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# The syntheses, structures and redox properties of phosphine-gold(I) and triruthenium-carbonyl cluster derivatives of tolans

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Dedicated to Professor Pierro Zanello, on the occasion of his 65th birthday, in recognition of his many contributions to organometallic chemistry.

#### Abstract

The syntheses of several ethynyl-gold(I)phosphine substituted tolans (1,2-diaryl acetylenes) of general form  $[Au(C \equiv CC_6H_4C \equiv CC_6H_4X)(PPh_3)]$  are described [X = Me (2a), OMe (2b), CO<sub>2</sub>Me (2c), NO<sub>2</sub> (2d), CN (2e)]. These complexes react readily with  $[Ru_3(CO)_{10}(\mu$ -dppm)] to give the heterometallic clusters  $[Ru_3(\mu$ -AuPPh<sub>3</sub>)( $\mu$ - $\eta^1$ , $\eta^2$ -C<sub>2</sub>C<sub>6</sub>H<sub>4</sub>C  $\equiv CC_6H_4X$ )(CO)<sub>7</sub>( $\mu$ -dppm)] (3a-e). The crystallographically determined molecular structures of 2b, 2d, 2e and 3a-e are reported here, that of 2a having been described on a previous occasion. Structural, spectroscopic and electrochemical studies were conducted and have revealed little electronic interaction between the remote substituent and the organometallic end-caps. © 2007 Elsevier B.V. All rights reserved.

Keywords: Tolan; Ruthenium cluster; Gold complex; Electrochemistry; Spectroelectrochemistry

#### 1. Introduction

Molecular and polymeric compounds featuring extended  $\pi$ -conjugated electronic structures are of considerable interest from the point of view of developing new materials for optical and electronic applications [1–5]. In this context, oligomeric phenylene ethynylenes have been particularly well studied [6]. The introduction of a metal centre into the  $\pi$ -conjugated framework offers many possibilities for further tuning of the physical properties, which are modified by mixing of the metal d and ligand-based  $\pi$  orbitals [7–10]. Although there are many discussions of

the capacity for  $\pi$ -conjugated ligands to transmit electronic effects between mono-metallic fragments, we were interested to discover if the tolan (1,2-diphenylacetylene) fragment was an efficient conduit for the transmission of electronic effects between a remote substituent and a cluster core [11]. However, whilst there are numerous examples of complexes derived from oligomeric phenylene ethynylenes and their various properties, especially non-linear optical response and excited state structures have been well described [12–28], cluster compounds featuring these "wire-like" ligands are particularly scarce [29,30].

Gold(I)phosphine acetylide complexes are efficient reagents for the transfer of acetylenic fragments to polymetallic clusters, either by addition of the Au–C bond across a metal–metal bond [31], or via elimination of gold(I)phosphine halide complexes upon Pd(0)/Cu(I) catalyzed reaction with halocarbynes [32]. In this work, a series of

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tolan derivatives  $Me_3SiC \equiv CC_6H_4C \equiv CC_6H_4X$  [X = Me (1a), OMe (1b), CO<sub>2</sub>Me (1c), NO<sub>2</sub> (1d), CN (1e)] have been prepared. converted to the gold(I) complexes  $[Au(C \equiv CC_6H_4C \equiv CC_6H_4X)(PPh_3)]$  [2a-e] and subsequently reacted with  $[Ru_3(CO)_{10}(\mu-dppm)]$  to give the cluster-substituted tolans  $[Ru_3(\mu-AuPPh_3)(\mu-\eta^1,\eta^2 C_2C_6H_4C \equiv CC_6H_4X(CO)_7(\mu-dppm)]$  (3a–e) which feature the desired cluster-tolan-substituent motif. The molecular structures, electrochemical and spectroscopic properties, and IR spectroelectrochemical response of these compounds are described herein.

# 2. Results and discussion

# 2.1. Syntheses

The trimethylsilyl-protected tolan  $Me_3SiC \equiv CC_6H_4C \equiv CC_6H_4Me-4$  (1a) was prepared by sequential reaction of lithium tolylacetylide and lithium trimethylsilylacetylide with benzoquinone and reduction of the mixture of diols thus formed, as described previously [30,33]. The other protected tolans,  $Me_3SiC \equiv CC_6H_4C \equiv CC_6H_4X$  [X = OMe (1b),  $CO_2Me$  (1c),  $NO_2$  (1d), CN (1e)] were prepared via Sonogashira Pd/Cu cross-coupling protocols, taking advantage of the availability of 1-trimethylsilylethynyl-4-ethynylbenzene (Scheme 1) [34]. Alternative synthetic pathways can also be employed [35], but we favour the approach described here for its simplicity. Compounds 1a–e were desilylated in conventional fashion (K<sub>2</sub>CO<sub>3</sub>/MeOH) to afford terminal alkynes (1-H). Reaction of either the Me<sub>3</sub>Si- or H-terminated ethynyl tolans with [AuCl(PPh<sub>3</sub>)] in the presence of NaOMe gave the gold complexes [Au(C=CC<sub>6</sub>H<sub>4</sub>C=CC<sub>6</sub>H<sub>4</sub>X)-(PPh<sub>3</sub>)] [X = Me (2a), OMe (2b), CO<sub>2</sub>Me (2c), NO<sub>2</sub> (2d), CN (2e)], the yield being comparable from both routes (70–84%) (Scheme 1). The complexes were characterized by the usual spectroscopic methods, which included singlet phosphorus resonances near  $\delta$  43 ppm and a single v(C=C) band slightly above 2200 cm<sup>-1</sup>, and by single crystal X-ray diffraction in the case of 2a, 2b, 2d and 2e (*vide infra*).

Reaction of the gold complexes 2a-e with  $[Ru_3(CO)_{10}(\mu$ dppm)] in refluxing THF, gave  $Ru_3(\mu-AuPPh_3)(\mu-AuPPh$  $C_2C_6H_4C \equiv CC_6H_4X(CO)_7(\mu\text{-dppm})$  (3a–e) (Scheme 2). Similar species have been obtained from reactions of gold acetylides with triangulo triruthenium clusters, [36] or through the auration of cluster anions obtained by deprotonation of the corresponding hydride clusters [37]. Spectroscopic parameters consistent with the proposed structure were obtained, and the characterization completed in each case by a single crystal X-ray diffraction study. The <sup>31</sup>P NMR spectrum was particularly informative, with the three chemically distinct phosphorus centres giving rise to a characteristic pattern in which the resonance arising from P(2) was split into a doublet of doublets by coupling to both the gold-bound phosphine P(1) and the dppm phosphorus centre P(3). The electrospray ionization



Scheme 1. The preparation of 1 and 2.



Scheme 2. The preparation of cluster compounds 3a-e.

mass spectra (ES-MS) of these clusters were characterized by the observation of the simple protonated species  $[M+H]^+$  or the aggregate ion  $[M+AuPPh_3]^+$ .

Interestingly, the electronic environment of the cluster core, as measured by the characteristic v(CO) band patterns, is almost the same in each member of the series 3a-e, with no apparent systematic shift in frequency that could be attributed to variation in  $\pi$ -back-bonding from the ruthenium centres brought about by the electron-donating or electron-withdrawing properties of the tolan substituent.

#### 2.2. Molecular structures

The molecular structure of **2a** has been reported recently, and only pertinent data are included here for purposes of comparison [30]. A molecule of **2d**, which is representative of the series, is illustrated in Fig. 1 to show to the atom labelling scheme. Selected bond lengths and angles are summarized in Table 1. Within the series **2a–e**, the Au–C(1) [1.999(2)–2.023(4) Å] and Au–P(1) [2.2652(14)–2.2752(5) Å] bond lengths are comparable with those of related acetylide complexes, such as [Au(C=CPh)(PPh<sub>3</sub>)] [Au–C 1.97(2)/2.02(2); Au–P 2.276(5)/2.282(4) Å, for two independent molecules] [38] and [Au(C=CSiMe<sub>3</sub>)(PPh<sub>3</sub>)] [Au–C 2.000(4); Au–P 2.2786(10) Å] [39]. There is no evidence for significant cumulene/quinoidal character within

the phenylene ethynylene portion of the molecule and the C(1)–C(2) [1.191(8)–1.204(3) Å] and C(9)–C(10) [1.198(3)– 1.207(7) Å] acetylide bond lengths are the same within the limits of precision of the structure determination. The P–Au–C moiety is essentially linear [171.6(2)–176.4(6)°], but there is a gentle curvature in the molecular backbone, particularly pronounced at C(1) [Au–C(1)–C(2) 168.2(5)– 175.3(2)°], brought about by crystal packing effects.

The complexes 2a-e offer an opportunity to examine systems in which Au···Au and  $\pi \cdot \cdot \pi$  interactions, together with other weak interactions such as  $CH \cdots \pi$ , may work to influence the solid-state structures. In this work, no aurophilic interactions were found in the extended solid-state structures, with  $\pi \cdots \pi$  interactions between the tolan moieties being more prevalent. In each structure the molecules lie in an anti-parallel arrangement with a number of CH(from various phenyl rings)  $\cdots \pi$ (phenyl or acetylene bond) interactions being evident (Fig. 2). Stacking  $\pi \cdots \pi$ interactions between the phenyl rings of the tolan moieties are observed only in the structures 2d and 2e, which also carry the most strongly electron-withdrawing terminal substituents ( $X = NO_2$  and CN). Whilst in the case of **2e** both tolan ring systems are stacked, only the more highly polarized terminal phenyl ring in 2d is involved in this motif. Steric constraints associated with the PPh<sub>3</sub> supporting ligand likely restrict the close approach of the gold centres, and Au...Au aurophilic interactions are superseded by these various  $\pi$ -hydrocarbon based interactions [40].



Fig. 1. A plot of a molecule of 2d illustrating the atom numbering scheme.

Table 1															
Selected	bond	lengths	(Å)	and	angles	(°)	associated	with	com	olexes	2a,	2b,	2d	and	2e

	2a	2b	2d	2e
Au(1)–P(1)	2.2752(5)	2.2652(14)	2.2889(12)	2.2764(5)
Au(1)-C(1)	1.999(2)	2.003(6)	2.023(4)	1.999(2)
C(1)–C(2)	1.204(3)	1.191(8)	1.195(6)	1.204(3)
C(2) - C(3)	1.441(3)	1.447(8)	1.439(6)	1.438(3)
C(9)–C(10)	1.198(3)	1.204(8)	1.207(7)	1.201(3)
P(1)-Au(1)-C(1)	176.4(6)	171.6(2)	176.3(1)	176.0(6)
Au(1)-C(1)-C(2)	170.5(2)	168.2(5)	172.8(4)	175.3(2)
C(1)-C(2)-C(3)	174.6(2)	177.3(6)	178.8(5)	178.0(2)
C(8)-C(9)-C(10)	178.8(2)	178.4(7)	178.8(6)	178.7(3)
C(9)-C(10)-C(11)	177.8(2)	177.3(6)	178.2(6)	179.3(3)



Fig. 2. Representative molecular packing diagrams for (a) 2d and (b) 2e.

There are few, if any, differences of note within the structures of 3a-e. The common cluster core geometry is illustrated schematically in Fig. 3, with a molecule of 3d shown in Fig. 4 as a representative example of the series. Selected bond lengths and angles are summarized in Table 2. The clusters **3a–e** feature a triangular Ru<sub>3</sub> metal framework, with the Au(PPh<sub>3</sub>) moiety bridging the  $Ru_B-Ru_C$ bond, and the Ru<sub>A</sub>-Ru<sub>B</sub> bond supported by the bridging dppm ligand. The gold supported metal-metal bond is the shortest of the three Ru-Ru bonds in the cluster, with the unsupported RuA-RuC bond generally being the longest. The C(1)-C(2) acetylide ligand caps the triangular face in the expected  $\mu_3$ - $\eta^1$ ,  $\eta^2$ ,  $\eta^2$  mode. As a consequence of the interaction with the metal centres, this bond is elongated in comparison to typical acetylenic  $C \equiv C$  bond lengths [1.318(6)-1.324(5) Å]. The tolan  $C(9) \equiv C(10)$ alkyne bond is in the normal range [1.191(5)-1.201(6) Å].



Fig. 3. A schematic representation of the cluster core in 3a-e.

Planar tolan structures are thought to be more conducting than conformers in which the phenyl ring systems are twisted with respect to one another [41]. Thus, whilst the barrier to rotation about the aryl-ethynyl single bond is small in the gas phase and in solution [42], much of the interest in the solid-state structures of tolan and related oligo(phenylene ethynylene) compounds lies in the analysis of the inter-ring torsion angles. In the case of the clusters **3a–e**, the dihedral angles between the planes of the tolan phenyl rings range from  $33.2^{\circ}$  to  $42.8^{\circ}$ .

In much the same way as observed in the structures of the parent compounds 2, the packing of the molecules 3a-e in the crystalline state is also determined by a number of relatively weak C-H···X (X = O, Cl,  $\pi$ ) interactions. However, the presence of carbonyl ligands and solvent molecules in the structures 3 results in a much more complicated 3D-network of these interactions than was observed in the structures of compounds 2. We note that there are no obvious stacking  $\pi \cdots \pi$  interactions between tolan ligand fragments in the case of the cluster structures.

# 2.3. UV-Vis spectroscopy

The electronic absorption spectra of the ligand precursors 1a-e, the mononuclear gold complexes 2a-e and the heterometallic clusters 3a-e were recorded as dilute (1–10 µmol dm<sup>-3</sup>) solutions in CH<sub>2</sub>Cl<sub>2</sub> (Table 3). The spectra



Fig. 4. A plot of a molecule of 3d, which is representative of the compounds in the series.

Table 2 Selected bond lengths (Å) and angles (°) for 3a-e

	3a	3b	3c	3d	3e
Ru <sub>A</sub> -Ru <sub>B</sub>	2.8345(5)	2.8271(4)	2.8248(6)	2.8140(6)	2.8175(3)
Ru <sub>A</sub> -Ru <sub>C</sub>	2.8330(5)	2.8394(4)	2.8451(7)	2.8321(6)	2.8353(3)
Ru <sub>B</sub> -Ru <sub>C</sub>	2.7994(4)	2.7861(4)	2.7933(6)	2.7987(5)	2.7987(3)
$Ru_A - C(1)$	1.939(4)	1.9747(3)	1.944(4)	1.952(4)	1.951(3)
C(1)–C(2)	1.322(6)	1.324(5)	1.318(6)	1.318(6)	1.322(4)
C(2)–C(3)	1.458(5)	1.460(5)	1.460(6)	1.459(6)	1.470(4)
$Ru_B - C(1)$	2.198(4)	2.193(3)	2.191(4)	2.186(4)	2.192(3)
$Ru_{C}-C(1)$	2.021(4)	2.210(3)	2.213(4)	2.223(4)	2.218(2)
$Ru_B-C(2)$	2.217(4)	2.231(3)	2.238(4)	2.229(4)	2.231(3)
$Ru_{C}-C(2)$	2.273(4)	2.243(3)	2.229(4)	2.242(4)	2.229(3)
Ru <sub>A</sub> -Ru <sub>B</sub> -Ru <sub>C</sub>	60.37(1)	60.77(1)	60.85(2)	60.61(2)	60.64(1)
Ru <sub>A</sub> -Ru <sub>C</sub> -Ru <sub>B</sub>	60.43(1)	60.33(1)	60.12(2)	59.96(2)	60.00(1)
Ru <sub>B</sub> -Ru <sub>A</sub> -Ru <sub>C</sub>	59.20(1)	58.90(1)	59.03(1)	59.43(1)	59.35(1)
Ru <sub>B</sub> -Au-Ru <sub>C</sub>	60.79(1)	59.97(1)	60.11(1)	60.48(1)	60.34(1)
$Ru_{A}-C(1)-C(2)$	154.8(3)	154.0(3)	154.0(3)	153.1(3)	152.8(2)
C(1)-C(2)-C(3)	139.4(4)	140.7(3)	142.2(4)	141.6(4)	141.8(3)

of 1a-c and 1e are characteristic of the tolan (1,2-diphenylacetylene) moiety, exhibiting three relatively intense transitions between ca. 280 and 350 nm [30,43]. The spectrum of nitro-substituted derivative 1d contains a broad absorption band from the nitrobenzene moiety centred near 340 nm. Substitution of the SiMe<sub>3</sub> group for Au(PPh<sub>3</sub>) resulted in little change to these spectroscopic profiles. As noted previously, the UV-Vis absorption spectra of the cluster derivatives 3a-e exhibit several new features that were not present in the spectra of the precursors 1a-e and 2a-e. The clusters all exhibit an absorption band of low intensity near 450 nm, which is associated with charge transfer transitions from the cluster to the unoccupied orbitals of the tolan moiety. This assignment is supported by the cyclic voltammetric investigations presented below. Two bands between 300 and 400 nm, which were not resolved in all cases (Table 3) and a higher energy absorption band near 280 nm were also observed. Given their similar energetic positions and

intensities as observed for **1a–e**, these absorption bands likely contain contributions from tolan-centred transitions.

#### 2.4. Electrochemical properties

Transition metal clusters typically offer closely spaced frontier orbitals with a significant metal character. This can lead to a rich electrochemical response in these systems, and has led to the description of cluster compounds as "electron sinks" [44]. This potential for redox activity, coupled with the ready spectroscopic probes offered by both the carbonyl ligands and several of the remote substituents (e.g., the ester and nitro groups) prompted us to examine the heterometallic (Ru<sub>3</sub>–Au) clusters **3a–d** and their mononuclear (phosphine)Au-tolan precursors **2a–d** using cyclic voltammetry and, in selected examples, IR spectroelectrochemical methods. Compounds **3e** and **2e** were not included in the spectroelectrochemical studies.

Table 3 The principal UV–Vis absorption bands observed from CH<sub>2</sub>Cl<sub>2</sub> solutions of **1a–e. 2a–e. 3a–e** 

Compound	$\lambda$ , nm ( $\varepsilon$ , M <sup>-1</sup>	$cm^{-1}$ )	
1a	290 (53 200)	306 (62 300)	326 (59 500)
1b	a	313 (62700)	332 (58300)
1c	285 (84200)	314 (59300)	335 (50800)
1d	280 (64900)	300sh (41200)	342 (42900)
1e	287 (30000)	315 (47300)	336 (45900)
2a	297 (41700)	315 (69400)	337 (68300)
2b	b	320 (65900)	341 (62500)
2c	310 (33 500)	327 (44900)	348 (39900)
2d	284 (42200)	299 (37100)	358 (30300)
2e	310 (39 500) <sup>c</sup>	328 (55 500)	349 (51400)
3a		324 (41 200)	450 (5500)
3b	275 (46600)	329 (22100)	450 (3000)
3c	283 (102000)	336 (43000) 376 (32000)	451 (8000)
3d	283 (65900)	390 (24500)	463 (9000)
3e	285 (84200)	331 (34700) 376 (25600)	440 (5800)

 $^{a}$  Several unresolved bands were also observed between 250 and 300 nm (ca. 43000  $M^{-1}\,cm^{-1}).$ 

<sup>b</sup> Several unresolved bands were also observed between 260 and 300 nm (ca.  $28000-48000 \text{ M}^{-1} \text{ cm}^{-1}$ ).

 $^{\rm c}$  Several unresolved bands were also observed between 260 and 300 nm (ca. 24000–34000  $M^{-1}\,cm^{-1}$ ).

#### 2.5. Cyclic voltammetry

The cyclic voltammograms of the mononuclear gold complexes **2a**-**d** in dichloromethane show totally irreversible anodic [O2, between 0.85 and 1.15 V versus  $Fc/Fc^+$ ] and cathodic [R2 < -2.20 V versus  $Fc/Fc^+$ ] waves close to, or beyond, the limits of the solvent potential window (Table 4). Indeed, for **2a** and **2b** which feature electrondonating tolan substituents X = Me and OMe, respectively, the cathodic waves are shifted beyond the limit of the electrochemical window. These irreversible redox processes were not studied in detail. Complex **2d** shows an additional cathodic wave R1 at -1.49 V, which is fully reversible and apparently belongs to the reduction of the remote X = NO<sub>2</sub> substituent.

The cyclic voltammograms of the heterometallic clusters 3a-d exhibit irreversible redox processes at very similar electrode potentials to those observed in the precursors



Fig. 5. Cyclic voltammogram of heterometallic cluster **3c** (Scheme 2; X = OMe). The asterisks denote two small cathodic peaks observed in addition to *r*O1 during the reverse cathodic scan triggered beyond O1. Experimental conditions: carefully polished Pt disk microelectrode, dichloromethane containing  $10^{-1}$  M Bu<sub>4</sub>NPF<sub>6</sub>, v = 100 mV s<sup>-1</sup> at 293 K.

**2a–d** (Table 4, Fig. 5). The similarity of these electrochemical events point to their localization at the terminal 1,2diphenylacetylene moiety, indicating that the tolan chain is not significantly affected by coordination to the triruthenium cluster core through the acetylide moiety. The anodic waves O2 partly overlap with higher-lying irreversible waves O3, which are not observed for **2a–d**. The chemically irreversible nature of R2 is further illustrated by the presence of a new anodic wave rR2 arising in the course of the reverse potential scan initiated beyond R2 (Fig. 5). This wave is shifted some 1.7–1.8 V positively relative to R2, and arises from oxidation of an unassigned secondary reduction product.

The nitro group in **3d** is reduced at essentially the same cathodic potential R1 as that in **2d** (Table 4). At room temperature, the peak-to-peak separation ( $\Delta E_p = E_{p,c} - E_{p,a}$ ) for this redox couple (100 mV) is only slightly larger than the value of 80 mV determined for the Fc/Fc<sup>+</sup> internal

able 4	
ectrochemical properties of the Au-tolan complexes 2a-d and corresponding heterometallic cluster compounds 3a-d	a

Compound	$E_{\rm p,c}$ (R2, tolan)	$E_{1/2}$ (R1, NO <sub>2</sub> )	$E_{\rm p,a}$ (O1, Ru <sub>3</sub> -core)	$E_{\rm p,a}$ (O2/O3, tolan)
2a	not observed			0.94
2b	not observed			0.88
2c	-2.37			1.14
2d	-2.23	-1.49		1.13
3a	-2.49		0.19	0.93/1.02
3b	-2.48		0.18	0.88/0.95
3c	-2.35		0.25	1.04/1.16
3d <sup>b</sup>	-2.16	-1.47	0.29	1.02/1.15

<sup>a</sup> Redox potentials (V vs. Fc/Fc<sup>+</sup>) were determined from cyclic voltammetric scans. Experimental conditions: Pt disk working microelectrode,  $v = 100 \text{ mV s}^{-1}$ , T = 293 K.  $E_p$  denotes peak potential of a chemically irreversible step.

standard. At 206 K, however, the  $\Delta E_{\rm p}$  value of the nitro reduction increases to 600 mV while that of the internal Fc/Fc<sup>+</sup> standard does not change. The electrochemically quasireversible to irreversible nature of the cathodic step R1 in **3d** may reflect some hindered access of the remote NO<sub>2</sub> group to the electrode surface, and in turn sluggish electron transfer kinetics.

The dominant new feature in the cyclic voltammograms of clusters 3a-d is the irreversible two-electron anodic wave O1 (Table 4, Fig. 5) that corresponds to oxidation of the triruthenium cluster core. The reverse cathodic scan at room temperature reveals the presence of three small cathodic peaks due to reduction of secondary oxidation products, which are shifted significantly more negatively from O1, for example in the case of 3a by 0.63, 1.13 and 1.81 V, respectively. The minor dependence of the anodic potentials O1 on the nature of the electron-donating or electron-withdrawing substituents X (Scheme 2) reflects a rather limited degree of electronic communication between the cluster core and the substituted tolan moiety, in agreement with the conclusions drawn from the IR spectra of the **3a**–**e** series (see above).

#### 2.6. IR spectroelectrochemistry

The triruthenium clusters **3a** (X = Me), **3c**  $(X = CO_2Me)$  and **3d** (X = NO<sub>2</sub>) were selected for IR spectroelectrochemical investigations aimed at obtaining more information about the electronic communication between the cluster core and the remote substituent X on the conjugated tolan chain. These experiments were carried out in dichloromethane solutions containing  $10^{-1}$  M NBu<sub>4</sub>PF<sub>6</sub> as supporting electrolyte. For reference purposes, the carbonyl stretching frequencies of the parent compounds in dichloromethane are listed in Section 4.

One-electron reduction of the nitro group in compound 3d at the electrode potential R1 (Table 4) led to the expected disappearance of the absorption bands at 1519 and 1344 cm<sup>-1</sup>, which can be attributed to the  $v_{as}(NO_2)$ and v<sub>s</sub>(NO<sub>2</sub>) modes, respectively [45]. A new band arose at 1367 cm<sup>-1</sup>, assigned to  $v_{as}(NO_2^{\cdot-})$  [46]. In addition, an absorption band at 1589 cm<sup>-1</sup> was replaced by a new one at  $1568 \text{ cm}^{-1}$  that may be due to a nitrobenzene ring v(C=C) mode. This NO<sub>2</sub>-localized reduction also results in a low-frequency shift of the  $v(C \equiv C)$  band from 2213 to 2186 cm<sup>-1</sup>. The v(C $\equiv$ O) band pattern of the carbonyltriruthenium fragment was almost unchanged by the reduction, with wavenumbers of individual bands decreasing by only  $1-2 \text{ cm}^{-1}$ , in agreement with the weak influence of the nitro group on the electronic properties of the metal centres and hence hardly affecting the ruthenium-to-CO  $\pi$ -backbonding interactions. Apparently, the NO<sub>2</sub> substituent is relatively strongly conjugated with the uncoordinated acetylene moiety of the cluster-anchored tolan ligand, while interactions with the cluster core are more limited.

The first oxidation event is clearly cluster centred (Table 4). The  $v_{as}(NO_2)$  and  $v_s(NO_2)$  bands shifted by 2 and



Fig. 6. IR spectral changes in the C $\equiv$ C and C $\equiv$ O stretching region observed during the irreversible oxidation of complex **3d** at the anodic wave O1 (Table 2) in CH<sub>2</sub>Cl<sub>2</sub> at 293 K, using an OTTLE cell. The asterisk denotes a product of a slow thermal reaction of the oxidized complex.

1 cm<sup>-1</sup>, respectively, to higher frequencies when the triruthenium cluster core in 3d was oxidized at the anodic potential O1 (Table 4). In addition, the oxidation at potential O1 was accompanied by a  $v(C \equiv C)$  shift to 2217 cm<sup>-1</sup> (Fig. 6), which is a significantly smaller absolute shift  $(3 \text{ cm}^{-1})$  than that induced by the NO<sub>2</sub> reduction  $(27 \text{ cm}^{-1})$ . Perhaps surprisingly, the irreversible oxidation of the cluster core largely preserved the  $v(C \equiv O)$  band pattern, with the oxidation product exhibiting v(CO) bands at 2100m, 2051s, 2014s, 1997sh, 1977mw, 1962sh and 1947w  $cm^{-1}$  (Fig. 6). The shift of the v(C $\equiv$ O) bands to higher wavenumbers by  $40-70 \text{ cm}^{-1}$ , the greatest shift being associated with the fully symmetric all-CO-stretching mode, is consistent with the two-electron nature of the oxidation wave O1. Whilst it is beyond the scope of this work to determine the structure of the oxidation product, we can, however, state firmly that the irreversible two-electron oxidation of 3d does not induce a rapid CO dissociation reaction and that the geometry of the triruthenium-carbonyl moiety remains largely preserved after this initial oxidation event. The initially observed oxidation product is, however, thermally unstable and slowly converts to another carbonyl cluster species, as judged from a new absorption at  $2081 \text{ cm}^{-1}$  (Fig. 6).

The oxidation products derived from **3a** and **3c** were significantly more chemically reactive, with rapid *in situ* electrochemical oxidation of either species resulting directly in a product with a v(C=0) band pattern (2083m, 2074sh, 2049m, 2035s, 2024m, 2008s, 1995m-s, 1983m, 1960m-w, 1946sh and 1917w cm<sup>-1</sup>) quite different from the parent clusters being observed in each case. In line with the very limited electronic communication between the X group and the cluster core, the v(C=0) band of the ester moiety in **3c** was almost unchanged, shifting from 1720 cm<sup>-1</sup> in

**3c** to  $1722 \text{ cm}^{-1}$  in the oxidized species. Interestingly, oxidation of **3a** and **3c** caused the  $v(C \equiv C)$  band to completely disappear. This observation is in sharp contrast with the *in situ* electrochemical oxidation of cluster **3d**, where the  $v(C \equiv C)$  band is initially preserved (Fig. 6). We assume that the ethynylene moiety in **3a** and **3c** features in fast chemical reactions that follow the initial two-electron oxidation. In contrast, the conjugation of the acetylene moiety to the nitro-phenyl-acetylene unit in **3d** appears to stabilize the initial oxidation product to such an extent that it can be observed by IR spectroelectrochemical methods at room temperature.

## 3. Conclusion

A series of gold(I)-phosphine complexes of ethynyl tolans has been prepared and structurally characterized. The solid-state packing of these compounds exhibits various intramolecular contacts between the tolan ligands. but not aurophilic interactions, which are presumably limited by the steric bulk of the triphenyl phosphine supporting ligand. The gold complexes are convenient reagents for use in the preparation of tolans bearing heterometallic cluster end-caps. The cluster carbonyl bands are insensitive to the electronic nature of the tolan substituent, including NO<sub>2</sub>-centred reduction in the case of 3d. Oxidation is centred on the cluster core, and in the case of the most stable system, 3d, IR spectroelectrochemistry reveals the oxidation product to retain the same carbonyl arrangement as the starting material. The tolan group does not act as a particularly efficient conduit for passage of the electronic effect of electron-donating or electron-withdrawing groups to the cluster core.

#### 4. 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, and degassed before use. No special precautions were taken to exclude air or moisture during work-up. Preparative TLC was performed on  $20 \times 20$  cm glass plates coated with silica gel (0.5 mm thick, Merck GF-254). The compounds  $[Ru_3(CO)_{10}(\mu\text{-dppm})]$  [47], [AuCl(PPh<sub>3</sub>)] [48], [PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] [49], 1-trimethylsilylethynyl-4-ethynylbenzene [34b], 1a, its analogous terminal alkyne and **3b** [30] were prepared by literature methods. Other reagents were purchased and used as received. Dichloromethane (Acros Chemicals) for the spectroelectrochemical experiments was freshly distilled from P2O5 under an atmosphere of dry nitrogen. Bu<sub>4</sub>NPF<sub>6</sub> electrolyte (TBAH; Aldrich) was recrystallized twice from absolute ethanol and dried overnight under vacuum at 80 °C before use.

IR spectra of the synthesized complexes were recorded using a Nicolet Avatar spectrometer from cyclohexane solutions in a cell fitted with CaF<sub>2</sub> windows, or from Nujol mulls suspended between NaCl plates. NMR spectra were obtained with Bruker Avance (<sup>1</sup>H 400.13 MHz, <sup>13</sup>C 100.61 MHz, <sup>31</sup>P 161.98 MHz) or Varian Mercury (<sup>31</sup>P 161.91 MHz) spectrometers from CDCl<sub>3</sub> solutions and referenced against solvent resonances (<sup>1</sup>H, <sup>13</sup>C) or external H<sub>3</sub>PO<sub>4</sub> (<sup>31</sup>P). Mass spectra were recorded using Thermo Quest Finnigan Trace MS-Trace GC or Thermo Electron Finnigan LTQ FT mass spectrometers or Matrix-Assisted Laser Desorption/Ionization-Time-of-Flight (Mass Spectrometry) (MALDI-TOF MS) ABI Voyager STR.

Cyclic voltammograms were recorded at  $v = 100 \text{ mV s}^{-1}$ from solutions of approximately  $10^{-4}$  M in analyte in dichloromethane containing  $10^{-1}$  M Bu<sub>4</sub>NPF<sub>6</sub>, using a gastight single-compartment three-electrode cell equipped with platinum disk working (apparent surface area of 0.42 mm<sup>2</sup>), coiled platinum wire auxiliary, and silver wire pseudo-reference electrodes. The working electrode surface was polished between scans with a diamond paste containing 0.25 um grains (Oberflächentechnologien Ziesmer, Kempen, Germany). The cell was placed in a Faraday cage and connected to a computer-controlled PAR Model 283 potentiostat. All redox potentials are reported against the standard ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) redox couple used as an internal reference system [50]. Cyclic voltammetric measurements at ca. 210 K were performed with the electrochemical cell immersed into a bath of acetone/dry ice.

IR spectroelectrochemical experiments at room temperature were performed with an air-tight optically transparent thin-layer electrochemical (OTTLE) cell equipped with a Pt minigrid working electrode (32 wires cm<sup>-1</sup>) and CaF<sub>2</sub> windows [51]. The cell was positioned in the sample compartment of a Bruker Vertex 70 FTIR spectrometer (1 cm<sup>-1</sup> spectral resolution, 16 scans). The controlledpotential electrolyses were carried out with a PA4 potentiostat (EKOM, Polná, Czech Republic).

Diffraction data were collected at 120K on a Bruker SMART 6000 (**2a,e, 3b,e**), SMART 1K (**2d**) and Bruker PROT-EUM-M (**3c,d**) three-circle diffractometers, using graphitemonochromated Mo K $\alpha$  radiation. The structures were solved by direct-methods and refined by full matrix leastsquares against  $F^2$  of all data using SHELXTL software [52]. All non-hydrogen atoms where refined in anisotropic approximation except the disordered ones, H atoms were placed into the calculated positions and refined in "riding" mode. The crystallographic data and parameters of the refinements are listed in Table 5.

## 4.1. Preparation of 1b

#### 4.1.1. General procedure

A nitrogen purged, 500 ml Schlenk flask was charged with 1-iodo-4-methoxybenzene (2.34 g, 10 mmol), 1-trimethylsilylethynyl-4-ethynylbenzene (2.18 g, 11 mmol),  $[PdCl_2(PPh_3)_2]$  (0.70 g, 0.1 mmol) and CuI (0.19 g, 0.1 mmol). Triethylamine (ca. 250 ml) was transferred to the reaction flask via cannula and the reaction mixture

Table 5 Crystal data and parameters of refinement of the structures 2b,d,e and 3b-e<sup>a</sup>

	2b	2d	2e	3b	3c	3d	3e
Formula	C35H26AuOP	C35H25AuCl2NO2P	C35H23AuNP	C67H48AuO8P3Ru3	C69H48AuCl3O9P3Ru3	C67H46AuCl3NO9P3Ru3	C68H46AuCl3NO7P3Ru3
Formula weight	690.49	790.40	685.48	1574.14	1720.51	1708.48	1688.49
Crystal system	triclinic	triclinic	triclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\overline{1}$	$P2_1/n$	$P2_1/c$	$P2_1/c$	$P2_1/n$
a (Å)	9.762(1)	11.750(4)	8.7340(8)	11.004(1)	11.095(2)	11.145(2)	11.0569(3)
b (Å)	17.617(3)	11.792(4)	9.8435(9)	27.520(3)	27.417(5)	27.492(4)	27.3570(7)
c (Å)	18.133(3)	13.058(4)	16.4629(15)	20.590(2)	23.226(4)	23.130(3)	20.6694(5)
α (°)	110.01(1)	64.42(3)	86.948(2)	90	90	90	90
β (°)	100.21(1)	76.49(3)	88.443(2)	90.54(3)	115.83(7)	118.25(1)	91.71(1)
γ (°)	101.30(1)	68.08(3)	82.302(2)	90	90	90	90
$V(Å^3)$	2770.4(7)	1508.2(9)	1400.3(2)	6235(1)	6359(2)	6242(1)	6249.4(3)
Ζ	4	2	2	4	4	4	4
$D_{\text{calc}}$ (Mg/m <sup>3</sup> )	1.656	1.740	1.626	1.677	1.797	1.818	1.795
Absorption coefficient (mm <sup>-1</sup> )	5.394	5.141	5.334	3.189	3.258	3.319	3.312
<i>F</i> (000)	1352	772	668	3080	3364	3336	3296
Reflections collected	26767	14640	19102	84736	71159	63851	65628
Independent reflections $(R_{int})$	10880(0.0423)	7531(0.0213)	8473(0.023)	19038(0.038)	17700(0.052)	15492(0.0532)	19840(0.0434)
Number of parameters	652	383	343	578	738	784	655
Absorption correction	SADABS	SADABS	SADABS	sadabs <sup>b</sup>	SADABS	SADABS	numerical
Goodness-of-fit	0.980	1.046	1.040	1.106	1.006	1.067	1.055
Final $R_1 [I > 2\sigma]$	0.0331	0.0236	0.0206	0.0350	0.0416	0.0423	0.0298
Final $wR_2$ (all data)	0.0797	0.0552	0.0489	0.0925	0.0991	0.0865	0.0714

<sup>a</sup> The structures **3b–e** are, in fact, isostructural – the  $P2_1/n$  setting is transformed into the standard  $P2_1/c$  one by usual (1,0,0,0,1,0,-1,0,1) operation. <sup>b</sup> The disordered solvent (CHCl<sub>3</sub>) has been taken into account by applying SQUEEZE procedure (PLATON).

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heated to reflux for 2 h. The solvent was removed *in vacuo* and the residue passed through a silica pad with hexane and CH<sub>2</sub>Cl<sub>2</sub>. The solvent was removed *in vacuo* to give a yellow solid of the title product (**1b**) which was recrystallized from hexane and CH<sub>2</sub>Cl<sub>2</sub> (1.90 g, 62%). IR (Nujol):  $v(C \equiv C)$  2215, 2158 cm<sup>-1</sup>. <sup>1</sup>H NMR:  $\delta$  0.25 (s, 9H; SiMe<sub>3</sub>), 3.83 (s, 3H; OMe), 6.88 (pseudo-d,  $J_{HH} = 8.6$  Hz, 2H; C<sub>6</sub>H<sub>4</sub>), 7.43 (s, 4H; C<sub>6</sub>H<sub>4</sub>), 7.46 (pseudo-d,  $J_{HH} = 8.6$  Hz, 2H; C<sub>6</sub>H<sub>4</sub>). <sup>13</sup>C NMR:  $\delta$  0.13 (s, SiMe<sub>3</sub>), 55.3 (OCH<sub>3</sub>), 85.7, 91.4, 96.0, 04.76 (4×s, C = C), 114.04, 115.09, 122.49, 123.70, 131.20, 131.80, 133.08, 159.81 (8×s, Ar). EI-MS: m/z 304, M<sup>+</sup>; 274, [M–OMe]<sup>+</sup>; 201, [M–OMe–SiMe<sub>3</sub>]<sup>+</sup>. C<sub>20</sub>H<sub>20</sub>OSi requires: C, 78.90; H, 7.11. Found: C, 78.24; H, 6.58%.

Compounds 1c-e were prepared in an entirely analogous fashion, full details of which will be published elsewhere. Compound 1c (crystallized from hot toluene, yield 49%). (Nujol):  $v(C \equiv C)$  2211, 2155 cm<sup>-1</sup>;  $v(C \equiv O)$ IR  $1715 \text{ cm}^{-1}$ . C<sub>21</sub>H<sub>20</sub>O<sub>2</sub>Si requires: C, 75.86; H, 6.05. Found: C, 75.85; H 5.95%. Compound 1d (purified by column chromatography, silica, hexane-CH2Cl2 70/30, yield 84%). IR (Nujol): v(C=C) 2209, 2149 cm<sup>-1</sup>. C<sub>19</sub>H<sub>17</sub>NO<sub>2</sub>Si requires: C, 71.47; H, 5.33; N, 4.39. Found C, 71.44; H, 4.62; N, 4.94%. Compound 1e (purified by column chromatography, Silica, hexane-CH2Cl2 60/40, yield 91%). IR (Nujol):  $v(C \equiv N)$  2224 cm<sup>-1</sup>;  $v(C \equiv C)$  2209, 2149 cm<sup>-1</sup>. C<sub>20</sub>H<sub>17</sub>NSi requires: C, 80.22; H, 5.72; N, 4.68. Found: C, 79.90; H, 5.63; N, 4.23%.

# 4.2. Desilylation of 1b

# 4.2.1. General procedure

A solution of **1b** (150 mg, 0.49 mmol) and potassium carbonate (273 mg, 1.97 mmol) in MeOH (30 ml) was stirred under nitrogen at room temperature overnight (ca. 12 h). The reaction mixture was partitioned between diethylether (50 ml) and water (50 ml), the organic layer collected, dried over MgSO<sub>4</sub>, and finally dried *in vacuo* to afford HC=CC<sub>6</sub>H<sub>4</sub>C=CC<sub>6</sub>H<sub>4</sub>OMe-4 (**1b-H**) as a yellow solid (102 mg, 89%). IR (Nujol): v(C=C) 2214, 2103 cm<sup>-1</sup>. <sup>1</sup>H NMR:  $\delta$  3.16 (s, 1H, C=CH); 3.83 (s, OMe); 6.90 (pseudo-d,  $J_{HH}$  = 8.8 Hz, 2H, C<sub>6</sub>H<sub>4</sub>); 7.48 (pseudo-d,  $J_{HH}$  = 9.6 Hz, 6H, C<sub>6</sub>H<sub>4</sub>). <sup>13</sup>C NMR:  $\delta$  55.3 (s, OCH<sub>3</sub>); 78.7, 83.3, 87.6, 91.5 (4 × s, 4 × C=C); 114.1, 115.1, 121.5, 124.2, 131.3, 132.0, 133.1, 159.9 (8 × s, Ar). EI-MS: *m/z* 232, M<sup>+</sup>; 217, [M–Me]<sup>+</sup>. C<sub>17</sub>H<sub>12</sub>O requires: C, 87.93; H, 5.17. Found: C, 87.24; H, 5.05%.

Compounds **1c–e** were desilylated in a similar fashion, full details of which will be reported elsewhere. Compound **1c-H** (yield 85%). IR (Nujol):  $v(C \equiv C)$  2211, 2101 cm<sup>-1</sup>;  $v(C \equiv O)$  1707 cm<sup>-1</sup>. C<sub>18</sub>H<sub>12</sub>O<sub>2</sub> requires: C, 83.08; H, 4.62. Found: C, 81.37; H, 4.59%. Compound **1d-H** (yield 89%). IR (Nujol):  $v(C \equiv C)$  2210, 2101 cm<sup>-1</sup>. C<sub>16</sub>H<sub>9</sub>NO<sub>2</sub> requires: C, 77.73; H, 3.64; N 5.67. Found: C, 77.72; H, 3.89; N, 5.31%. Compound **1e-H** (yield 51%). IR (Nujol):  $v(C \equiv N)$  2227 cm<sup>-1</sup>;  $v(C \equiv C)$  2209, 2100 cm<sup>-1</sup>. C<sub>17</sub>H<sub>9</sub>N requires: C, 89.87; H, 3.96; N 6.17. Found: C, 89.43; H, 3.98; N, 5.74%.

### 4.3. Preparation of 2b

#### 4.3.1. General procedure

A suspension of 1b (135 mg, 0.44 mmol) and NaOH (162 mg, 4.05 mmol) in MeOH (25 ml) was allowed to stir for 30 min, to give a clear solution, which was treated with [AuCl(PPh<sub>3</sub>)] (200 mg, 0.40 mmol) and allowed to stir for a further 3 h. The resulting cloudy solution was filtered, the precipitate washed with MeOH (6 ml), diethylether (6 ml) and pentane (6 ml) and dried in vacuo to afford 2b (180 mg, 65%). IR (Nujol):  $v(C \equiv C)$  2204, 2113 cm<sup>-1</sup>. <sup>1</sup>H NMR:  $\delta$  3.82 (s, 3H, OMe); 6.88 (pseudo-d,  $J_{HH} = 8.8$  Hz, 2H, C<sub>6</sub>H<sub>4</sub>); 7.38–7.58 (m, 21H, Ar). <sup>13</sup>C NMR:  $\delta$  55.6 (s, OCH<sub>3</sub>); 88.5, 90.8 (2×s, 2×C $\equiv$ C); 104.3 (d, = 27 Hz, Au-C=C), 129.7 (d,  $J_{CP} = 56$  Hz, Au-C=C); 114.2, 115.7, 122.0, 124.7, 131.3, 132.5, 133.5, 135.1 (8×s, Ar); 129.4 (d,  $J_{CP} = 11$  Hz), 131.9 (d,  $J_{CP} = 3$  Hz), 134.6 (d,  $J_{CP} = 14$  Hz), 159.8 (s) (P–Ar). <sup>31</sup>P NMR:  $\delta$  43.4. ES-MS: m/z 721,  $[Au(PPh_3)_2]^+$ ; 713,  $[M+Na]^+$ .  $C_{35}H_{26}NO-$ PAu requires: C, 60.87; H, 3.77. Found: C, 60.43; H, 3.73%.

Compounds 2c-e were prepared in a similar fashion. 2c (yield 78%). IR (Nujol):  $v(C \equiv C)$  2210, 2111 cm<sup>-1</sup>; v(C = O)1776 cm<sup>-1</sup>. <sup>1</sup>H NMR:  $\delta$  3.92 (s, 3H, OMe); 7.28–7.58 (m, 21H, Ar); 8.02 (pseudo-d,  $J_{\rm HH} = 8.8$  Hz, 2H, C<sub>6</sub>H<sub>4</sub>). <sup>13</sup>C NMR:  $\delta$  52.5 (s, OCH<sub>3</sub>); 90.00, 92.9 (2×s, 2×C=C); 104.2 (d, = 27 Hz, Au–C $\equiv$ C), 130.1 (d,  $J_{CP}$  = 56 Hz, Au-C=C); 121.0, 125.7, 128.3, 129.8, 130.1, 131.6, 132.6, 135.0 (8×s, Ar); 129.5 (d,  $J_{CP} = 11 \text{ Hz}$ ), 131.9 (d,  $J_{\rm CP} = 2$  Hz), 134.6 (d,  $J_{\rm CP} = 14$  Hz), 136.0 (s) (P–Ar); 166.8(s, C=OCH<sub>3</sub>). <sup>31</sup>P NMR:  $\delta$  43.3. ES-MS: m/z 1635,  $[M+(AuPPh_3)_2]^+; 1177, [M+AuPPh_3]^+; 721, [Au(PPh_3)_2]^+.$ C<sub>36</sub>H<sub>26</sub>O<sub>2</sub>PAu requires: C, 60.17; H, 3.62. Found: C, 60.31; H, 3.66%. Compound 2d (yield 69%). IR (Nujol): v(C=C) 2214, 2109 cm<sup>-1</sup>. <sup>1</sup>H NMR:  $\delta$  7.43–7.58 (m, 19H, Ar); 7.65 (pseudo-d,  $J_{\rm HH} = 8.8$  Hz, 2H, C<sub>6</sub>H<sub>4</sub>); 8.22 (pseudo-d,  $J_{\rm HH} = 9.2$  Hz, 2H, C<sub>6</sub>H<sub>4</sub>). <sup>13</sup>C NMR:  $\delta$  88.9, 95.3 (2×s,  $2 \times C \equiv C$ ; 130.1 (d,  $J_{CP} = 56$  Hz, Au-C  $\equiv C$ ); 120.3, 123.9, 126.3, 130.6, 131.8, 132.4, 132.7 (7×s, Ar); 129.5 (d,  $J_{CP} = 11$  Hz), 131.9 (d,  $J_{CP} = 2$  Hz), 134.6 (d,  $J_{CP} = 14$  Hz); 147.1 (s) (P-Ar). <sup>31</sup>P NMR:  $\delta$  43.3. ES-MS: m/z 1625,  $[M+(AuPPh_3)_2]^+$ ; 1164,  $[M+AuPPh_3]^+$ ; 721, [Au(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup>. C<sub>34</sub>H<sub>23</sub>NO<sub>2</sub>PAu requires: C, 57.87; H, 3.26; N 1.99. Found: C, 57.46; H, 3.23; N, 1.80%. Compound **2e** (yield 71%). IR (Nujol):  $v(C \equiv N)$  2217 cm<sup>-1</sup>;  $v(C \equiv C)$  2169, 2113 cm<sup>-1</sup>. <sup>1</sup>H NMR:  $\delta$  7.41–7.63(m, 19H, Ar). <sup>13</sup>C NMR:  $\delta$  89.1, 94.3 (2×s, 2×C=C); 104.0 (d, = 22 Hz, Au–C $\equiv$ C), 130.0 (d,  $J_{CP} = 55$  Hz, Au–C $\equiv$ C); 111.5, 118.8, 126.1, 126.8, 128.5, 131.6, 131.7, 132.6  $(8 \times s, Ar)$ ; 129.5 (d,  $J_{CP} = 12 \text{ Hz}$ ), 131.9 (d,  $J_{CP} = 2 \text{ Hz}$ ), 134.6 (d,  $J_{CP} = 14$  Hz), 168.4 (s) (P–Ar). <sup>31</sup>P NMR:  $\delta$ 43.3. ES-MS: *m*/*z* 1144, [M+AuPPh<sub>3</sub>]<sup>+</sup>; 721, [Au(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup>. C<sub>35</sub>H<sub>23</sub>NPAu requires: C, 61.31; H, 3.36; N 2.04. Found: C, 61.61; H, 3.33; N, 1.93%.

#### 4.4. Preparation of 3b

## 4.4.1. General procedure

A solution of  $Ru_3(CO)_{10}$  (µ-dppm) (100 mg, 0.10 mmol) and **2b** (71 mg, 0.10 mmol) in THF (15 ml) was heated at reflux, with the progress of the reaction being monitored by TLC and IR spectroscopy. When adjudged complete (ca. 3 h), the solvent was removed and the residue purified by preparative TLC (hexane-CH<sub>2</sub>Cl<sub>2</sub> 60:40) and the yellow band collected, and recrystallized (CHCl<sub>3</sub>/hexane) to afford orange crystals of **3b** (67 mg, 41%) suitable for X-ray crystallography. IR (cyclohexane): v(CO) 2038s, 1993s, 1972s, 1956m, 1939m, 1909w cm<sup>-1</sup>. <sup>1</sup>H NMR:  $\delta$  2.36 (s, 3H, OMe), 3.35, 4.26 ( $2 \times dt$ ,  $J_{HP} = 12$  Hz,  $J_{HH} = 11$  Hz, 2H, dppm), 6.39–7.94 (m, 43H, Ar). <sup>31</sup>P NMR:  $\delta$  38.5 (d,  $J_{\rm PP} = 62$  Hz); 40.8 (dd,  $J_{\rm PP} = 62$  Hz,  $J_{\rm PP} = 39$  Hz); 61.1 (d,  $J_{PP} = 39$  Hz). ES-MS: m/z 1575,  $[M+H]^+$ ; 721,  $[Au(PPh_3)_2]^+$ . C<sub>67</sub>H<sub>48</sub>O<sub>8</sub>P<sub>3</sub>Ru<sub>3</sub>Au requires: C, 51.12; H, 3.07. Found: C, 51.33; H, 3.10%.

The clusters 3c-e were prepared in a similar fashion, and crystallized from CHCl<sub>3</sub>/MeOH to give single crystals suitable for X-ray crystallography. Compound 3c IR (cyclohexane): v(CO) 2034s, 1991s, 1971s, 1959m, 1938m, 1912w cm<sup>-1</sup>, v(C=O) 1730 cm<sup>-1</sup>; (CH<sub>2</sub>Cl<sub>2</sub>): v(CO) 2029s, 1984s, 1965vs, 1950sh, 1931m-w, 1907w cm<sup>-1</sup>; v(C≡C) 2213 cm<sup>-1</sup>; v(C=0) 1720 cm<sup>-1</sup>. <sup>1</sup>H NMR:  $\delta$  2.64 (s, 3H, OMe), 3.52, 4.26 (2 × dt,  $J_{HP} = 11$  Hz,  $J_{HH} = 10$  Hz, 2H, dppm), 6.38–8.04 (m, 43H, Ar). <sup>31</sup>P NMR:  $\delta$  38.7 (d,  $J_{\rm PP} = 62 \text{ Hz}$ ; 41.3 (dd,  $J_{\rm PP} = 62 \text{ Hz}$ ,  $J_{\rm PP} = 38 \text{ Hz}$ ); 61.3 (d,  $J_{PP} = 39$  Hz). ES-MS: m/z 1603,  $[M+H]^+$ ; 721,  $[Au(PPh_3)_2]^+$ . C<sub>68</sub>H<sub>48</sub>O<sub>9</sub>P<sub>3</sub>Ru<sub>3</sub>Au requires: C, 50.97; H, 3.00. Found: C, 50.67; H, 3.34%. Compound 3d IR (cyclohexane): v(CO) 2034s, 1992s, 1971s, 1955m, 1940m, 1910w cm<sup>-1</sup>; (CH<sub>2</sub>Cl<sub>2</sub>): v(CO) 2030s, 1985s, 1966vs, 1953sh, 1931m-w, 1906w cm<sup>-1</sup>;  $v(C \equiv C)$  2213 cm<sup>-1</sup>;  $v_{as}(NO_2)$ 1519 cm<sup>-1</sup> and  $v_s(NO_2)$  1344 cm<sup>-1</sup>. <sup>1</sup>H NMR:  $\delta$  3.39, 4.30  $(2 \times dt, J_{HP} = 11 \text{ Hz}, J_{HH} = 10 \text{ Hz}, 2\text{ H}, \text{ dppm}),$ 6.38–8.24 (m, 43H, Ar). <sup>31</sup>P NMR:  $\delta$  38.7 (d,  $J_{PP} = 62$  Hz); 40.6 (dd,  $J_{PP} = 62$  Hz,  $J_{PP} = 38$  Hz); 61.3 (d,  $J_{PP} = 39$  Hz). ES-MS: m/z 1590,  $[M+H]^+$ ; 721  $[Au(PPh_3)_2]^+$ . C<sub>66</sub>H<sub>45</sub>O<sub>9</sub>NP<sub>3</sub>Ru<sub>3</sub>Au requires: C, 49.84; H, 2.83; N, 0.88. Found: C, 49.54; H, 2.64; N, 0.78%. Compound 3e IR (cyclohexane):  $v(C \equiv N)$  2212 cm<sup>-1</sup>, v(CO) 2035s, 1991s, 1973s, 1941m, 1918w cm<sup>-1</sup>. <sup>1</sup>H NMR:  $\delta$  3.37, 4.28 (2 × dt,  $J_{\rm HP} = 11$  Hz,  $J_{\rm HH} = 10$  Hz, 2H, dppm), 6.36–8.06 (m, 43H, Ar). <sup>31</sup>P NMR:  $\delta$  38.5 (d,  $J_{PP} = 62$  Hz); 41.0 (dd,  $J_{\rm PP} = 62$  Hz,  $J_{\rm PP} = 39$  Hz); 61.1 (d,  $J_{\rm PP} = 39$  Hz). ES-MS: m/z2028, [M+AuPPh<sub>3</sub>]<sup>+</sup> 1570,  $[M+H]^+$ . C<sub>67</sub>H<sub>45</sub>O<sub>7</sub>P<sub>3</sub>Ru<sub>3</sub>Au requires: C, 51.24; H, 2.87; N, 0.89. Found: C, 51.08; H, 2.86; N, 0.93%.

## 5. Supplementary material

CCDC 632295, 632296, 632297, 632298, 632299, 632300 and 632301 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving. html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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