



Iodo-alkynyl- and iodo-butadiynyl-ruthenium complexes

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ABSTRACT

Addition of $[I(py)_2]BF_4$ to $Ru(C\equiv CH)(dppe)Cp^*$ gave the iodovinylidene $[Ru(=C=CHI)(dppe)Cp^*]BF_4$ **1**, which could be deprotonated to $Ru(C\equiv C)(dppe)Cp^*$ **2**. The attempted preparation of $Ru(C\equiv C-C\equiv C)(dppe)Cp^*$, followed by derivatisation with tcne, gave the diynyl $Ru\{C\equiv CC[=C(CN)_2]-C\equiv C(CN)_2\}(dppe)Cp^*$ **3**. The Pd(0)/Cu(I)-catalysed reaction of **3** with $Ru\{C\equiv CC\equiv CAu(PPh_3)\}(dppe)Cp^*$ afforded $Ru\{C\equiv CC\equiv C(CN)_2C\equiv C(CN)_2Au(PPh_3)\}(dppe)Cp^*$ **4** by formal replacement of I^+ by $[Au(PPh_3)]^+$. XRD structures of **1–4** are reported.

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1. Introduction

Iodo-di- and poly-yne have developed into useful reagents for a variety of syntheses, ranging from linear carbon allotropes [1] through ordered poly(diiodobutadiyne) [2] to a variety of highly unsaturated organic molecules including natural products [3]. Considerable interest has been evinced in their spectroscopic properties [4], while their formulation as iodine-capped carbon chains renders them also suitable for molecular assembly [5]. Metal complexes have included systems such as $\{ML_n\}_2(\mu-\eta^2:\eta^2-IC_2C_2I)$ ($ML_n = WCl_5$ [6], $Rh_2(\mu-O_2CCF_3)_4(OCMe_2)$ [7]), and iododiyne have been employed in the Cadiot–Chodkiewicz reaction [8]. Several hypervalent iodonium derivatives are known [9]. The syntheses of bis(carbene) complexes via iododiyne such as $IC\equiv CC\equiv CSiMe_3$ has been reported [10], while thermolysis within molecular sieves such as MCM-41 results in polymerisation to form novel oligo-yne [11].

More recently, we described a methodology towards long carbon chains end-capped by transition metal groups which involves elimination of phosphine–gold(I) halides between compounds containing $C(sp)-$ or $C(sp^2)-X$ bonds and alkynyl or poly-ynyl-gold(I) complexes [12]. While we have used this approach on

numerous occasions with organic halo-alkenes or -alkynes [13], we considered that a desirable target would be the reverse reaction in which iodo-alkynyl- or -poly-ynyl-metal complexes could be employed. There appear to be relatively few iodo-alkynyl-metal complexes described, of which recent examples are $Ru(C\equiv C)Cl-L_2(\eta^5-C_9H_7)$ [$L_2 = (PPh_3)_2, dppe$], obtained from the corresponding lithiated ethynyl complexes and $[I(py)_2]BF_4$ [14]. Hitherto, our experience has been that iodoethynyl-metal complexes are somewhat unstable and do not readily lend themselves to isolation and further characterisation. However, by using the bulky and electron-rich $Ru(dppe)Cp^*$ fragment as an end-group, we have been able to synthesise $Ru(C\equiv C)(dppe)Cp^*$, and to obtain evidence for the formation of the next homologue, $Ru(C\equiv CC\equiv C)(dppe)Cp^*$.

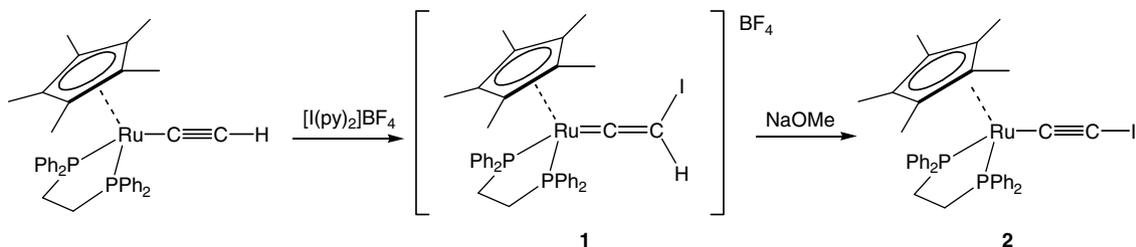
2. Results and discussion

We sought to prepare an iodoethynyl complex from the reaction between $Ru(C\equiv CH)(dppe)Cp^*$ and $[I(py)_2]BF_4$. However, the only product obtained was the iodovinylidene $[Ru(=C=CHI)(dppe)Cp^*]BF_4$ **1** (Scheme 1). This complex was identified by microanalysis and from its ES-MS, which contained M^+ and $[M-I]^+$ at m/z 787 and 660, respectively. In the IR spectrum, there was no $\nu(C\equiv C)$ band, but a medium intensity band at 1612 cm^{-1} can be assigned to $\nu(C=C)$. In the 1H NMR spectrum, the vinylidene proton is found at δ 4.62, while the characteristic downfield triplet C_α resonance at δ_c 323.94 also lends support to the structural interpretation. Confirmation of the nature of this compound was achieved by a

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Scheme 1.

single-crystal XRD structure determination. Addition of positive iodine to the Ru–C≡CH fragment to give Ru=C=CHI⁺ follows the precedent established many years ago in the reaction of Ru(C≡CPh)(PPh₃)₂Cp with I₂ [19].

Treatment of **1** with base (KOBU^t) resulted in ready deprotonation to afford orange Ru(C≡CI)(dppe)Cp* **2** in 86% yield, characterised by microanalysis and spectroscopic methods, together with a single-crystal XRD structure determination. A strong ν(C≡C) band is found at 1995 cm⁻¹, while the NMR spectra contained the resonances characteristic of the Ru(dppe)Cp* group. In addition, a singlet at δ_C –13.42 could be assigned to C_α, but the resonance of C_β was not distinguishable. In the ES-MS, notable ions included [2(M–I)+Na]⁺ and [2(M–I)]⁺ at *m/z* 1341 and 1318, respectively.

Lithiation of Ru(C≡CC=CH)(dppe)Cp* readily affords a derivative which can be considered to be Ru(C≡CC=CLi)(dppe)Cp*, although it is unlikely that the molecular structure is as simple as this representation implies. Similar lithio-poly-ynyl complexes have also been described by Wong [15], Akita [16] and Gladysz [17]. When the lithio derivative was made in situ, followed by addition of [I(py)₂]BF₄ at –78 °C, a yellow solution was obtained. Several attempts to isolate the supposed iodobutadiynyl complex were unsuccessful, but addition of the electrophilic alkene tcne resulted in a rapid colour change to dark purple. Separation by preparative t.l.c. (silica gel, acetone–dichloromethane, 1/99) afforded two products, of which the major component **3** formed dark purple crystals. The minor product has not yet been fully characterised.

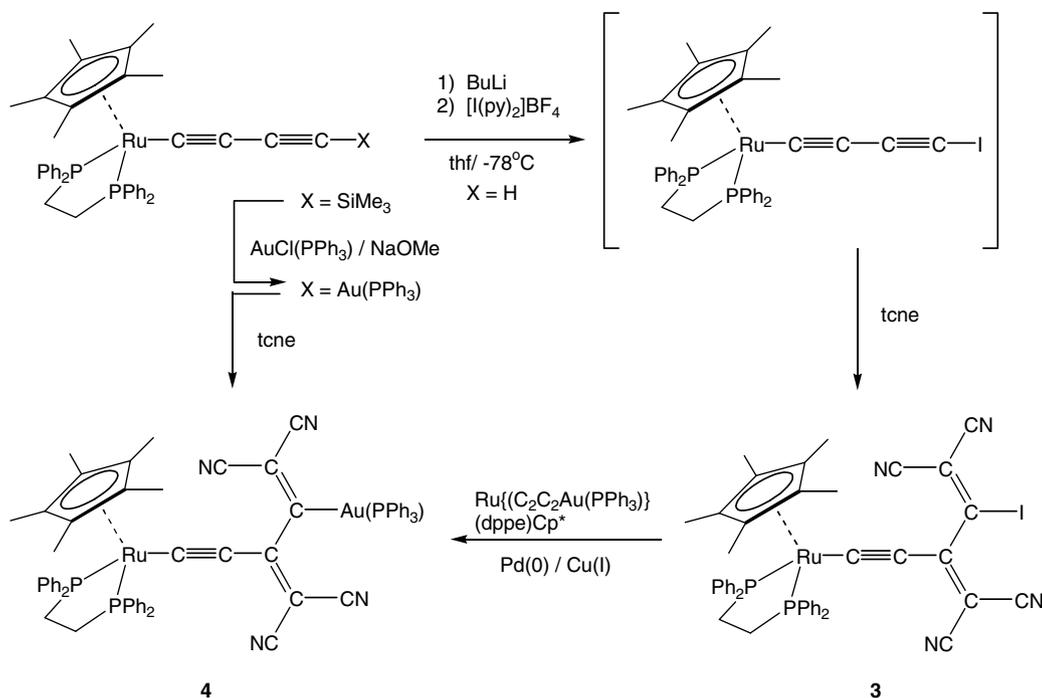
Compound **3** was characterised as the tetracyanoiodobutadienyl complex Ru{C≡CC=C(CN)₂}Cl=C(CN)₂(dppe)Cp* by means of elemental analyses and a single-crystal XRD study (see below). The spectroscopic properties were in accord with the solid-state structure, including ν(CN) at 2206 and 2188 cm⁻¹, and a broad ν(C≡C) band at 1965 cm⁻¹. The ¹H NMR spectrum contained resonances for Cp* (δ 1.25), dppe–CH₂ (δ 1.97–2.06 and 2.53–2.62) and Ph protons (δ 6.78–7.25). The ¹³C NMR spectrum contains resonances at δ 10.01 and 97.32 (Cp*), 29.30–29.91 (dppe CH₂), four singlets between δ 110.44 and 115.77 (CN) and multiple aromatic signals between δ 127.97 and 133.56. The skeletal carbons of the C₄ chain were found at δ 98.62, 134.24–136.46 and 144.71. The dppe ³¹P nuclei formed an AB quartet at δ 80.3 and 80.7 [J(PP) = 17 Hz]. The EI-MS, from a solution in MeOH and MeCN containing NaOMe, contained a strong ion at *m/z* 961, assigned to [M+Na]⁺, together with weak M⁺ and [M–I]⁺. Unusually, at higher *m/z*, ions corresponding to [2M+Na]⁺ (*m/z* 1899) suggest that some association occurs in solution. The redox properties include an irreversible wave at –0.78 V [assigned to reduction of the =C(CN)₂ groups] and two oxidation processes at +0.86 and +1.28 V, occurring at the Ru–C_n chain.

The chemistry described above is summarised in Scheme 2. Metallation of Ru(C≡CC=CH)(dppe)Cp* with LiBu affords the lithio derivative, which is iodinated at the terminal carbon using [I(py)₂]BF₄ as reported earlier for Ru(C≡CLi)(PPh₃)₂(η⁵-C₉H₇) [14]. By keeping the mixture at low temperatures, we were able to perform the subsequent reaction with tcne in reasonable con-

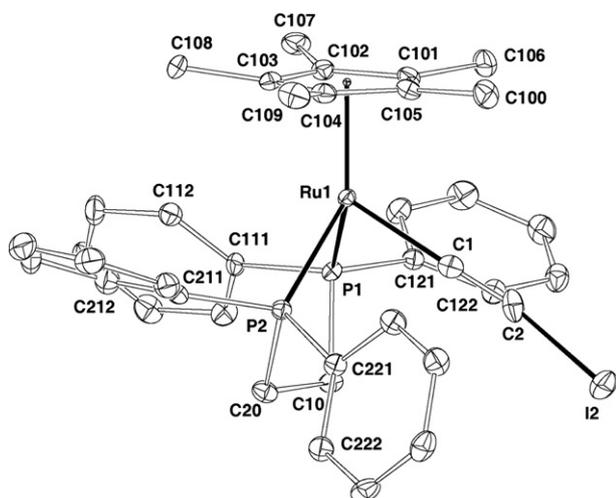
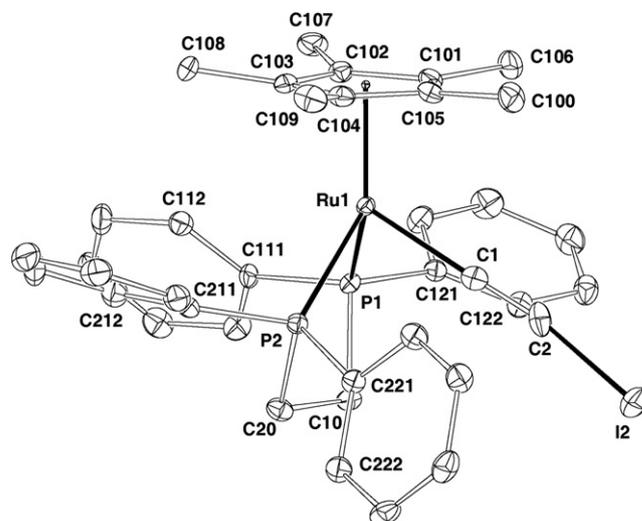
version, although the identity of a second pink product also formed is presently unknown. Addition of tcne to transition metal alkynyl complexes often proceeds through a radical intermediate [18], although in the present case we were not able to observe this independently, the reaction mixture becoming dark green within five minutes and changing to the deep purple colour of the major product after 30 min. It is presumed that the first-formed adduct is the cyclobutenyl complex, often observed in related reactions, but that this undergoes a rapid ring-opening reaction to afford the isolated complex.

The isolation of the tcne adduct is reasonable evidence that the iododienyl-ruthenium complex is formed and further experiments were designed to explore the chemistry of this unusual species. In the first of these, we considered whether the iodo complex **3** would undergo loss of phosphine–gold(I) iodide in a Pd(0)/Cu(I)-catalysed reaction with Ru{C≡CC=CAu(PPh₃)}(dppe)Cp*. Somewhat to our surprise, we found instead that the orange-red product was formed by replacement of the I atom in **3** with a Au(PPh₃) group, i.e., Ru{C≡CC=C(CN)₂C=C(CN)₂Au(PPh₃)}(dppe)Cp* **4** (61% yield). The fate of the ‘Ru(C₄)(dppe)Cp*’ fragment could not be determined: possibly it was contained in the extensive dark baseline (perhaps formed by oxidation) observed during the t.l.c. purification of **4**. Complex **4** was also obtained from a conventional addition of tcne to Ru{C≡CC=CAu(PPh₃)}(dppe)Cp* (41% yield). The molecular formula was established by microanalysis and from its ES-MS (M⁺ at *m/z* 1270), and the molecular structure was determined from a single-crystal XRD study. The spectroscopic properties were consistent with this structure, with ν(CN) at 2207, ν(C≡C) at 1980 and ν(C=C) at 1440 cm⁻¹. The Ru(dppe)Cp* group showed the usual resonances [Cp* at δ_H 1.53, δ_C 10.23 and 96.22; dppe at δ_H 2.14, 2.96 and between 7.12 and 7.57, δ_C 29.87 (CH₂), multiple aromatic signals between δ_C 127.87–134.74 (Ph), and δ_P 40.3 (PPh₃), 80.3, 81.0 (AB q, dppe)]. While four singlets between δ_C 111.8–117.33 can be assigned to the CN groups, only one carbon chain signal can be assigned, at δ_C 121.18.

Molecular structures: Characterisation of the four complexes **1–4** was achieved by single-crystal XRD studies (Figs. 1–4, Table 1). To our knowledge, **2** is the first structurally characterised complex containing an iodoethynyl group, which has the normal parameters Ru–C 2.007(3), C(1)–C(2) 1.196(4) and C(2)–I 2.022(3) Å, with angles at C(1) and C(2) of 176.5(3)° and 168.3(3)°. The organic ligand in **3** is confirmed as the tetracyanoiodobutadienylethynyl group, with C(1)–C(2) 1.241(6), C(2)–C(3) 1.375(5), C(3)–C(30) 1.393(7), C(3)–C(4) 1.484(3), C(4)–C(40) 1.342(5) Å (< >, all molecules, both solvates). Angles at atoms C(1, 2) are 170.6–176.1(4)° as expected for the C≡C triple bond, while those around C(3, 4) range between 115.2° and 125.9(3)°, with torsion angles C(30)–C(3)–C(4)–C(40) –69.0(5) to –78.5(5)°, consistent with their being C(sp²) atoms with the *s-trans* configuration found in previous examples of this type of complex. These values can be compared with values found in somewhat related compounds (NC)₂C=C₆H₂I₂=C(CN)₂, which has C=C(CN)₂, Cl=CH and C–I bonds of 1.388, 1.356 and 2.080(2) Å [20], and Bu^tC₆H₄C≡C–



Scheme 2.

Fig. 1. Projection of the cation in $[\text{Ru}(=\text{C}=\text{CHI})(\text{dppe})\text{Cp}]\text{BF}_4$ (**1**).Fig. 2. Projection of a molecule of $\text{Ru}(\text{C}=\text{Cl})(\text{dppe})\text{Cp}^*$ (**2**).

$\text{Cl}=\text{C}(\text{C}_6\text{H}_4\text{Bu}^t)$, which has $\text{C}=\text{C}$, $\text{C}(\text{sp})=\text{C}(\text{sp}^2)$, $\text{C}=\text{Cl}$ and $\text{C}-\text{I}$ of 1.208(7), 1.427(9), 1.317(9) and 2.111, 2.123(7) Å, respectively, [21].

In **2**, the $\text{Ru}-\text{C}(1)$ and $\text{C}(1)-\text{C}(2)$ distances are 2.007(3) and 1.196(4) Å, respectively, in the normal range for $\text{Ru}-\text{C}(\text{sp})$ and $\text{C}=\text{C}$ triple bonds. However, in **3** and **4**, these distances are shorter [$\text{Ru}-\text{C}(1)$ 1.921(7) **3** (< >), 1.945(2) Å **4**] and longer [$\text{C}(1)-\text{C}(2)$ 1.241(6) **3** (< >), 1.235(3) Å **4**], which suggests a relatively large contribution from the allenylidene tautomer. In the three iodine-containing compounds, the $\text{C}-\text{I}$ distances range between 2.022(3) [$\text{C}(\text{sp})-\text{I}$] and 2.108(2) Å [$\text{C}(\text{sp}^2)-\text{I}$]. The considerable bending at $\text{C}(2)$ in **4** [167.4(2)°, 167.0(2)°] probably results from intramolecular interactions between phenyl groups.

The $\text{Ru}(\text{dppe})\text{Cp}^*$ groups have pseudo-octahedral geometry, the structural parameters being similar to those found in many other related complexes. In the neutral complexes **2–4**, $\text{Ru}-\text{P}$ separations range between 2.2544(7) and 2.3028(7) Å, while in the cation of **1**,

these distances are longer, at 2.3123, 2.3314(4) Å. The lengthening may be ascribed to reduction in back-bonding from Ru to P , caused by either or both of the presence of the positive charge on the metal centre and the strongly electron-accepting vinylidene ligand. Similarly, the $\text{Ru}-\text{C}(\text{cp})$ distances are longer in **1**, although the unusually wide range of these distances (ca. 0.1 Å) masks the difference. Note that in all of **1–4**, the shorter $\text{Ru}-\text{C}(\text{cp})$ distances lie, in projection, in the vicinity of the unsaturated substituent.

3. Conclusions

This work has described the preparation and isolation of the iodoethynyl complex $\text{Ru}(\text{C}=\text{Cl})(\text{dppe})\text{Cp}^*$ **2** by reaction of $[\text{l}(\text{py})_2]\text{BF}_4$ to $\text{Ru}(\text{C}=\text{CH})(\text{dppe})\text{Cp}^*$ to give the iodovinylidene complex $[\text{Ru}(=\text{C}=\text{CHI})(\text{dppe})\text{Cp}^*]\text{BF}_4$ **1**, followed by deprotonation

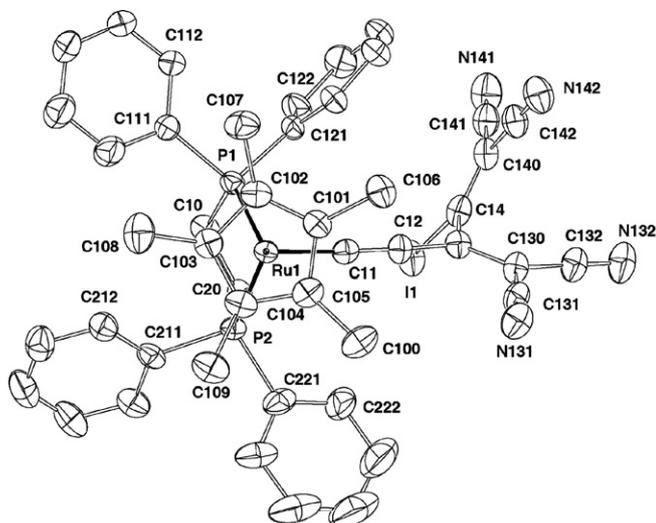


Fig. 3. Projection of a molecule of $\text{Ru}\{\text{C}\equiv\text{CC}[\text{=C}(\text{CN})_2]\text{Cl}=\text{C}(\text{CN})_2\}(\text{dppe})\text{Cp}^*$ (**3**).

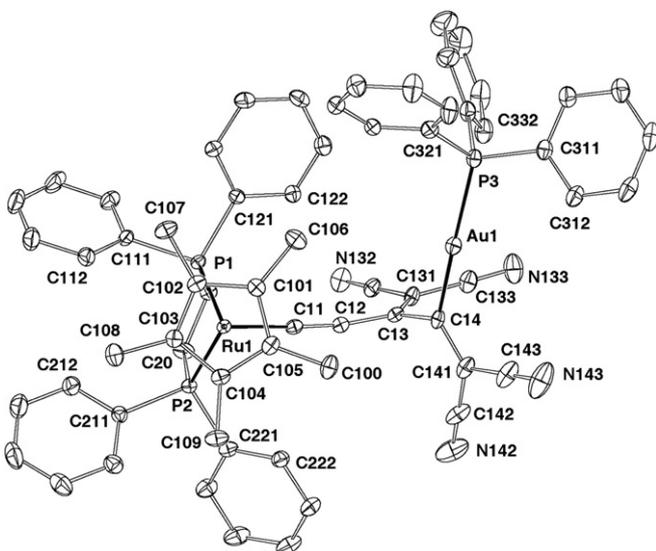


Fig. 4. Projection of a molecule of $\text{Ru}\{\text{C}\equiv\text{CC}[\text{=C}(\text{CN})_2]\text{C}[\text{Au}(\text{PPh}_3)]\text{C}(\text{CN})_2\}(\text{dppe})\text{Cp}^*$ (**4**).

with NaOMe. The putative preparation of $\text{Ru}(\text{C}\equiv\text{CC}=\text{Cl})(\text{dppe})\text{Cp}^*$, derivatised with tcne to give the dienyne $\text{Ru}\{\text{C}\equiv\text{CC}[\text{=C}(\text{CN})_2]\text{Cl}=\text{C}(\text{CN})_2\}(\text{dppe})\text{Cp}^*$ **3**, is also reported. A Pd(0)/Cu(I)-catalysed reaction of **1** with afforded $\text{Ru}\{\text{C}\equiv\text{CC}=\text{CAu}(\text{PPh}_3)\}(\text{dppe})\text{Cp}^*$ **4** by formal replacement of I^+ by $[\text{Au}(\text{PPh}_3)]^+$.

4. Experimental

4.1. General

All reactions were carried out under dry nitrogen, although normally no special precautions to exclude air were taken during subsequent work-up. Common solvents were dried, distilled under nitrogen and degassed before use. Separations were carried out by preparative thin-layer chromatography on glass plates ($20 \times 20 \text{ cm}^2$) coated with silica gel (Merck, 0.5 mm thick). Spectroscopic and electrochemical data were acquired using instrumentation which is fully described elsewhere [13]; unless otherwise stated, NMR spectra were measured on CDCl_3 solutions. Electrochemistry was carried out with a 263 potentiostat, using a cell containing a

Pt-mesh working electrode, Pt wire counter and pseudo-reference electrodes; scan rate 100 mV s^{-1} . Samples (1 mM) were dissolved in CH_2Cl_2 containing 0.1 M $[\text{NBu}_4]\text{PF}_6$ as the supporting electrolyte. Potentials are given in V vs SCE, determined using ferrocene as internal calibrant ($\text{FeCp}_2/[\text{FeCp}_2]^+ = +0.46 \text{ V}$). Elemental analyses were by CMAS, Belmont, Vic., Australia.

4.2. Reagents

$\text{Ru}(\text{C}\equiv\text{CH})(\text{dppe})\text{Cp}^*$ [23], $\text{Ru}(\text{C}\equiv\text{CC}=\text{CX})(\text{dppe})\text{Cp}^*$ [$\text{X} = \text{H}$, SiMe_3 , $\text{Au}(\text{PPh}_3)$] [22] and $[\text{I}(\text{py})_2]\text{BF}_4$ [24] were made as previously described.

4.2.1. $[\text{Ru}(\text{C}\equiv\text{CHI})(\text{dppe})\text{Cp}^*]\text{BF}_4$ **1**

To a solution of $\text{Ru}(\text{C}\equiv\text{CH})(\text{dppe})\text{Cp}^*$ (150 mg, 0.227 mmol) in CH_2Cl_2 (10 mL) was added $[\text{I}(\text{py})_2]\text{BF}_4$ (89 mg, 0.239 mmol) and the stirred solution was protected from light. The solution turned from yellow to dark green and after 30 min, half the solvent was removed under reduced pressure and hexane (20 mL) was layered on top of the solution. After 1 d the crude product was collected and recrystallised ($\text{CH}_2\text{Cl}_2/\text{hexane}$) to give dark orange crystals of $[\text{Ru}(\text{C}\equiv\text{CHI})(\text{dppe})\text{Cp}^*]\text{BF}_4$ **1** (141 mg, 71%). X-ray quality crystals were grown from (acetone/hexane). Anal. Calc. ($\text{C}_{38}\text{H}_{40}\text{BF}_4\text{IN}_2\text{Ru}$): C, 52.25; H, 4.62; I, 787. Found: C, 51.95; H, 4.76%. IR (Nujol, cm^{-1}): $\nu(\text{C}=\text{C})$ 1612s, $\nu(\text{BF})$ 1052s (br). ^1H NMR (acetone- d_6): δ 1.74 (s, 15H, Cp*), 2.81, 3.02 ($2 \times \text{m}$, $2 \times \text{CH}_2$, dppe), 4.62 (s, 1H, C=CH), 7.12–7.24, 7.59–7.82 (m, 20H, Ph), ^{13}C NMR (acetone- d_6): δ 10.43 (C_5Me_5), 103.56 (s, =CH), 104.86 (s, C_5Me_5), 128.94–134.92 (m, Ph), 323.94 [t, $J(\text{CP}) = 16 \text{ Hz}$, $\text{Ru}=\text{C}$]. ^{31}P NMR (acetone- d_6): δ 74.6 [s, 2P, $\text{Ru}(\text{dppe})$]. ES-MS (MeOH, m/z): 635, $[\text{Ru}(\text{dppe})\text{Cp}^*]^+$; 660, $[\text{M}-\text{I}]^+$; 787, M^+ .

4.2.2. $\text{Ru}(\text{C}\equiv\text{Cl})(\text{dppe})\text{Cp}^*$ **2**

A solution of $[\text{Ru}(\text{C}\equiv\text{CHI})(\text{dppe})\text{Cp}^*]\text{BF}_4$ (50 mg, 0.057 mmol) in CH_2Cl_2 (8 mL) was treated with KOBu^t (8 mg, 0.063 mmol) and the mixture was stirred for 30 min. Solvent was removed, the residue taken up in CH_2Cl_2 , filtered and evaporated, and extracted with benzene–hexanes (1/3). Evaporation of the filtered solution afforded yellow $\text{Ru}(\text{C}\equiv\text{Cl})(\text{dppe})\text{Cp}^*$ **2** (38 mg, 86%). X-ray quality crystals were obtained from benzene–hexanes. Anal. Calc. ($\text{C}_{38}\text{H}_{39}\text{IP}_2\text{Ru}$): C, 58.09; H, 5.00; I, 786. Found: C, 60.03; H, 5.33%. IR (CH_2Cl_2 , cm^{-1}): $\nu(\text{C}\equiv\text{C})$ 1995s. ^1H NMR (C_6D_6): δ 1.59 (s, 15H, Cp*), 1.85, 2.55 ($2 \times \text{m}$, $2 \times \text{CH}_2$, dppe), 7.03–7.31, 7.80–7.86 (m, 20H, Ph), ^{13}C NMR (C_6D_6): δ -13.42 (s, Cl), 10.68 (C_5Me_5), 29.71–30.31 (m, CH_2P), 93.15 (s, C_5Me_5), 127.85–139.85 (m, Ph). ^{31}P NMR (C_6D_6): δ 81.9 (s, 2P, dppe). ES-MS (positive ion mode, MeOH + NaOMe, m/z): 1341, $[\text{M}-\text{I}+\text{Na}]^+$; 1318, $[\text{M}-\text{I}]^+$; 786, M^+ ; 659, $[\text{M}-\text{I}]^+$; 635, $[\text{Ru}(\text{dppe})\text{Cp}^*]^+$.

4.2.3. $\text{Ru}\{\text{C}\equiv\text{CC}[\text{=C}(\text{CN})_2]\text{Cl}=\text{C}(\text{CN})_2\}(\text{dppe})\text{Cp}^*$ **3**

LiBu (0.10 mL, 2.5 M solution in hexanes, 0.25 mmol) was added to a solution of $\text{Ru}(\text{C}\equiv\text{CC}=\text{CH})(\text{dppe})\text{Cp}^*$ (156 mg, 0.23 mmol) in THF (10 mL) at -78°C . After stirring the mixture for 5 min, $[\text{I}(\text{py})_2]\text{BF}_4$ (88 mg, 0.24 mmol) was added and stirring was continued for a further 20 min. Addition of tcne (33 mg, 0.26 mmol) at -78°C was followed by warming the reaction mixture to r.t. Removal of solvent under vacuum and purification by preparative t.l.c. (silica gel, acetone–dichloromethane, 1/99) afforded a dark purple band containing $\text{Ru}\{\text{C}\equiv\text{CC}[\text{=C}(\text{CN})_2]\text{Cl}=\text{C}(\text{CN})_2\}(\text{dppe})\text{Cp}^*$ **3** (99 mg, 46%), together with a pink fraction containing as yet unidentified material (20 mg). Crystals for the XRD studies were obtained from Et₂O/hexane or from benzene/hexane. Anal. Calc. for $\text{C}_{46}\text{H}_{39}\text{IN}_4\text{P}_2\text{Ru}$: C, 58.92; H, 4.19; N, 5.97; I, 938. Found: C, 59.01; H, 4.23; N, 5.93%. IR (Nujol, cm^{-1}): $\nu(\text{CN})$ 2206m, 2188w; $\nu(\text{C}\equiv\text{C})$ 1965s (br), 1545w, 695m. ^1H NMR: δ 1.25 (s, 15H, Cp*), 1.97–2.06, 2.53–2.62 ($2 \times \text{m}$, $2 \times 2\text{H}$, PCH₂), 6.78–7.25 (m, 20H,

Ph). ^{13}C NMR: δ 10.01 (s, C_5Me_5), 29.3–29.9 (m, CH_2), 97.32 (C_5Me_5), 98.62, 144.71 ($2 \times$ s, $\text{C}=\text{C}$), 110.44, 113.80, 115.71, 115.77 ($4 \times$ s, CN), 127.97–128.47, 129.66–130.55, 132.11–132.47, 132.94–133.56 ($4 \times$ m, Ph), 134.24–136.46 (m), 144.71 ($\text{C}=\text{C}$). ^{31}P NMR: δ 80.3, 80.9 [AB q, $J(\text{PP}) = 17$ Hz]. ES-MS (MeOH + MeCN + NaOMe, m/z): 1899, $[2\text{M}+\text{Na}]^+$; 961, $[\text{M}+\text{Na}]^+$; 811, $[\text{M}-\text{I}]^+$. Electrochemistry: -0.78 (rev.), $+0.86$, $+1.28$ V (quasi-rev.).

4.2.4. $\text{Ru}\{\text{C}\equiv\text{CC}=\text{C}(\text{CN})_2\text{C}=\text{C}(\text{CN})_2\text{Au}(\text{PPh}_3)\}(\text{dppe})\text{Cp}^* \mathbf{4}$

(a) To a mixture of $\text{Ru}\{\text{C}\equiv\text{CC}=\text{C}(\text{CN})_2\text{C}=\text{C}(\text{CN})_2\text{I}\}(\text{dppe})\text{Cp}^*$ (17 mg, 0.018 mmol), $\text{Ru}\{\text{C}\equiv\text{CC}=\text{CAu}(\text{PPh}_3)\}(\text{dppe})\text{Cp}^*$ (21 mg, 0.018 mmol), CuI (1 mg, 0.005 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (4 mg, 0.004 mmol) was added THF (8 mL). The whole was stirred at r.t. for 2 h. Solvent was removed and the residue taken up in CH_2Cl_2 and purified by column chromatography (flash silica, CH_2Cl_2 –hexane, 3:1). The major orange red fraction contained

$\text{Ru}\{\text{C}\equiv\text{CC}=\text{C}(\text{CN})_2\text{C}=\text{C}(\text{CN})_2\text{Au}(\text{PPh}_3)\}(\text{dppe})\text{Cp}^* \mathbf{4}$ (14 mg, 61%), isolated as a dark red solid. Anal. Calc. ($\text{C}_{64}\text{H}_{54}\text{AuN}_4\text{P}_3\text{Ru} + 0.5\text{CH}_2\text{Cl}_2$): C, 59.07; H, 4.19; N, 4.27; M, 1270. Found: C, 59.24; H, 4.30; N, 5.3%. IR (CH_2Cl_2 , cm^{-1}): $\nu(\text{CN})$ 2207, $\nu(\text{C}=\text{C})$ 1980vs, $\nu(\text{C}=\text{C})$ 1440m. ^1H NMR: δ 1.53 (s, 15H, Cp^*), 2.14, 2.96 ($2 \times$ m, $2 \times \text{CH}_2$, dppe), 7.12–7.57 (m, 35H, Ph). ^{13}C NMR: δ 10.23 (C_5Me_5), 29.87 (m, PCH_2), 96.22 (s, C_5Me_5), 111.81, 116.61, 116.91, 117.33 ($4 \times$ s, CN), 121.18 (s, C) 127.87–134.74 (m, Ph). ^{31}P NMR: δ 40.3 (s, 1P, Au PPh_3), 80.3, 81.0 [AB q, $J(\text{PP}) = 15$ Hz, 2P, Ru(dppe)]. ES-MS (MeOH/NaOMe, m/z): 635, $[\text{Ru}(\text{dppe})\text{Cp}^*]^+$; 1270, M^+ ; 1293, $[\text{M}+\text{Na}]^+$.

(b) A solution of $\text{Ru}\{\text{C}\equiv\text{CC}=\text{CAu}(\text{PPh}_3)\}(\text{dppe})\text{Cp}^*$ (35 mg, 0.031 mmol) and tcne (8 mg, 0.062 mmol) in benzene (6 mL) was stirred at r.t. overnight to give a burgundy-red solution containing some red-orange precipitate. The latter was removed by filtration, washed with benzene, and the combined filtrates were evaporated.

Table 1
Selected bond parameters

Complex	1	2	3 · C_6H_6 (molecule 1)	4 (molecule 1)
<i>Bond distances</i> (Å)				
Ru–P(1,2)	2.3123(4), 2.3314(4)	2.2544(7), 2.2743(7)	2.2950(7), 2.2846(7)	2.2614(5), 2.2750(5)
<Ru–C(cp)>	2.29(5)	2.25(2)	2.27(2)	2.26(3)
Range	2.242(1)–2.340(1)	2.211–2.266(3)	2.237–2.298(3)	2.228(2)–2.293(2)
Ru–C(1)	1.840(1)	2.007(3)	1.921(3)	1.945(2)
C(1)–C(2)	1.312(2)	1.196(4)	1.246(4)	1.235(3)
C(2)–C(3)			1.373(4)	1.392(3)
C(3)–C(30)			1.401(4)	1.392(3) [C(31)]
C(3)–C(4)			1.488(4)	1.478(3)
C(4)–C(40)			1.348(4)	1.352(3) [C(41)]
C(4)–X	2.108(2) [C(2), I]	2.022(3) [C(2), I]	2.079(3) [I]	2.037(2) [Au]
<i>Bond angles</i> (°)				
P(1)–Ru–P(2)	82.18(1)	83.48(3)	83.47(2)	82.40(2)
P(1,2)–Ru–C(1)	85.19(5), 93.09(5)	84.81(8), 83.88(8)	84.96(7), 86.18(7)	84.26(6), 88.45(6)
Ru–C(1)–C(2)	172.7(1)	176.5(3)	174.2(2)	174.5(2)
C(1)–C(2)–C(3)			175.1(3)	167.4(2)
C(2)–C(3)–C(30, 4)			125.5(2), 116.1(2)	124.1(2), 116.7(2) [C(31)]
C(4)–C(3)–C(30)			118.4(2)	119.0(2) [C(31)]
C(3)–C(4)–C(40)			121.8(2)	119.2(2) [C(41)]
C(3,40)–C(4)–X	118.7(1) [C(1)–C(2)–I]	168.3(3) [C(1)–C(2)–I]	115.3(2), 122.9(2) [I]	126.9(2) [C(41), Au]

For 4: Au–P(3) 2.2801(6) Å; C(4)–Au–P(3) 170.56(6)°.

Table 2
Crystal data and refinement details

Complex	1 · $0.5\text{C}_6\text{H}_{14}$	2	3 · $0.5\text{Et}_2\text{O}$	3 · $0.5\text{C}_6\text{H}_6$	4 · $0.5\text{CH}_2\text{Cl}_2$
Formula	$\text{C}_{38}\text{H}_{40}\text{IP}_2\text{Ru}^+ \cdot \text{BF}_4^- \cdot 0.5\text{C}_6\text{H}_{14}$	$\text{C}_{38}\text{H}_{39}\text{IP}_2\text{Ru}$	$\text{C}_{46}\text{H}_{39}\text{IN}_4\text{P}_2\text{Ru} \cdot 0.5\text{C}_4\text{H}_{10}\text{O}$	$\text{C}_{46}\text{H}_{39}\text{IN}_4\text{P}_2\text{Ru} \cdot 0.5\text{C}_6\text{H}_6$	$\text{C}_{64}\text{H}_{54}\text{AuN}_4\text{P}_3\text{Ru} \cdot 0.5\text{CH}_2\text{Cl}_2$
M_w	916.51	785.60	974.78	976.78	1312.52
Crystal system	Triclinic	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	12.6322(3)	10.2764(2)	15.786(2)	15.706(2)	14.9285(2)
b (Å)	13.0458(3)	22.7746(4)	16.885(2)	16.891(2)	18.6541(2)
c (Å)	13.8756(3)	14.8638(3)	17.620(2)	17.669(2)	21.2289(2)
α (°)	74.163(2)		100.297(3)	100.360(2)	82.111(1)
β (°)	73.837(2)	109.469(2)	102.623(3)	102.755(2)	85.412(1)
γ (°)	61.872(2)		99.801(3)	98.698(2)	74.736(1)
V (Å ³)	1910	3280	4401	4407	5643
ρ_c (g cm^{-3})	1.594	1.591	1.471	1.472	1.545
Z	2	4	4	4	4
$2\theta_{\text{max}}$ /deg.	80	68	66	66	72
$\mu(\text{MoK}\alpha)$ (mm^{-1})	1.35	1.54	1.17	1.17	3.04
$T_{\text{min/max}}$	0.86	0.94	0.90	0.84	0.77
Crystal dimensions (mm^3)	$0.48 \times 0.42 \times 0.37$	$0.36 \times 0.18 \times 0.03$	$0.45 \times 0.42 \times 0.31$	$0.55 \times 0.48 \times 0.42$	$0.36 \times 0.28 \times 0.25$
N_{tot}	89091	62072	59067	59196	208826
$N(R_{\text{int}})$	23327 (0.024)	13225 (0.065)	31102 (0.033)	31118 (0.027)	51040 (0.032)
N_o	17373	9166	19182	22869	37912
R1	0.035	0.043	0.052	0.044	0.028
wR2 (a, b)	0.105 (0.055, 0.86)	0.114 (0.061, –)	0.14 (0.07, 1.07)	0.12 (0.06, 2.29)	0.076 (0.03, 2.90)
S	1.11	0.95	1.05	1.08	1.09
T (K)	100	100	153	153	100

Purification of a CH₂Cl₂ extract of the residue by preparative t.l.c. (acetone-hexane, 3/7) gave a major burgundy-red band ($R_f = 0.33$) which contained Ru{C≡CC=C(CN)₂C=C(CN)₂Au(PPh₃)₃}-
(dppe)Cp* **4** (16 mg, 41%), obtained as red crystals (CH₂Cl₂/hexane).

4.3. Structure determinations

Full spheres of diffraction data were measured using a CCD area-detector instrument. N_{tot} reflections were merged to N unique (R_{int} cited) after “empirical”/multiscan absorption correction (proprietary software), N_o with $F > 4\sigma(F)$ considered “observed”. All data were measured using monochromatic Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å. In the full matrix least squares refinements on F^2 , anisotropic displacement parameter forms were refined for the non-hydrogen atoms, (x, y, z, U_{iso})_H being included following a “riding” model [reflection weights: $(\sigma^2(F^2) + (aP)^2 + (bP)^2)^{-1}$, $P = (F_o^2 + 2F_c^2)/3$]. Neutral atom complex scattering factors were used within the SHELXL 97 program [25]. Pertinent results are given in the figures (which show non-hydrogen atoms with 50% probability amplitude displacement ellipsoids) and Tables 1 and 2.

4.3.1. Variata

In the benzene solvate of **3**, the solvent was modelled as disordered over two sets of sites, occupancies 0.5. In both (isomorphous) solvates there are weak interactions from the I atoms of one molecule to C(n31) of the other [I(1)⋯C(231) ($1 - x, y, 1 - z$) 2.969(4), 3.010(3); I(2)⋯C(131) ($1 - x, 1 - y, 1 - z$) 2.958(4), 2.974(3) Å (Et₂O, C₆H₆ solvates).

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Appendix A. Supplementary material

CCDC 667568, 667569, 667739, 667740 and 690141 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2008.06.008](https://doi.org/10.1016/j.jorganchem.2008.06.008).

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