.313(2); Ru–C(Cp) 2.214–2.273(6), 2.202–2.289(6) [<av.> 2.24(3), 2.25(4)]; Ru–C(1) 1.997(6), 2.006(7); C(1)–C(2) 1.187(7), 1.198(7); C(2)–C(3) 1.429(8), 1.455(8); P(1)–Ru–C(1) 85.0(2), 82.2(2); Ru–C(1)–C(2) 178.7(6), 178.8(6); C(1)–C(2)–C(3) 176.0(7), 177.6(7).

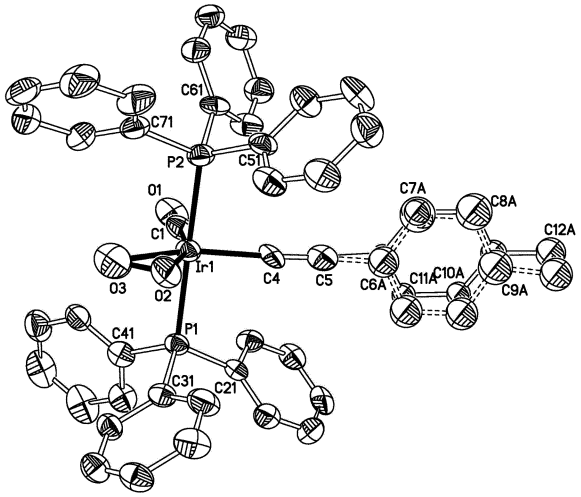

Fig. 4 Molecular structure of Ir(C≡CC$_6$H$_4$Me)(η^2-O$_2$)(CO)(PPh$_3$)$_2$ (**5b**). Selected bond lengths (Å) and angles (°): Ir–P(1) 2.351(2); Ir–P(2) 2.350(2); Ir–C(1) 1.844(10); Ir–C(4) 2.011(10); C(4)–C(5) 1.186(12); C(5)–C(6A) 1.466(16); C(5)–C(6B) 1.484(18); Ir–O(2) 2.030(7); Ir–O(3) 2.036(7); O(2)–O(3) 1.492(9); P(1)–Ir–P(2) 175.58(8); C(1)–Ir–C(4) 94.5(4); C(4)–Ir–O(2) 106.9(3); C(4)–Ir–O(3) 149.8(3); C(1)–Ir–O(3) 115.7(4); Ir–C(4)–C(5) 177.4(7); C(4)–C(5)–C(6A)172.5(12); C(4)–C(5)–C(6B) 178.3(12).

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over two independent molecules], and similar to those in IrCl(η^2-O_2)(CO)(PPh_3)$_2$ [2.38(1), 2.36(1) Å]. Thus, whilst formalised descriptions of metal oxidation states in organometallic chemistry are not always especially useful, it seems appropriate to consider **5b** and compounds of this type as Ir(III), with a significant distortion from the trigonal bipyramidal geometry towards an octahedral structure.

The molecular structures of nickel(II) complexes Ni(C≡CR)-(PPh_3)Cp have been studied on previous occasions, with data often interrogated for evidence of the nature of the metal–acetylide bond.[61,62] The structure of **6a** has been reported by the Humphrey group,[61] and unsurprisingly, the structure of **6b** (Fig. 5) is similar. The Ni(1)–C(1) bond lengths in **6a** [1.856(3), 1.850(3) Å] and **6b** [1.8537(14) Å] are indistinguishable, and whilst there is greater variation in the lengths of the Ni(1)–P(1) [**6a** 2.1350(9), 2.1378(9); **6b** 2.1456(3) Å] and C(1)≡C(2) [**6a** 1.191(4), 1.193(4); **6b** 1.2150(19) Å] bonds, the parameters associated with **6b** fall within the ranges defined by many other similar compounds. The Ni(1)–C(1)–C(2)–C(3) moiety is essentially linear with angles at C(1) and C(2) being 175.1(1) and 172.2(1)°, respectively.

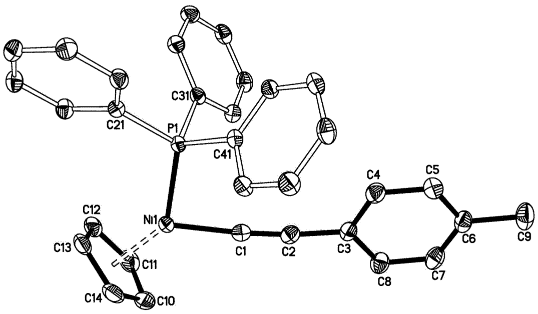

Fig. 5 A plot of a molecule of Ni(C≡CC_6H_4Me-4)(PPh_3)Cp (**6b**). Selected bond lengths (Å) and angles (°): Ni(1)–P(1) 2.1456(3); Ni(1)–C(1) 1.8537(14); C(1)–C(2) 1.2150(19); C(2)–C(3) 1.4416(18); C(1)–Ni(1)–P(1) 89.10(4); Ni(1)–C(1)–C(2) 175.1(1); C(1)–C(2)–C(3) 172.2(1).

In each of the Pt(II) complexes **7a** (Fig. 6) and **7b** (Fig. 7), the metal atoms of the molecules are located in special positions at the crystallographic inversion centre, the platinum centres being in square-planar arrangements, with bond lengths comparable to those in many other similar platinum bis(acetylide) complexes.[63] The ethynyl moieties are essentially linear [Pt(1)–C(1)–C(2) 172.78(15) (**7a**); 175.9(2) (**7b**)°, C(1)–C(2)–C(3) 173.27(18) (**7a**); 177.32(18) (**7b**)°] and the acetylenic (C≡C) and Pt(1)–C(1) bond lengths fall in a narrow range [1.188(2)–1.207(2) and 2.0017(17)–2.0252(17) Å, respectively] typical for these systems.

While there are examples of platinum bis(acetylide) complexes known, there is only one previous example of the structurally characterised *trans*-Pt(C≡CR)$_2$(PMe_3)$_2$ system.[64] A comparison of the structural parameters of **8b** (Fig. 8) and the Pt moiety in the cyclic heteronuclear complex [{Au{Pt(PMe_3)$_2$}$_2$}{1,2-μ-C_6H_4(C≡C)$_2$}$_3$] reveals little differences and indicates that the constraining effect at the Pt atom in the cyclic complex is negligible. The change of the phosphine ligand in **7b** and **8b** has little effect on the overall molecular structure.

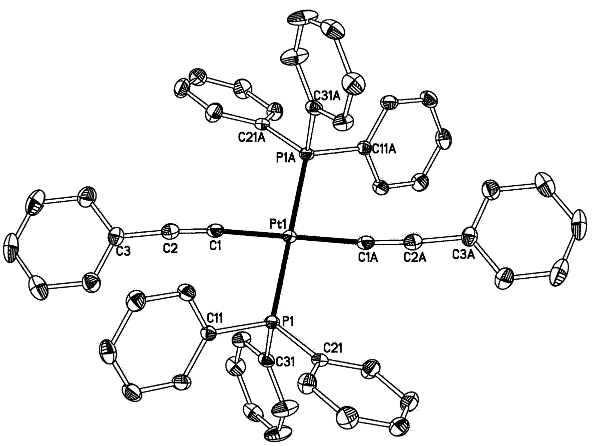

Fig. 6 A projection of the molecular structure of centrosymmetric *trans*-Pt(C≡CC_6H_5)$_2$(PPh_3)$_2$ (**7a**). Selected bond lengths (Å) and angles (°): Pt–P(1) 2.3121(4); Pt–C(1) 2.0017(17); C(1)–C(2) 1.207(2); C(2)–C(3) 1.441(2); P(1)–Pt–C(1) 93.27(5); Pt–C(1)–C(2) 172.78(15); C(1)–C(2)–C(3) 173.27(18). [symmetry operations (−*x*, 1 − *y*, −*z*)].

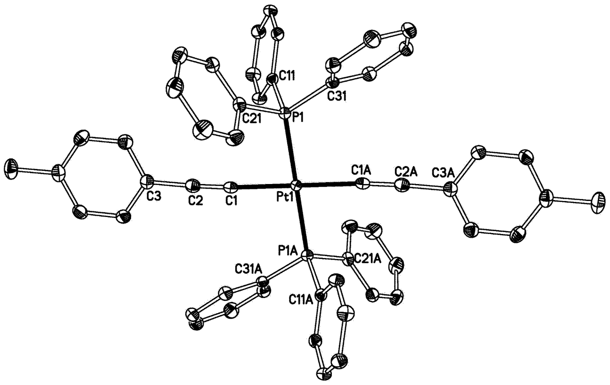

Fig. 7 The molecular structure of centrosymmetric *trans*-Pt(C≡CC_6H_4Me)$_2$(PPh_3)$_2$ (**7b**). Selected bond lengths (Å) and angles (°): Pt–P(1) 2.2887(4); Pt–C(1) 2.0252(17); C(1)–C(2) 1.188(2); C(2)–C(3) 1.445(2); P(1)–Pt–C(1) 85.90(5); Pt–C(1)–C(2) 175.88(15); C(1)–C(2)–C(3) 177.32(18). [symmetry operations (1 − *x*, −*y*, −*z*)].

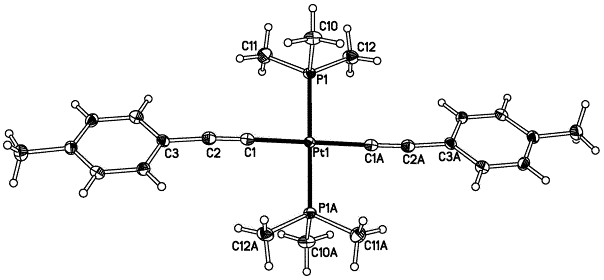

Fig. 8 A plot of a molecule of centrosymmetric *trans*-Pt(C≡CC_6H_4Me)$_2$(PMe_3)$_2$ (**8b**). Selected bond lengths (Å) and angles (°): Pt–P(1) 2.2929(6); Pt–C(1) 2.0001(3); C(1)–C(2) 1.214(4); C(2)–C(3) 1.437(3); P(1)–Pt–C(1) 89.55(7); Pt–C(1)–C(2) 178.7(2); C(1)–C(2)–C(3) 175.3(3). [symmetry operations (1 − *x*, 2 − *y*, −*z*)].

Considering the intermolecular interactions in these three platinum complexes, stacking-type $\pi\cdots\pi$ interactions between tolyl groups were observed only in the structure **7b** (Fig. 9) (interplanar distance is equal to 3.64 Å) where they are combined with additional CH(Me)$\cdots$C(sp) close intermolecular contacts (C$\cdots$H 2.83 Å). In molecule **7a**, no methyl groups are present while in the structure **8b**, trimethylphosphine groups take part in intermolecular CH$\cdots\pi$ contacts and impede parallel arrangement of tolyl groups. It seems that in the case of these Pt complexes,

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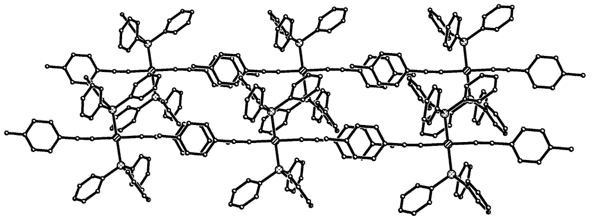

Fig. 9 A fragment of the crystal structure of (**7b**) showing the stacking interactions between tolyl groups.

stacking interactions alone are insufficient to determine the packing of molecules in the crystal.

The series of acetylide complexes reported here all feature small deviations from linearity along the M–C≡C–C$_{Ar}$ chain, which are consequently gently curved or bowed. In a comprehensive review of polyyne conformation and structure, Szafert and Gladysz have noted a lack of systematic variation in structure within the solid state within a large array of yne-based compounds.[65] Given the low bending force constants associated with M–C≡C and C≡C–C, crystal packing effects are thought likely to be responsible for the specific conformation adopted by any one compound.

Finally, we note that while our work was in progress, the structure of **9** was independently reported by Horvarth and Raubenheimer.[43] The conclusions drawn by these authors are consistent with our own observations from an essentially identical structure determination, and no further comment is necessary.

Conclusions

A series of preparative scale, stoichiometric transmetallation reactions involving alkynyl–gold(I) complexes, Au(C≡CR)(PPh$_3$) (R = Ph, C$_6$H$_4$Me-4), and inorganic or organometallic compounds MXL$_n$ (M = metal, X = halide, L$_n$ = supporting ligands), have afforded the corresponding metal alkynyl complexes M(C≡CR)L$_n$, (35–90% yields), with representative examples featuring metals from groups 8–11 being described for the first time. The alkynyl products were fully characterised by the usual spectroscopic methods and molecular structural analyses in several cases. Looking ahead, we note that easily prepared phosphine–gold(I) complexes featuring highly conjugated carbon-rich and all-carbon ligands are known, and which are usually easier and safer to handle than their analogous protio, lithio, tin, copper, mercury or Grignard derivatives. The AuX(PPh$_3$) by-products can be isolated from the reaction mixture and recycled. The transmetallation process has not been as successful with Au(C≡CC$_6$F$_5$)(PPh$_3$) based on one exploratory reaction here. Further investigations are desirable with other Au(C≡CAr)(PR$_3$) complexes to assess the generality of the alkynyl–gold transmetallation process and also to understand the alkynyl–gold transmetallation mechanism.

Experimental

All reactions were carried out under an atmosphere of nitrogen using standard Schlenk techniques. Reaction solvents were purified and dried using an Innovative Technology SPS-400 system, and degassed before use. No special precautions were taken to exclude air or moisture during work-up. Preparative TLC was performed on 20 × 20 cm glass plates coated with silica gel (0.5 mm thick, Merck GF-254). The reagents FeCl(dppe)Cp,[66] RuCl(PPh$_3$)$_2$Cp,[67] RuCl(PPh$_3$)$_2$Cp*,[32] RuCl(dppe)Cp*,[68] NiBr(PPh$_3$)Cp,[69] *cis*-PtCl$_2$(PPh$_3$)$_2$,[70] *cis*-PtCl$_2$(PMe$_3$)$_2$,[71] IrCl(CO)(PPh$_3$),[72] Au(C≡CC$_6$H$_5$)(PPh$_3$) (**1a**),[18] Au(C≡CC$_6$H$_4$Me-4)(PPh$_3$) (**1b**)[18] and Au(C≡CC$_6$F$_5$)(PPh$_3$) (**1c**)[18] were prepared by literature methods. Other reagents were purchased and used as received.

IR spectra were recorded from dichloromethane solutions in a cell fitted with CaF$_2$ windows, from KBr discs, or from Nujol mulls between NaCl plates using a Nicolet Avatar spectrometer. NMR spectra were obtained with Bruker Avance and Varian Mercury spectrometers from CDCl$_3$ solutions and referenced against solvent resonances (^{1}H, ^{13}C) or external H$_3$PO$_4$ (^{31}P). The ^{31}P chemical shift values for the gold starting materials **1a** and **1b** are at 43.4 ppm. Mass spectra were recorded using Thermo Quest Finnigan Trace MS-Trace GC or Thermo Electron Finnigan LTQ FT mass spectrometers.

Preparation of Fe(C≡CC$_6$H$_5$)(dppe)Cp (2a)

A suspension of FeCl(dppe)Cp (50 mg, 0.09 mmol), **1a** (51 mg, 0.09 mmol) and NH$_4$PF$_6$ (15 mg, 0.09 mmol) in MeOH (10 ml) was heated at reflux for *ca.* 1 h, the progress of the reaction being monitored by TLC (hexane–acetone = 7 : 3). The resulting clear orange solution was treated with 2–3 drops of DBU and the reaction mixture was taken to dryness. The crude solid was extracted with benzene, and the extracts purified by preparative TLC (hexane–acetone = 7 : 3). The red band was collected and afforded **2a** (24 mg, 43%). IR (CH$_2$Cl$_2$) ν/cm^{-1}: (C≡C) 2060. ^{1}H NMR δ/ppm: 2.23 (m, 2H, dppe), 2.63 (m, 2H, dppe); 4.25 (s, 5H, Cp), 6.49 (2H, d, phenyl C2H of C≡CC$_6$H$_5$), 6.81 (1H, t, C4H), 6.92 (2H, dd, C3H), 7.26 (m, 10H, dppe), 7.41 (m, 6H, dppe), 7.94 (m, 4H, dppe). ^{31}P{^{1}H} NMR δ/ppm: 107.5 (s, dppe). ^{13}C{^{1}H} NMR δ/ppm: 28.6 (m, dppe CH$_2$); 79.3 (Cp); 120.7 (C$_\beta$); 123.1 (C4), 125.3 (br, C$_\alpha$), 127.5 (C3); 127.8, 128.1 (dd, $^3J_{CP}$,$^5J_{CCP}$~5 Hz, C$_{m,m'}$); 129.0, 129.4 (C$_{p,p'}$); 130.1 (C1); 130.5 (C2); 132.0, 134.0 (dd, $^2J_{CP}$,$^4J_{CCP}$~5, C$_{o,o'}$); 138.2, 142.5 (m, C$_{i,i'}$). Found: C 75.2, H 5.6%. C$_{39}$H$_{34}$P$_2$Fe requires: C 75.5, H 5.5%. ES-MS: *m*/*z* 621 [M + H]$^+$, 519 [M − C≡CPh]$^+$. High resolution calculated for FeC$_{39}$H$_{34}$P$_2$: [M]$^+$: 620.14797; found: 620.14757.

Preparation of Fe(C≡CC$_6$H$_4$Me-4)(dppe)Cp (2b)

Complex **2b** (62 mg, 54%) was formed from FeCl(dppe)Cp (100 mg, 0.18 mmol), **1b** (103 mg, 0.18 mmol) and NH$_4$PF$_6$ (30 mg, 0.18 mmol) in MeOH (20 mL) using a similar procedure as described for **2a**. Crystals of **2b** suitable for X-ray crystallography were grown from slow diffusion of hexane into a CH$_2$Cl$_2$ solution. IR (CH$_2$Cl$_2$) ν/cm^{-1}: (C≡C) 2067. ^{1}H NMR δ/ppm: 2.16 (s, 3H, CH$_3$), 2.21 (m, 2H, dppe), 2.60 (m, 2H, dppe), 4.23 (s, 5H, Cp), 6.38 (2H, d, tolyl C2H), 6.72 (2H, dd, C3H), 7.26 (m, 10H, dppe), 7.40 (m, 6H, dppe), 7.93 (m, 4H, dppe). ^{31}P{^{1}H} NMR δ/ppm: 107.3 (s, dppe). ^{13}C{^{1}H} NMR δ/ppm: 21.0 (s, CH$_3$), 28.3 (m, dppe CH$_2$), 78.9 (Cp), 120.3 (C$_\beta$), 122.0 (br, C$_\alpha$), 126.9 (C1), 127.5, 127.8 (dd, $^3J_{CP}$,$^5J_{CCP}$~5 Hz, C$_{m,m'}$), 128.0 (C3), 128.6, 129.0 (C$_{p,p'}$), 130.0 (C2), 132.3 (C4), 131.7, 133.7 (dd, $^2J_{CP}$,$^4J_{CCP}$~5, C$_{o,o'}$), 138.1, 142.3 (m, C$_{i,i'}$). Found: C 75.6, H 5.7%. C$_{40}$H$_{36}$P$_2$Fe requires: C 75.7, H 5.7%. ES-MS(+): *m*/*z* 635 [M + H]$^+$.

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Preparation of Ru(C≡CC$_6$H$_5$)(PPh$_3$)$_2$Cp (3a)

A suspension of RuCl(PPh$_3$)$_2$Cp (100 mg, 0.14 mmol), **1a** (77 mg, 0.14 mmol) and NH$_4$PF$_6$ (22 mg, 0.14 mmol) in MeOH (10 mL) was heated at reflux point for 30 min to form a bright red solution. Addition of 2–3 drops of DBU caused a yellow precipitate to form, which was collected by filtration, washed with cold MeOH (3 mL), and air-dried to afford **3a** as a yellow solid (88 mg, 81%) and characterised by comparison of spectroscopic data with those reported elsewhere.[24,31]

Preparation of Ru(C≡CC$_6$H$_4$Me-4)(PPh$_3$)$_2$Cp (3b)

Complex **3b** (84 mg, 74%) was formed from **1b** and RuCl(PPh$_3$)$_2$Cp, using a similar procedure to that described for **3a**, and identified by comparison with an authentic sample.[31]

Preparation of Ru(C≡CC$_6$H$_5$)(dppe)Cp* (4a)

A suspension of RuCl(dppe)Cp* (100 mg, 0.15 mmol), **1a** (84 mg, 0.15 mmol) and NH$_4$PF$_6$ (24 mg, 0.15 mmol) in MeOH (10 mL) was heated at reflux point for 1 h to form a bright red solution, which was treated with 2–3 drops of DBU and allowed to stir for a further 1 h. The yellow precipitate that formed over this time was collected by filtration, washed with cold MeOH (3 mL), and air-dried to afford **4a** as a yellow solid (56 mg, 51%). Characterisation data for **4a** were identical to that reported elsewhere.[31,55]

Preparation of Ru(C≡CC$_6$H$_4$Me-4)(dppe)Cp* (4b)

Complex **4b** was prepared (63 mg, 56%) from **1b** and RuCl(dppe)Cp* in a manner identical to that described for **4a**, and characterised by comparison of spectroscopic data with that reported elsewhere.[31]

Formation of Ru(C≡CC$_6$F$_5$)(η^2-O$_2$)(PPh$_3$)Cp* (4c)

A mixture of RuCl(PPh$_3$)$_2$Cp* (50 mg, 0.063 mmol) and **1c** (86.6 mg, 0.127 mmol) was heated in refluxing benzene (13 mL) for 2.5 h to give a red-brown solution. Conventional work-up gave numerous unidentified products, appearing as multi-coloured bands on preparative TLC plates, together with AuCl(PPh$_3$) (5 mg). One yellow band afforded yellow crystals (from hexane) (1.1 mg, 2.4%), identified by a single-crystal X-ray diffraction structure determination as Ru(C≡CC$_6$F$_5$)(η^2-O$_2$)(PPh$_3$)Cp* (**4c**). The small amount obtained precluded further characterisation.

Preparation of Ir(C≡CC$_6$H$_5$)(η^2-O$_2$)(CO)(PPh$_3$)$_2$ (5a)

A suspension of IrCl(CO)(PPh$_3$)$_2$ (100 mg, 0.13 mmol) and **1a** (73 mg, 0.13 mmol) were stirred at room temperature in THF (12 mL) for *ca.* 6 h to give an orange-brown solution. The progress of the reaction was monitored by TLC and ^{31}P NMR [26.0 for IrCl(CO)(PPh$_3$)$_2$ and 25.2 ppm for Ir(C≡CC$_6$H$_5$)(CO)(PPh$_3$)$_2$]. When the reaction was adjudged complete, 7 mL of the solvent was removed to give a cloudy brown solution. Acetone (5 mL) was added to the solution and the mixture stirred for 10 min followed by filtration to give a yellow solid that was recrystallised (CHCl$_3$/hexane) to afford small pale yellow crystals of **5a** (71 mg, 62%). IR (CH$_2$Cl$_2$) ν/cm^{-1}: (C≡C) 2134; (C≡O) 2005, (O–O) 883. ^{1}H NMR δ/cm^{-1}: 2.23 (s, 3H, Me), 6.24 (d, 2H, J_{HH} = 8 Hz, C$_6$H$_4$), 6.81 (d, 2H, J_{HH} = 8 Hz, C$_6$H$_4$), 7.39 (m, 12H, PPh$_3$), 7.45 (m, 6H, PPh$_3$), 7.59 (m, 12H, PPh$_3$). ^{31}P{^{1}H} NMR δ/ppm: 8.3 (s). ^{13}C{^{1}H} NMR δ/ppm: 67.8 (t, $^2J_{CP}$ 11 Hz, C$_\alpha$), 108.5 (s, C$_\beta$), 125.1 (C4), 127.3 (C3), 128.1 (dd, $^3J_{CP}$, $^5J_{CP}$~5 Hz, C$_m$), 128.1 (m, C$_i$), 128.2 (C1), 130.8 (C$_p$), 131.3 (C2), 134.7 (dd, $^2J_{CP}$, $^4J_{CP}$~5 Hz, C$_o$), 167.1 (s, C≡O). ES-MS: *m/z* 879 [M + H]$^+$, 920 [M + H + MeCN]$^+$.

Preparation of Ir(C≡CC$_6$H$_4$Me-4)(η^2-O$_2$)(CO)(PPh$_3$)$_2$ (5b)

A suspension of IrCl(CO)(PPh$_3$)$_2$ (100 mg, 0.13 mmol) and **1b** (74 mg, 0.13 mmol) were stirred at room temperature in THF (12 mL) for *ca.* 6 h to give an orange solution. After the same work-up as described above for **5a**, the yellow solid was recrystallised from CHCl$_3$/hexane to yield yellow crystals of **5b** (46 mg, 40%) suitable for X-ray crystallography. IR (CH$_2$Cl$_2$) ν/cm^{-1}: (C≡C) 2128; (C≡O) 2008, (O–O) 834. ^{1}H NMR δ/ppm: 2.23 (s, 3H, Me), 6.24 (d, 2H, J_{HH} = 8 Hz, C$_6$H$_4$), 6.81 (d, 2H, J_{HH} = 8 Hz, C$_6$H$_4$), 7.39 (m, 12H, PPh$_3$), 7.45 (m, 6H, PPh$_3$), 7.59 (m, 12H, PPh$_3$). ^{31}P{^{1}H} NMR δ/ppm: 8.2 (s). ^{13}C{^{1}H} NMR δ/ppm: 21.1 (s, Me), 66.0 (t, $^2J_{CP}$ 11 Hz, C$_\alpha$), 109.1 (s, C$_\beta$), 125.0 (C1), 128.1 (C3), 131.1 (C2), 134.8 (C4), 128.1 (dd, $^3J_{CP}$, $^5J_{CP}$~5 Hz, C$_m$), 128.1 (m, C$_i$), 130.7 (C$_p$), 134.6 (dd, $^2J_{CP}$, $^4J_{CP}$~5 Hz, C$_o$), 167.1 (s, C≡O). Found: C 61.5, H 4.1%. C$_{46}$H$_{37}$P$_2$O$_3$Ir requires: C 62.0, H 4.2%. ES-MS: *m/z* 893 [M + H]$^+$, 934 [M + H + MeCN]$^+$. High resolution calculated for IrC$_{46}$H$_{38}$O$_3$P$_2$: [M + H]$^+$ 893.19199, found 893.19242.

Preparation of Ni(C≡CC$_6$H$_5$)(PPh$_3$)Cp (6a)

A solution of NiBr(PPh$_3$)Cp (100 mg, 0.21 mmol) in THF (10 mL), was treated with **1a** (120 mg, 0.21 mmol) and the mixture allowed to stir at ambient temperature in the dark, the progress of the reaction being monitored by TLC (hexane–acetone, 8 : 2) and by ^{31}P NMR [34.2 ppm for AuBr(PPh$_3$)]. The solution colour became pale brown after 1 h. After 4 h, the solution was distinctly green. After stirring for 6 h, the reaction was adjudged complete and the mixture was taken to dryness, followed by purification by preparative TLC. A green band was isolated, which was recrystallised (chloroform/MeOH) to afford green crystals of **6a** (55 mg, 53%). IR (CH$_2$Cl$_2$) ν/cm^{-1}: (C≡C) 2097 cm^{-1}. ^{1}H NMR δ/ppm: 5.25 (s, 5H, Cp), 6.64 (d, 2H, phenyl C2H at ≡CPh), 6.91 (t, 1H, C4H), 6.93 (m, 2H, C3H), 7.38 (m, 9H, PPh$_3$), 7.74 (m, 6H, PPh$_3$). ^{31}P NMR δ/ppm: 41.8 (s, PPh$_3$). ^{13}C NMR δ/ppm: 85.8 (d, $^2J_{PC}$ = 50 Hz, C$_\alpha$), 92.5 (d, $^3J_{PC}$ = 2 Hz, Cp), 119.7 (d, $^3J_{PC}$ = 2 Hz, C$_\beta$), 124.5 (C4), 127.2 (C3), 128.0 (C1), 128.1 (d, $^3J_{PC}$ = 10 Hz, C$_m$), 130.1 (d, $^4J_{PC}$ = 2 Hz, C$_p$), 130.9 (C2), 133.8 (d, $^2J_{PC}$ = 10 Hz, C$_o$), 134.0 (d, $^2J_{PC}$ = 49 Hz, C$_i$). ES-MS: *m/z* 995 [2M + Na]$^+$, 509 [M + Na]$^+$, 486 [M]$^+$, 385 [M – C≡CPh]$^+$.

Preparation of Ni(C≡CC$_6$H$_4$Me)(PPh$_3$)Cp (6b)

The modestly air- and light-sensitive green complex **6b** was prepared (44 mg, 42%) from **1b** and NiBr(PPh$_3$)Cp using the method described for **6a**. IR (CH$_2$Cl$_2$) ν/cm^{-1}: (C≡C) 2100. ^{1}H NMR δ/ppm: 2.17 (s, 3H, CH$_3$), 5.25 (s, 5H, Cp), 6.56 (d, 2H, tolyl C2H), 6.74 (d, 2H, C3H), 7.40 (m, 9H, PPh$_3$), 7.76 (m, 6H, PPh$_3$). ^{31}P NMR δ/ppm: 41.7 (s, PPh$_3$). ^{13}C NMR δ/ppm: 21.2 (CH$_3$), 83.5 (d, $^2J_{PC}$ = 50 Hz, C$_\alpha$), 92.6 (d, $^3J_{PC}$ = 2 Hz, Cp), 119.7 (d, $^3J_{PC}$ = 2 Hz, C$_\beta$), 125.2 (C1), 128.0 (C3), 128.1 (d, $^3J_{PC}$ = 10 Hz,

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C_m), 130.1 (d, $^4J_{PC} = 2$ Hz, C_p), 130.7 (C2), 133.9 (d, $^2J_{PC} = 10$ Hz, C_o), 134.0 (d, $^2J_{PC} = 47$ Hz, C_i), 134.1 (C4). ES-MS: *m*/*z* 501 $[M + 1]^+$. Found: C 76.7, H 5.5%. $C_{32}H_{27}PNi$ requires: C 76.7, H 5.5%.

Preparation of *trans*-$Pt(C{\equiv}CC_6H_5)_2(PPh_3)_2$ (7a)

To a stirred aliquot of MeOH (15 mL), *cis*-$PtCl_2(PPh_3)_2$ (141 mg, 0.18 mmol) and **1a** (200 mg, 0.36 mmol) were added to form a pale yellow suspension. The reaction mixture was allowed to stir for *ca.* 15 h, after which time it was filtered and the precipitate collected and washed with acetone to give a yellow solid, which was recrystallised (CH_2Cl_2/hexane) to afford pale yellow crystals of **7a** (86 mg, 59%). IR (nujol) ν/cm^{-1}: (C≡C) 2107. ^{1}H NMR δ/ppm: 6.28 (m, 4H, phenyl C2H at CCPh), 6.89 (m, 2H, C4H), 6.91 (m, 4H, C3H), 7.37 (m, 18H, PPh_3), 7.81 (m, 12H, PPh_3). $^1P\{^1H\}$ NMR ($CDCl_3$, 80.96 MHz) δ/ppm: 19.7 (s + d, $^1J_{PtP} = 2640$ Hz, PPh_3). $^{13}C\{^1H\}$ NMR δ/ppm: 109.7 (t, $^2J_{CP}$~16 Hz, C_α), 113.2 (C_β), 124.5 (C4), 127.0 (C3), 127.8 (dd, $^3J_{CP/}$ $^5J_{CP}$~5 Hz, C_m), 128.5 (C1), 130.8 (C2), 130.1 (C_p), 131.4 (dd, $^1J_{CP/}$ $^3J_{CP}$~29 Hz C_i), 135.1 (dd, $^2J_{CP/}$ $^4J_{CP}$~5 Hz, C_o). Found: C 68.0, H 4.4%. $C_{52}H_{40}P_2Pt$ requires: C 67.8, H 4.4%. ES-MS: *m*/*z* 922 $[M + H]^+$, 944 $[M + Na]^+$. High resolution calculated for $PtC_{52}H_{41}P_2$: $[M + H]^+$ 922.23257, found 922.23318, calculated for $PtC_{52}H_{40}P_2Na$: $[M + Na]^+$ 944.21452, found 944.21662.

Preparation of *trans*-$Pt(C{\equiv}CC_6H_4Me)_2(PPh_3)_2$ (7b)

A reaction similar to that described for **7a** between *cis*-$PtCl_2(PPh_3)_2$ (200 mg, 0.25 mmol) and **1b** (291 mg, 0.51 mmol) gave **7b** as a pale yellow precipitate, which was recrystallised (CH_2Cl_2/MeOH) to afford pale yellow crystals (83 mg, 35%). IR (nujol) ν/cm^{-1}: (C≡C) 2106. ^{1}H NMR δ/ppm: 2.17 (s, 6H, Me), 6.16 (d, J_{HH}~7 Hz, C_6H_4), 6.70 (d, J_{HH}~7 Hz, C_6H_4), 7.36 (m, 18H, PPh_3), 7.80 (m, 12H, PPh_3). $^1P\{^1H\}$ NMR δ/ppm: 19.7 (s + d, $^1J_{PtP} = 2660$ Hz, PPh_3). $^{13}C\{^1H\}$ NMR δ/ppm: 21.2 (Me), 127.7 (dd, $^3J_{CP}$, $^5J_{CP}$~5 Hz, C_m), 127.9 (C3), 130.1 (C2), 130.8 (C_p), 131.9 (dd, $^1J_{CP}$, $^3J_{CP}$~29 Hz, C_i), 135.1 (dd, $^2J_{CP}$, $^4J_{CP}$~5 Hz C_o), other ^{13}C peaks were not observed due to poor solubility. Found: C 68.8, H 4.6%. $C_{54}H_{44}P_2Pt$ requires: C 68.3, H 4.7%. ES-MS: *m*/*z* 950 $[M + H]^+$, 972 $[M + Na]^+$, 982 $[M + H + MeOH]^+$. High resolution calculated for $^{194}PtC_{54}H_{45}P_2$: $[M]^+$ 949.256611, found 949.26387.

Preparation of *trans*-$Pt(C{\equiv}CC_6H_5)_2(PMe_3)_2$ (8a)

To a stirred aliquot of MeOH (15 mL), *trans*-$PtCl_2(PMe_3)_2$ (100 mg, 0.24 mmol) and **1a** (269 mg, 0.48 mmol) were added under nitrogen to afford a pale green suspension, which was stirred at rt for *ca.* 15 h, filtered and washed with cold MeOH (3 mL) and hexane (3 mL), and recrystallised ($CHCl_3$/MeOH) to afford pale yellow crystals of **8a** (99 mg, 73%). IR (nujol) ν/cm^{-1}: (C≡C) 2108. ^{1}H NMR δ/ppm: 1.77 (dd, $^2J_{PH}$, $^4J_{PH}$~4 Hz, and Pt satellites, $^3J_{Pt\text{–}H}$~30 Hz, PMe_3), 1.80 (dd, $^3J_{Pt\text{–}H}$~30 Hz), 2.29 (s, 6H, Me), 7.03 (d, $J_{HH} = 8$ Hz, C2H of tolyl), 7.23 (d, $J_{HH} = 8$ Hz, C3H). $^{31}P\{^1H\}$ NMR δ/ppm: −19.4 (s + d, $^1J_{PtP} = 2300$ Hz, PMe_3). $^{13}C\{^1H\}$ NMR δ/ppm: 15.3 (dd, $^2J_{CP}$,$^4J_{CP}$~20 Hz, and Pt satellites, $^2J_{Pt\text{–}C}$~81 Hz, PMe_3), 107.2 (t, $^2J_{CP} = 15$ Hz, C_α), 108.5 (C_β), 125.3 (C4), 127.9 (C3), 128.2 (C1), 130.9 (C2). Found: C 47.1, H 5.1%. $C_{24}H_{32}P_2Pt$ requires: C 48.1, H 5.1%. ES-MS: *m*/*z* 1162 $[2M + Na]^+$; 550 $[M + H]^+$.

Preparation of *trans*-$Pt(C{\equiv}CC_6H_4Me\text{-}4)_2(PMe_3)_2$ (8b)

Complex **8b** was prepared from **1b** (275 mg, 0.48 mmol) and $PtCl_2(PMe_3)_2$ and isolated as pale yellow-green crystals (93 mg, 67%). IR (nujol) ν/cm^{-1}: (C≡C) 2108. ^{1}H NMR δ/ppm: 1.77 (dd, $^2J_{PH}$, $^4J_{PH}$~4 Hz, and Pt satellites, $^3J_{Pt\text{–}H}$~30 Hz, PMe_3), 1.80 (dd, $^3J_{Pt\text{–}H}$~30 Hz), 2.29 (s, 6H, Me), 7.03 (d, $J_{HH} = 8$ Hz, C2H of tolyl), 7.23 (d, $J_{HH} = 8$ Hz, C3H). $^{31}P\{^1H\}$ NMR δ/ppm: −19.4 (s + d, $^1J_{PtP} = 2310$ Hz, PMe_3). $^{13}C\{^1H\}$ NMR δ/ppm: 15.4 (dd, $^2J_{CP}$,$^4J_{CP}$~20 Hz, and Pt satellites, $^2J_{Pt\text{–}C}$~83 Hz, PMe_3), 21.3 (s, Me), 106.0 (t, $^2J_{CP} = 15$ Hz, C_α), 108.4 (C_β), 125.2 (C1), 128.6 (C3), 130.9 (C2), 135.0 (C4). Found: C 49.3, H 5.6%. $C_{24}H_{32}P_2Pt$ requires: C 49.9, H 5.6%. ES-MS: *m*/*z* 1177 $[2M + Na]^+$, 632 $[M + Na + MeOH]^+$, 578 $[M + H]^+$. High resolution calculated for $PtP_2C_{24}H_{33}$: $[M + H]^+$ 578.16997, found 578.17067.

Isolation of $Au(PMe_3)_2[PF_6]$ (9)

A suspension of $PtCl_2(PMe_3)_2$ (200 mg, 0.48 mmol), **1a** (130 mg, 0.23 mmol) and NH_4PF_6 (78 mg, 0.48 mmol) in MeOH (15 mL) was allowed to stir at rt for *ca.* 8 h to give a white precipitate, which was collected by filtration, washed with a small quantity of cold MeOH (3 mL) followed by hexane (3 mL) and dried *in vacuo*. Crystallisation of the precipitate from MeCN/MeOH gave white crystals of **9** (14 mg, 0.028 mmol, 12%) suitable for X-ray crystallography. ^{1}H NMR δ/ppm: 1.70. $^{31}P\{^1H\}$ NMR δ/ppm: 5.0 (s), −144.1 (septet, $J_{PF} = 710$ Hz). $^{13}C\{^1H\}$ NMR δ/ppm: 16.4 (br). ES-MS: *m*/*z* 721 $[2M + Na]^+$, 349 $[M]^+$ $C_6H_{18}AuP_2 = [M]^+$. High resolution calculated for $C_6H_{18}AuP_2$: $[M]^+$ 349.05439, found 349.05424.

Preparation of $\{Cu(C{\equiv}CC_6H_5)\}_n$ (10a)

An aliquot of THF (25 mL) was rapidly stirred and treated with CuI (100 mg, 0.50 mmol) and **1a** (280 mg, 0.50 mmol) to form a white suspension, which gradually changed to yellow after *ca.* 2 h. The reaction was allowed to stir for *ca.* 24 h to ensure complete reaction. The yellow suspension was filtered and the solid was washed with hexane (5 mL) to give a bright yellow solid (71 mg, 86%) identified as $\{Cu(C{\equiv}CC_6H_5)\}_n$ **10a**. IR (KBr) ν/cm^{-1}: (C≡C) 1940 (vw), 1481 (m), 742 (s), 679 (s), 520 (m), 511 (m).[73] Found: C 58.1, H 3.1%. C_8H_5Cu requires: C 58.4, H 3.0%.

Preparation of $\{Cu(C{\equiv}CC_6H_4Me\text{-}4)\}_n$ (10b)

A stirred suspension of CuI (200 mg, 1.05 mmol) in THF (60 mL) was treated with **1b** (600 mg, 1.05 mmol) to form a white suspension, which gradually changed to yellow after *ca.* 2 h. Using a similar work-up procedure as described for **10a**, a yellow solid (175 mg, 94%) was isolated and identified as $\{Cu(C{\equiv}CC_6H_4Me\text{-}4)\}_n$ (**10b**). IR (KBr) ν/cm^{-1}: (C≡C) 1937 (w), 1504 (s), 808 (s), 526 (m), 520 (m). Found: C 63.6, H 4.1%. C_9H_7Cu requires: C 60.5, H 3.9%.

Structure determinations†

Single-crystal X-ray data were collected using an Oxford Diffraction Xcalibur CCD (**11**), Rigaku R-AXIS Spider IP (**2b** and **5b**), Bruker Smart CCD 1 K (**6b** and **8b**) and 6 K (**4b**, **7a**, **7b** and **9**) diffractometers at low temperature and using monochromatic

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MoKα radiation, $\lambda = 0.71073$ Å. All structures were solved by direct methods and refined by full matrix least squares refinement on F^2. Anisotropic displacement parameters were refined for the non-hydrogen atoms, excepting the disordered ones in the structures **5b** and **9**; hydrogen atom treatment followed a riding model. The $C{\equiv}CC_6H_4Me$-4 fragment of molecule **5b** is disordered over two equally occupied positions, which correspond to two different directions of the flexing in the alkyne moiety. The inclinations of the planar aryl rings are also slightly different. The disorder does not affect the geometry of rest of the molecule. Neutral atom complex scattering factors were employed within the SHELXL-97 program.[74] Pertinent results are given in the tables and figures, the latter showing non-hydrogen atoms with 50% probability amplitude displacement ellipsoids.

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