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Journal of Organometallic Chemistry 592 (1999) 74–83

Journal of Organo metallic Chemistry

Some ruthenium complexes derived from 1,4-diethynylbenzene: molecular structure of $Ru\{\eta^3\text{-}C[{=}C(CN)_2]C(C_6H_4C{\equiv}CH\text{-}4){=}C(CN)_2\}(PPh_3)Cp$

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Received 23 June 1999; accepted 8 August 1999

Abstract

Reactions of $Ru(C{\equiv}CC_6H_4C{\equiv}CR\text{-}4)(PPh_3)_2Cp$ [R = $SiMe_3$ (**1**), H (**3**)] are described. With $Co_2(CO)_8$ reactions occur at the C≡C triple bond furthest from the ruthenium centre; in contrast, tetracyanoethene gave $Ru\{\eta^3\text{-}C[{=}C(CN)_2]C(C_6H_4C{\equiv}CR\text{-}4){=}C(CN)_2\}(PPh_3)Cp$ (R = $SiMe_3$, H), the molecular structure of the latter being determined. Protonation or methylation of **3** occurs at C_β to give the expected vinylidene complexes. With **3**, metallation (LiBu), Sonogashira and oxidative coupling reactions were demonstrated. Coupling with appropriate metal substrates gave a variety of complexes containing $RuC{\equiv}CC_6H_4C{\equiv}CM$ (M = W, Rh, Ir, Pt, Au, Hg) moieties. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Ruthenium; 1,4-Diethynylbenzene; Cobalt; Vinylidene

1. Introduction

The electronic properties and structures of metal centres linked by unsaturated carbon chains is a topic of much current interest [1–4]. Such links can also be achieved by combinations of alkynyl groups and unsaturated cyclic systems, such as aryl or heterocyclic groups, particularly thiophenes [5]. In addition, the consequences of introducing two or more alkynyl groups on an organic substrate on the chemistry of these systems is also of interest. In this connection, the prototypical dialkyne is 1,4-diethynylbenzene, $1,4\text{-}(HC{\equiv}C)_2C_6H_4$. Over the past two decades, homobinuclear derivatives of most of the transition metals have been described, those of most interest containing metals of Groups 8–11 [6–10]. Among these, some have been shown to possess appreciable non-linear optical properties [11], while unusual luminescent complexes containing copper or silver clusters linked by the $C{\equiv}CC_6H_4C{\equiv}C$ group have been described [12]. Heterometallic systems of this type are relatively rare [13], largely because of the difficulty in preparing suitable precursor complexes $\{ML_n\}\text{–}C{\equiv}C\text{–}Y\text{–}C{\equiv}CH$. For instance, attempts to remove a single $SiMe_3$ group from the readily available $Me_3SiC{\equiv}CC{\equiv}CSiMe_3$ lead to mixtures of products [14]. Our own interests in the chemistry of the $Ru(PR_3)_2Cp$ and related systems has recently led us to make several derivatives of this dialkyne: these studies are reported below.

2. Results and discussion

We have recently described the ready displacement of $SiMe_3$ from trimethylsilyl-substituted alkynes in their reactions with $RuCl(PPh_3)_2Cp$, carried out in methanol in the presence of potassium fluoride [15]. This reaction has afforded either of the complexes $Ru(C{\equiv}CC_6H_4C{\equiv}CSiMe_3)(PPh_3)_2Cp$ (**1**; Scheme 1) or $\{Ru(PPh_3)_2Cp\}_2(\mu\text{-}C{\equiv}CC_6H_4C{\equiv}C)$ (**2**), according to stoichiometry. The $SiMe_3$ group in **1** can be replaced by H in the reaction with $[NBu_4]F$ [16], from which yellow $Ru(C{\equiv}CC_6H_4C{\equiv}CH)(PPh_3)_2Cp$ (**3**) was obtained in 89% yield. Characteristic spectroscopic features (Table 1) include $\nu({\equiv}CH)$ and

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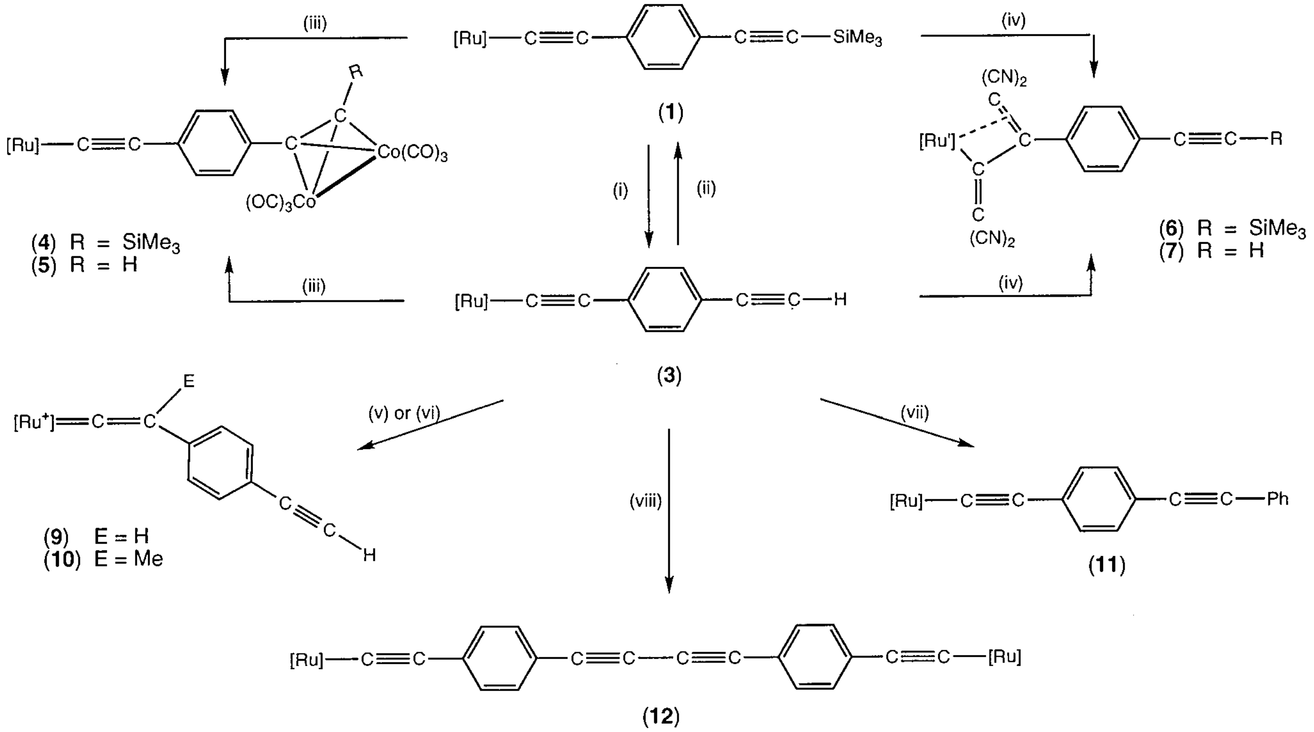
PII: S0022-328X(99)00487-8

ν(C≡C) bands at 3289 and 2071 cm^{-1}, respectively, singlet Cp resonances at δ_H 4.35 and δ_C 85.34, and the acetylenic carbons at δ 54.50, 94.93, 115.08 and 115.78. The electrospray (ES) mass spectrum of a solution with added NaOMe contained $[M + Na]^+$ at *m*/*z* 839. Complex **1** can be regenerated from **3** by treatment with LiBu^n and SiClMe$_3$, in 89% yield, indicating that the remaining ≡CH group can be metallated readily and is thus a potential source of many related complexes.

Reactions between **1** or **3** and $Co_2(CO)_8$ afforded the expected adducts $Co_2\{\mu\text{-}\eta^2\text{-}RC_2C{\equiv}C[Ru(PPh_3)_2Cp]\}(CO)_6$ [R = SiMe$_3$ (**4**), H (**5**)] as dark green crystalline solids. The IR spectra contained ν(CO) bands between 2065 and 2018 cm^{-1} and, for **4** only, a ν(C≡C) absorption at 2084 cm^{-1}. In **4**, the SiMe$_3$ group gave signals at δ_H 0.07 and δ_C 0.92, while in **5**, the ≡CH proton resonance was at δ 1.26. Singlet Cp resonances were found at δ_H 4.33 and 4.30 and at δ_C 85.41 and 85.44, respectively. The acetylenic carbon resonances are found between δ 84.26 and 115.68. For **5**, the CO groups resonated as a singlet at δ 212.74. The ES mass spectra contained M^+ at *m*/*z* 1101 (for **4**) and $[M + Na]^+$ at *m*/*z* 1197 (for **5**). While these data do not unequivocally indicate the site of addition, we suggest that it is the least hindered C≡CR group which is attached to the $Co_2(CO)_6$ fragment.

A characteristic reaction of transition metal alkynyl complexes is cycloaddition of tetracyanoethene to the C≡C triple bond to give a cyclobutenyl complex, which may undergo subsequent ring-opening to give a buta-1,3-dien-3-yl derivative, which in turn may displace a 2-e ligand from the metal centre to give an η^3-enyl complex [17,18]. The reactions of **1** and **3** with tetracyanoethene both proceed readily at ambient temperature to give deep green solutions, which turn orange–yellow when heated. Both isolated products were obtained as yellow crystals and were identified as the η^3-enyl complexes $Ru\{\eta^3\text{-}C(CN)_2C(C_6H_4C{\equiv}CH\text{-}4)C{=}C(CN)_2\}(PPh_3)Cp$ [R = SiMe$_3$ (**6**), H (**7**)]. The loss of one PPh$_3$ ligand suggested by the elemental analyses was confirmed by the ES mass spectra, which showed $[M + Na]^+$ ions at *m*/*z* 776 and 704, respectively. The spectra also contained aggregate ions formed by clustering of two or three molecules of the complex about the Na$^+$ ion. In their IR spectra, ν(CN) bands were found between 2223 and 2162 cm^{-1} and ν(C≡C) bands around 2140 cm^{-1}. The NMR spectra also confirmed that there was only one PPh$_3$ ligand present. In addition, characteristic singlet Cp resonances were found in the ^{1}H- and ^{13}C-NMR spectra; for **6**, the SiMe$_3$ group gave signals at δ_H 0.26 and δ_C −0.24, while the ≡CH proton signal was at δ 3.23. In **7**, the acetylenic carbons were found between δ 110.96 and 115.61, the CN



Reagents: (i) [NBu$_4$]F; (ii) LiBu, SiClMe$_3$; (iii) Co$_2$(CO)$_8$; (iv) tcne; (v) HPF$_6$ (E = H); (vi) MeOTf (E = Me); (vii) PhI/CuI/NHEt$_2$; (viii) O$_2$/Cu(I)/tmed.

Scheme 1.

Table 1
Analytical and spectroscopic data

Complex, analysis	IR (cm^{-1})	NMR (CDCl$_3$)	Mass spectrum (m/z)
3 Ru(C$\equiv$CC$_6$H$_4$C$\equiv$CH)(PPh$_3$)$_2$Cp Found: C, 73.87; H, 5.21, C$_{51}$H$_{40}$P$_2$Ru, calc.: C, 73.57; H, 5.23; M, 816	(Nujol): ν($\equiv$CH) 3289ms, ν(C$\equiv$C) 2071s	^{1}H-NMR: δ 3.10 (s, 1H, $\equiv$CH), 4.35 (s, 5H, Cp), 7.0–7.50 (m, 30H, aromatic H) ^{13}C-NMR: δ 54.50 (s, C4), 94.93 (s, C2), 85.34 (s, Cp), 115.08 (s, C3), 115.78 (s, C1), 127.21–139.71 (m, PPh$_3$ and C$_6$H$_4$)	(MeOH, with NaOMe): 839, [M+Na]$^+$
4 Co$_2${μ-η^2-SiMe$_3$C$_2$C$_6$H$_4$C$\equiv$C-[Ru(PPh$_3$)$_2$Cp]}(CO)$_6$ Found: C, 61.11; H, 3.93. C$_{60}$H$_{48}$Co$_2$O$_6$P$_2$RuSi calc.: C, 61.33; H, 4.12; M, 1174	(CH$_2$Cl$_2$): ν(C$\equiv$C) 2084m ν(CO) 2065m, 2048s, 2018m	^{1}H-NMR: δ 0.07 (s, 9H, SiMe$_3$), 4.33 (s, 5H, Cp), 7.06–7.48 (m, 34H, aromatic) ^{13}C-NMR: δ 0.92 (s, SiMe$_3$), 85.41 (s, Cp), 91.50, 115.68 (2 × s, C$\equiv$C), 127.22–139.35 (m, C$_6$H$_4$ and PPh$_3$)	(MeOH): 1101, [M]$^+$; 718, [M–C$_2$SiMe$_3$–Co$_2$(CO)$_6$]$^+$
5 Co$_2${μ-η^2-HC$_2$C$_6$H$_4$C$\equiv$C-[Ru(PPh$_3$)$_2$Cp]}(CO)$_6$ Found: C, 63.71; H, 3.93, C$_{57}$H$_{40}$Co$_2$P$_2$Ru·C$_6$H$_6$ calc.: C, 64.13; H, 3.93; M, 1102	(CH$_2$Cl$_2$): ν(C$\equiv$C) 2084m ν(CO) 2065m, 2048s, 2018s	^{1}H-NMR: δ 1.26 (s, 1H, $\equiv$CH), 4.30 (s, 5H, Cp), 7.16–7.47 (m, 34H, aromatic) ^{13}C-NMR: δ 84.26 (s, C2), 85.44 (s, Cp), 103.33 (C2), 113.17 (s, C2), 127.22–139.37 (m, C$_6$H$_4$ and PPh$_3$), 212.74 (s, CO)	(MeOH, with NaOMe): 1197, [M+Na]$^+$
6 Ru{η^3-C[=C(CN)$_2$]C(C$_6$H$_4$C$\equiv$C-SiMe$_3$)=C(CN)$_2$}(PPh$_3$)Cp Found: C, 66.24; H, 4.58; N, 7.43. C$_{42}$H$_{33}$N$_4$PRuSi calc.: C, 66.83; H, 4.41; N, 7.43; M, 754	(Nujol): ν(CN) 2223s, 2162m, ν(C$\equiv$C) 2147w	^{1}H-NMR: δ 0.26 (s, 9H, SiMe$_3$), 4.75 (s, 5H, Cp), 7.26–7.57 (m, 19H, aromatic) ^{13}C-NMR: δ −0.24 (s, SiMe$_3$), 6.99 (s, C2), 65.70 (s, C4), 85.27 (s, C1), 92.34, (s, Cp), 97.73 (S, C$\equiv$C), 103.95 (s, C$\equiv$C), 115.61 (s, CN), 118.43 (s, CN), 118.57 (s, CN), 118.69 (s, CN), 124.37–134.62 (m, C$_6$H$_4$ and PPh$_3$), 220.35 (s, C3)	MeOH, with added NaOMe): 1531, [2M+Na]$^+$; 776, [M+Na]$^+$
7 Ru{η^3-C[=C(CN)$_2$]C(C$_6$H$_4$C$\equiv$C-H)=C(CN)$_2$}(PPh$_3$)Cp Found: C, 66.95; H, 3.70; N, 8.03. C$_{39}$H$_{25}$N$_4$PRu·MeOH calc.: C, 67.21; H, 4.09; N, 7.85; M, 682	(CH$_2$Cl$_2$): ν(CN) 2220s, 2199m, 2177m, ν(C$\equiv$C) 2110m	^{1}H-NMR: δ 3.23 (s, 1H, $\equiv$CH), 4.77 (s, 5H, Cp), 7.45–7.56 (m, 19H, aromatic) ^{13}C-NMR: δ 6.97 (s, C2), 65.47 (s, C4), 82.62 (s, C1), 92.36 (s, Cp), 110.96 (s, C$\equiv$C), 115.61 (s, C$\equiv$C), 118.38 (s, CN), 118.52 (s, CN), 118.70 (s, CN), 124.25–134.62 (m, C$_6$H$_4$ and PPh$_3$)	(MeOH, with added NaOMe): 2067, [3M+Na]$^+$; 1386, [2M+Na]$^+$; 704, [M+Na]$^+$
9 Ru{=C=CH(C$_6$H$_4$C$\equiv$CH)}-(PPh$_3$)$_2$Cp][PF$_6$] Found: C, 63.55; H, 4.46 C$_{51}$H$_{41}$F$_6$P$_3$Ru·MeOH calc.: C, 63.68; H, 4.29; M, 962 (cation)	(Nujol): ν(C=C) 1675m, 1630m, 1591m	^{1}H-NMR: δ 3.15 (s, 1H, =CHR), 3.71 (s, 1H, $\equiv$CH), 5.40 (s, 5H, Cp), 7.04–7.78 (m, 3H, aromatic) ^{13}C-NMR: δ 92.20 (s, C$_\delta$), 95.46 (s, Cp), 111.84 (s, C$_\chi$), 119.53 (s, C$_\gamma$), 126.68–133.99 (m, Ph+C$_6$H$_4$), 273.09 [t, J(CP) 69, C$_\alpha$]	(MeOH): 817, [M–PF$_6$]$^+$; 429, [Ru(PPh$_3$)Cp]$^+$
10 Ru{=C=CMe(C$_6$H$_4$C$\equiv$CH)}-(PPh$_3$)$_2$Cp][OTf] Found: C, 63.37; H, 3.60 C$_{52}$H$_{43}$F$_6$O$_3$P$_2$RuS·0.5CH$_2$Cl$_2$ calc.: C, 62.81; H, 4.30; M, 980 (cation)	(Nujol): ν(C=C) 1661m, 1546m, (OTf) 1273m	^{1}H-NMR: δ 1.91 (s, 3H, Me), 3.04 (s, 1H, $\equiv$CH), 5.17 (s, 5H, Cp), 6.88–7.41 (m, 34H, aromatic) ^{13}C-NMR: δ 11.84 (s, Me), 83.10 (s, Cp), 94.47 (s, C), 95.46 (s, C), 121.37–134.39 (m, Ph)	(MeOH): 831, [M–PPh$_3$–CF$_3$SO$_3$]$^+$; 569, [M–PPh$_3$]$^+$

Table 1 (Continued)

Complex, analysis	IR (cm^{-1})	NMR ($CDCl_3$)	Mass spectrum (m/z)
11 $Ru\{C{\equiv}CC_6H_4C{\equiv}CPh)\}(PPh_3)_2Cp]$ Found: C, 72.43; H, 5.21 $C_{57}H_{44}P_2Ru\cdot 0.5PhI$ calc.: C, 72.50; H, 4.71; M, 892	(Nujol): $\nu(C{\equiv}C)$ 2148m, 2065m	^{1}H-NMR: δ 4.46 (s, 5H, Cp), 7.10–7.72 (m, 34H, aromatic) ^{13}C-NMR: δ 85.64 (s, Cp), 106.18 (s, $C{\equiv}C$), 127.78–134.46 (m, Ph and C_6H_4)	(MeOH): 888, M^+; 630, $[M–PPh_3]^+$
12 1,4$\{Ru(PPh_3)_2Cp(C{\equiv}C)\}_2C_6H_4$ Found: C, 68.24; H, 4.93 $C_{102}H_{78}P_4Ru_2\cdot 2.5CH_2Cl_2$ calc.: C, 68.13; H, 4.54; M, 1630	(Nujol): $\nu(C{\equiv}C)$ 2067s		(MeOH): 1630, M^+
13 $\{Cp(OC)_3W\}(\mu\text{-}C{\equiv}CC_6H_4C{\equiv}C)\{Ru(PPh_3)_2Cp\}$ Found: C, 62.01; H, 4.41 $C_{59}H_{44}O_3P_2RuW$ calc.: C, 61.74; H, 3.86; M, 1148	(Nujol): $\nu(C{\equiv}C)$ 2070m, ν(CO) 2034m, 1951m (br)	^{1}H-NMR: δ 4.31 (s, 5H, RuCp), 5.63 (s, 5H, WCp), 7.06–7.46 (m, 34H, aromatic) ^{13}C-NMR: δ 85.16 (s, Cp), 91.63 (s, Cp), 115.14 (s, CC), 121.48 (s, CC), 127.16–139.38 (m, C_6H_4 and PPh_3), 211.48 (s, CO)	(MeOH, with added NaOMe): 1170, $[M+Na]^+$; 1148, $[M]^+$
14 $\{Cp(Ph_3P)_3Ru\}(\mu\text{-}C{\equiv}CC_6H_4C{\equiv}C)\{Rh(\eta\text{-}O_2)(CO)(PPh_3)_2\}$ Found: C, 66.62; H, 4.81 $C_{88}H_{69}O_3P_4RhRu\cdot CH_2Cl_2$ calc.: C, 67.33; H, 4.51; M, 1505	(Nujol): $\nu(C{\equiv}C)$ 2065m ν(CO) 1961s (CO), ν(OO) 833m	^{1}H-NMR: δ 4.35 (s, 5H, Cp), 7.11–7.71 (m, 64H, aromatic) ^{13}C-NMR: δ 85.43 (s, Cp), 93.50 (s, $C{\equiv}C$), 103.37 (s, $C{\equiv}C$), 127.40–138.90 (m, C_6H_4 and PPh_3), 212.80 (s, CO)	(MeOH): 1505, M^+; 1243, $[M–PPh_3]^+$
15 $\{Cp(Ph_3P)_2Ru\}(\mu\text{-}C{\equiv}CC_6H_4C{\equiv}C\text{-}\{Ir(\eta\text{-}O_2)(CO)(PPh_3)_2\}$ Found: C, 66.41; H, 4.36 $C_{88}H_{69}IrO_3P_4Ru$ calc.: C, 66.32; H, 4.37; M, 1594	(Nujol): $\nu(C{\equiv}C)$ 2069m ν(CO) 1953ms ν(OO) 833m	^{1}H-NMR: δ 4.30 (s, 5H, Cp), 7.04–8.30 (m, 64H, aromatic) ^{13}C-NMR: δ 85.38 (s, Cp), 97.98 (s, $C{\equiv}C$), 115.68 (s, $C{\equiv}C$), 127.38–139.54 (m, C_6H_4 and PPh_3), 211.80 (s, CO)	(MeOH): 1631, $[M+MeCN]^+$
16 $Pt\{C{\equiv}CC_6H_4C{\equiv}C[Ru(PPh_3)_2Cp\}\}_2$ (dppe) Found: C, 69.16; H, 4.74 $C_{128}H_{102}P_6PtRu_2$ calc.: C, 69.08; H, 4.63; M, 2223	(Nujol): $\nu(C{\equiv}C)$ 2074s	^{1}H-NMR: δ 2.43 (s, 4H, CH_2) 4.31 (s, 10H, Cp), 6.93–7.49 (m, 88H, aromatic) ^{13}C-NMR: δ 36.26 (s, CH_2), 85.16 (s, Cp), 93.42 (s, $C{\equiv}C$), 103.29 (s, $C{\equiv}C$), 113.16 (s, $C{\equiv}C$), 115.26 (s, $C{\equiv}C$), 127.13–139.44 (m, C_6H_4 and Ph)	(MeOH, with added Ag^+): 2331, $[2M+Ag]^+$
17 $\{Cp(Ph_3P)_2Ru\}(\mu\text{-}C{\equiv}CC_6H_4C{\equiv}C\{Au(PPh_3)$ Found: C, 65.20; H, 4.40 $C_{69}H_{54}P_6AuP_3Ru$ calc.: C, 65.04; H, 4.27; M, 1274	(Nujol): $\nu(C{\equiv}C)$ 2068m	^{1}H-NMR: δ 4.60 (s, 5H, Cp) 7.20–7.57 (m, 49H, aromatic) ^{13}C-NMR: δ 85.42 (s, Cp), 127.59–133.95 (m, C_6H_4 and Ph)	(MeOH): 1275, M^+
18 $Hg\{C{\equiv}CC_6H_4C{\equiv}C[Ru\{PPh_3)_2Cp]\}_2$ Found: C, 70.98; H, 5.09 $C_{102}H_{78}HgP_4Ru_2$ calc.: C, 70.51; H, 4.53; M, 1830	(Nujol): $\nu(C{\equiv}C)$ 2068m		(MeOH, m/z): 1830, M^+; 429, $[Ru(PPh_3)Cp]^+$

carbons between δ 118.38 and 118.70. Final confirmation of the molecular structure was achieved by a single-crystal X-ray determination carried out on **7**, which showed that, in contrast to the reaction with $Co_2(CO)_8$, the cyano-olefin adds to the ruthenium-bonded $C{\equiv}C$ triple bond.

2.1. Molecular structure of *Ru{η³-C(CN)₂C(C₆H₄C≡CH-4)C=C(CN)₂}(PPh₃)Cp* (**7**)

A plot of a molecule of **7** is shown in Fig. 1, which also indicates the atom numbering scheme. Table 2 collects significant bond distances and angles, together with corresponding values for the closely related complex $Ru\{\eta^3\text{-}C(CF_3)_2CPhC{=}C(CN)_2\}(PPh_3)Cp$ (**8**) [18]. The metal is coordinated by the η-C_5H_5 group [Ru–C(cp) 2.195(7)–2.237(9), av. 2.22 Å] (av. 2.24 Å in **8**), the PPh_3 ligand [Ru–P(1) 2.383(1) Å; cf. 2.411(2) Å in **8**] and the cyanocarbon ligand [Ru–C(1), 2.212(6), Ru–C(2) 2.118(5), Ru–C(3) 1.980(7) Å; corresponding values for **8**: 2.202(7), 2.138(7), 1.977(7) Å]. The mode of attachment of this ligand is essentially identical to that found in **8** and is similar to several other examples [17,18]. The pattern of C–C separations along the chain is also similar, with values of 1.471(8), 1.422(8) and

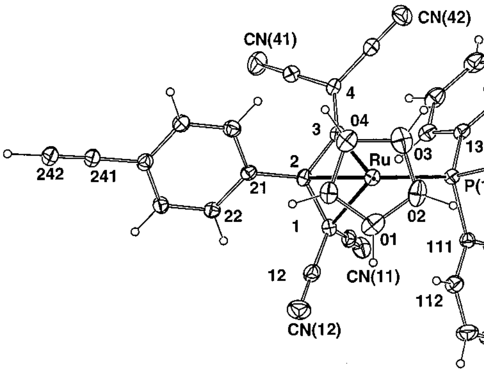


Fig. 1. Plot of a molecule of Ru{η^3-C[=C(CN)$_2$]C(C$_6$H$_4$C≡CH)=C(CN)$_2$}(PPh$_3$)Cp (**7**), showing the atom numbering scheme. Non-hydrogen atoms are shown with 20% thermal envelopes; hydrogen atoms have arbitrary radii of 0.1 Å.

1.341(9) Å for C(1)–C(2), C(2)–C(3) and C(3)–C(4), respectively. These values are consistent with an Ru-η^2-C(1)=C(2) interaction and a degree of multiple bonding in the Ru–C(3) bond. The substituent at C(2) has normal C–C separations, with C(2)–C(21) 1.497(6), C(24)–C(241) 1.438(7) and C(241)–C(242) 1.159(8) Å, the latter being an unperturbed C≡C triple bond.

The reactivity of **3** was further investigated with other electrophiles. Addition of HPF$_6$ to the orange solution of **3** in methanol resulted in a rapid colour change to cherry red. The reddish–pink solid which was isolated from the reaction mixture was identified as the expected vinylidene complex [Ru{=C=CH-(C$_6$H$_4$C≡CH)}(PPh$_3$)$_2$Cp][PF$_6$] (**9**). The characteristic low-field triplet resonance for the Ru–C atom was found at δ 273.09, while in the ^{1}H-NMR spectrum, resonances at δ 3.15 and 3.71 are assigned to the vinylidene and ethynyl protons, respectively. In the ES mass spectrum, [M–PF$_6$]$^+$ is found at m/z 817. Similarly, addition of methyl triflate to **3** afforded pink [Ru{=C=CMe(C$_6$H$_4$C≡CH)}(PPh$_3$)$_2$Cp][OTf] (**10**). The ES mass spectrum contained [M–OTf]$^+$ at m/z 831, while the ≡CH and =CMe protons resonated at δ 3.04 and 1.91, respectively. In the ^{13}C-NMR spectrum, the Me and Cp singlets were at δ 11.84 and 83.10, respectively; the Ru–C signal was not observed.

Table 2
Selected bond parameters for Ru{η^3-C[=C(CN)$_2$]C(C$_6$H$_4$R)=C(CN)$_2$}(PPh$_3$)Cp [R = C≡CH (**7**), H (**8**)]

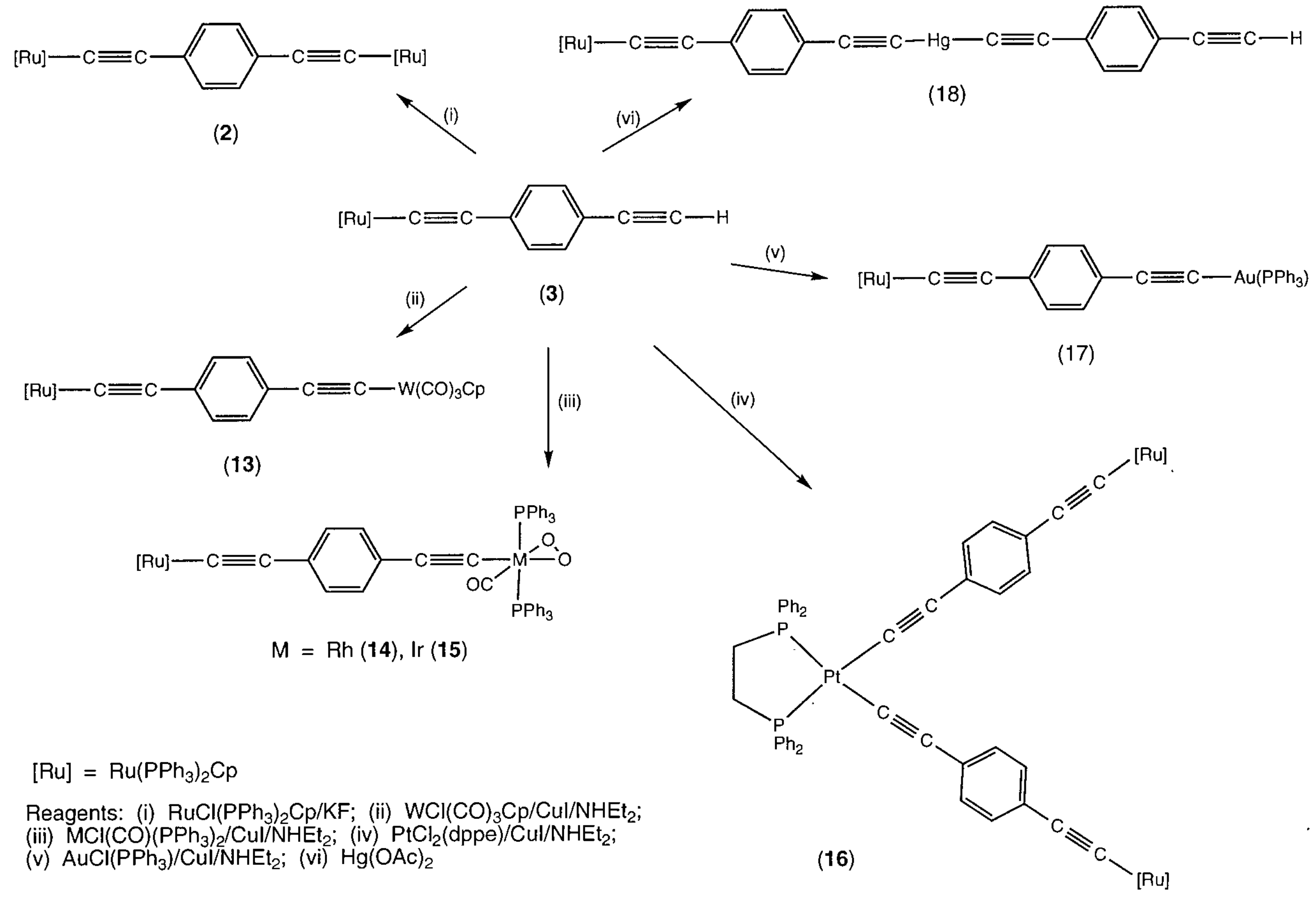
	7	8
Bond lengths		
Ru–P	2.383(1)	2.411(2)
Ru–C(1)	2.212(6)	2.202(7)
Ru–C(2)	2.118(5)	2.138(7)
Ru–C(3)	1.980(7)	1.977(7)
Ru–C(cp)	2.195–2.237(9)	2.218–2.273(8)
(av.)	2.22	2.24
C(1)–C(2)	1.471(8)	1.46(1)
C(2)–C(3)	1.422(8)	1.42(1)
C(2)–C(21)	1.497(6)	1.499(9)
C(3)–C(4)	1.341(9)	1.37(1)
C(24)–C(241)	1.438(7)	–
C(241)–C(242)	1.159(8)	–
C–CN	1.422–1.444(8)	1.43(1) (×2)
(av.)	1.437	
C–N	1.133(8)–1.15(1)	1.12, 1.13(1)
(av.)	1.143	
Bond angles		
P(1)–Ru–C(1)	96.1(5)	101.0(2)
P(1)–Ru–C(2)	115.5(1)	122.0(2)
P(1)–Ru–C(3)	92.3(1)	98.7(2)
C(1)–Ru–C(3)	70.5(2)	70.3(3)
Ru–C(1)–C(2)	66.7(3)	68.0(4)
Ru–C(2)–C(21)	128.0(4)	130.9(4)
Ru–C(3)–C(2)	75.0(4)	76.0(4)
Ru–C(3)–C(4)	146.9(4)	149.9(6)

As described above, metallation of the ethynyl group in **3** can be achieved with LiBu. Conventional coupling of the alkyne with iodobenzene, using a combined palladium(0)/copper(I) catalyst (Sonogashira coupling) [19] afforded Ru(C≡CC$_6$H$_4$C≡CPh)(PPh$_3$)$_2$Cp (**11**) in 98% yield. This complex was identified by elemental analysis, from its ES MS (M$^+$ at m/z 888) and from the NMR spectra, which contained the appropriate resonances. The IR spectrum contained ν(C≡C) bands at 2148 and 2065 cm^{-1}.

Oxidative coupling of **3**, using dioxygen and a Cu(I)/tmed catalyst [20], afforded a yellow powder tentatively identified as {Cp(Ph$_3$P)$_2$Ru}(μ-C≡CC$_6$H$_4$C≡CC≡CC$_6$H$_4$C≡C){Ru(PPh$_3$)$_2$Cp} (**12**) from its ES mass spectrum, which contained M$^+$ at m/z 1630. The IR spectrum contained a ν(C≡C) band at 2067 cm^{-1}; the compound was not soluble enough for meaningful NMR spectra to be obtained.

The electronic properties of oligomeric metal-yne polymers based upon the {M–C≡CC$_6$H$_4$C≡C–} repeat unit have recently been theoretically examined [21]. The synthesis of **2** demonstrates that symmetrical species containing two ruthenium(II) centres can be obtained from **3**. We have extended these studies to complexes containing ruthenium linked to tungsten(II), rhodium(I), iridium(I), platinum(II), gold(I) and mercury(II) moieties (Scheme 2). These materials were made via copper(I)-catalysed coupling reactions between **3** and WCl(CO)$_3$Cp, MCl(CO)(PPh$_3$)$_2$ (M = Rh, Ir), PtCl$_2$(dppe) and AuCl(PPh$_3$); the mercury derivative was obtained directly from **3** and Hg(OAc)$_2$.

The W–Ru complex {Cp(OC)$_3$W}(μ-C≡CC$_6$H$_4$C≡C)-{Ru(PPh$_3$)$_2$Cp} (**13**) was isolated as a yellow powder in 90% yield. The IR spectrum contained a ν(C≡C) band at 2070 cm^{-1} and two terminal ν(CO) bands at 2034 and 1951 cm^{-1} as expected for the W(CO)$_3$Cp group. The two Cp singlets were found at δ_H 4.31 and 5.63 and at δ_C 85.16 and 91.63, assigned



[Ru] = Ru(PPh$_3$)$_2$Cp

Reagents: (i) RuCl(PPh$_3$)$_2$Cp/KF; (ii) WCl(CO)$_3$Cp/CuI/NHEt$_2$; (iii) MCl(CO)(PPh$_3$)$_2$/CuI/NHEt$_2$; (iv) PtCl$_2$(dppe)/CuI/NHEt$_2$; (v) AuCl(PPh$_3$)/CuI/NHEt$_2$; (vi) Hg(OAc)$_2$

Scheme 2.

to the Ru–Cp and W–Cp groups, respectively. The ES mass spectrum of a solution containing NaOMe contained M$^+$ and [M + Na]$^+$ ions at *m*/*z* 1148 and 1170, respectively.

The Group 8/9 complexes were identified as the dioxygen adducts {Cp(Ph$_3$P)$_2$Ru}(μ-C≡CC$_6$H$_4$C≡C)-{M(η-O$_2$)(CO)(PPh$_3$)$_2$} [M = Rh (**14**), Ir (**15**)], as shown by the *ν*(OO) bands around 830 cm^{-1}. Single *ν*(CO) absorptions at ca. 2065 cm^{-1} confirmed the presence of the oxidised M(III) centre. Other spectroscopic properties were consistent with the proposed structures, including M$^+$ at *m*/*z* 1505 (**14**) and [M + MeCN]$^+$ at *m*/*z* 1632 (**15**). The ready formation of dioxygen adducts of similar complexes, such as {Cp(OC)$_3$M}(μ - C≡CC≡C){M′(η - O$_2$)(CO)(PPh$_3$)$_2$} (M = Mo, W; M′ = Rh, Ir) has been observed previously [22] and is probably a result of the increased electron density on the M(I) centre in the alkynyl complexes.

The reaction between **3** and PtCl$_2$(dppe) afforded the dialkynyl compound Pt{C≡CC$_6$H$_4$C≡C[Ru(PPh$_3$)$_2$-Cp]}$_2$(dppe) (**16**) in 90% yield as a yellow powder. The compound was characterised by microanalysis, from its ES mass spectrum obtained in the presence of Ag$^+$ ([M + Ag]$^+$ at *m*/*z* 2331) and from the expected resonances in the ^{1}H- and ^{13}C-NMR spectra. This complex is another example of the now large class of ‘tweezer complexes’ [23], exemplified by the *cis*-bis-alkynyl derivatives of titanium [24] and platinum [25], for example.

Ready replacement of the ethynyl hydrogen in **3** by the isolobal Au(PPh$_3$) group gave yellow {Cp(Ph$_3$P)$_2$Ru}(μ-C≡CC$_6$H$_4$C≡C){Au(PPh$_3$)} (**17**). As expected, the spectroscopic properties of **17** do not differ much from those of **3**, with the exception of the contributions from the Au(PPh$_3$) group; the *ν*(C≡C) absorption is at 2068 cm^{-1}. The ES mass spectrum contains M$^+$ at *m*/*z* 1275.

Direct reaction between **3** and Hg(OAc)$_2$ in THF solution occurred on heating to give a yellow precipitate, which was purified by chromatography (Al$_2$O$_3$ column). Its insolubility precluded our obtaining NMR spectra, but a *ν*(C≡C) at 2068 and M$^+$ at *m*/*z* 1830 in the ES mass spectrum support the proposed structure of the product as the mercury-bridged complex Hg{C≡CC$_6$H$_4$C≡C[Ru(PPh$_3$)$_2$Cp]}$_2$ (**18**).

The homo- and heterometallic complexes **12**–**15** and **17** are novel examples of compounds in which an extensive unsaturated carbon-rich chain bridges two metal centres, or in the case of **16** and **18**, two such chains attached to a single metal centre (Pt, Hg) are each capped by the ruthenium fragment. The electronic and optical properties of such extended systems are currently of great interest and are being investigated. However, we note that in the related iron complex $\{Cp^*(dppe)Fe\}(\mu\text{-}C{\equiv}CC_6H_4C{\equiv}C)\{Fe(dppe)Cp^*\}$ [26], the degree of electronic interaction between the iron centres, as shown by electrochemical studies, appears to be considerably less than that found in analogous systems containing all-carbon links such as C_4. In the present case, preliminary CV data indicate that **2** undergoes two reversible one-electron oxidations.

3. Conclusions

This work demonstrates the differing reactivities of the two C≡C triple bonds in **1** and **3**, $Co_2(CO)_8$ adding to the least hindered one, while tcne adds to the ruthenium-bonded and thereby activated one. The use of **3** as a source of heterobimetallic complexes in which a $C{\equiv}CC_6H_4C{\equiv}C$ moiety bridges the two metal centres is shown by syntheses of complexes containing Ru/W, Ru/Rh. Ru/Ir, Ru/Pt, Ru/Au and Ru/Hg pairs.

4. Experimental

4.1. General conditions

All reactions were carried out under dry, high-purity nitrogen unless otherwise stated, using standard Schlenck techniques. Common solvents were dried, distilled under nitrogen and degassed before use. Light petroleum refers to a fraction of b.p. 60–80°C. Elemental analyses were performed by the Canadian Microanalytical Service, Delta, BC. Preparative TLC was carried out on glass plates (20 × 20 cm) coated with silica gel (Merck 60 GF_{254}, 0.5 mm thick).

4.2. Instrumentation

Analytical and spectroscopic data are collected in Table 1. IR spectra were obtained on a Perkin–Elmer 1720X FTIR spectrometer. NMR spectra of solutions in $CDCl_3$ were recorded on Bruker ACP 300 (^1H at 300.13 MHz, ^{13}C at 75.47 MHz) or Varian Gemini 200 (^1H at 199.8 MHz, ^{13}C at 50.29 MHz) spectrometers. Electrospray mass spectra (ES MS) were obtained from samples dissolved in MeOH unless otherwise indicated. Solutions were injected into a VG Platform II spectrometer via a 10 ml injection loop, or by direct infusion into a Finnegan LCQ instrument. Nitrogen was used as the drying and nebulising gas. Samples were examined at cone voltages in the range 20–80 V to find the best conditions. Chemical aids to ionisation are indicated where used [27].

4.3. Reagents

Complex **1** was prepared as described previously [14]. Copper(I) iodide (Ajax), $IrCl_3{\cdot}3H_2O$ and $K_2[PtCl_4]$ (Johnson Matthey), triphenylphosphine and RhCl(CO)-$(PPh_3)_2$ (Strem), tetracyanoethene (Fluka) and iodomethane (Ajax) were used as received.

4.4. Preparation of $Ru(C{\equiv}CC_6H_4C{\equiv}CH)(PPh_3)_2Cp$ (3)

The silylated complex **1** (0.5 g, 0.56 mmol) was stirred in degassed THF (40 ml) and methanol (10 ml) with $[NBu_4]F$ (0.6 mg, 0.6 mmol) overnight. The solvent was removed under reduced pressure and the residue passed down an alumina column (3:7 acetone–hexane). The first yellow fraction was evaporated and the resulting yellow solid was collected to give $Ru(C{\equiv}CC_6H_4C{\equiv}CH)(PPh_3)_2Cp$ (**3**) (407 mg, 89%).

4.5. Reactions of $Co_2(CO)_8$

4.5.1. With 1

$Co_2(CO)_8$ (39 mg, 0.113 mmol) in benzene (10 ml) was added to complex **1** (100 mg, 0.113 mmol) in benzene (10 ml). The resulting solution turned dark green in colour after stirring 30 min at room temperature (r.t.). The solvent was removed and the resulting residue was recrystallised from CH_2Cl_2–*n*-hexane. Green crystals of $Co_2\{\mu\text{-}\eta^2\text{-}SiMe_3C_2C_6H_4C{\equiv}C[Ru(PPh_3)_2Cp]\}(CO)_6$ (**4**) (89 mg, 71%) were obtained.

4.5.2. With 3

Similarly, $Co_2(CO)_8$ (43 mg, 0.123 mmol) and complex **3** (100 mg, 0.123 mmol) in benzene (20 ml), stirring for 20 min gave a deep green solid, which was purified by preparative TLC (3:7 acetone–hexane). The green band (R_f 0.80) was recrystallised from CH_2Cl_2–*n*-hexane to give olive-green crystals of $Co_2\{\mu\text{-}\eta^2\text{-}HC_2C_6H_4C{\equiv}C[Ru(PPh_3)_2Cp]\}(CO)_6$ (**5**) (77.4 mg, 57%).

4.6. Reactions of tetracyanoethene

4.6.1. With 1

Tetracyanoethene (15 mg, 0.113 mmol) was added to a solution of **1** (100 mg, 0.113 mmol) in THF (20 ml) and the mixture was then heated under reflux for 3 h. Initially the yellow solution turns green, but after the reflux the solution was orange–yellow. Solvent was removed and the residue purified by preparative TLC (3:7 acetone–hexane). An orange–yellow band (R_f 0.65) was crystallised (CH_2Cl_2–*n*-hexane) to give yellow crystals of Ru{η^3-C[=C(CN)$_2$]C($C_6H_4C{\equiv}CSiMe_3$)=C(CN)$_2$}(PPh$_3$)Cp (**6**) (90 mg, 97%).

4.6.2. *With* **3**

Similarly, complex **3** (100 mg, 0.123 mmol) and tcne (16 mg, 0.123 mmol) in THF (20 ml) were heated under reflux for 3 h. A bright yellow band (R_f 0.4) gave yellow crystals of Ru{η^3-C[=C(CN)$_2$]C($C_6H_4C{\equiv}CH$)=C(CN)$_2$}(PPh$_3$)Cp (**7**) (57 mg, 68%) from CH_2Cl_2–MeOH. Crystals suitable for X-ray analysis were grown from CH_2Cl_2–hexane.

4.7. *Reactions of Ru(C≡CC$_6$H$_4$C≡CH)(PPh$_3$)$_2$Cp* (**3**)

4.7.1. *With HPF$_6$*

A few drops of HPF$_6$ were added to a solution of **3** (100 mg, 0.123 mmol) in MeOH (20 ml) and the mixture was stirred at r.t. for 10 min, after which the solution turned cherry red. Solvent was removed and the residue was dissolved in CH_2Cl_2; the solution was added dropwise to cold rapidly stirred Et$_2$O to give a reddish–pink precipitate of [Ru{=C=CH($C_6H_4C{\equiv}CH$)}(PPh$_3$)$_2$Cp][PF$_6$] (**9**) (101 mg, 85%).

4.7.2. *With methyl triflate*

Addition of CF$_3$SO$_3$Me (20 mg, 0.123 mmol) to a solution of **3** (100 mg, 0.123 mmol) in CH_2Cl_2 (10 ml) at r.t.; after 20 min, the solution turned red. Solvent was removed and the residue was dissolved in CH_2Cl_2 and added to rapidly stirred cold Et$_2$O, to give a pink precipitate which was collected and air-dried. This solid was identified as [Ru{=C=CMe($C_6H_4C{\equiv}CH$)}(PPh$_3$)$_2$Cp][OTf] (**10**) (76 mg, 63%).

4.7.3. *With WCl(CO)$_3$Cp*

A mixture of **3** (100 mg, 0.123 mmol) and WCl(CO)$_3$Cp (45 mg, 0.123 mmol) was stirred vigorously with CuI (ca. 3 mg) in degassed diethylamine (20 ml) in the dark for 1 h. The yellow precipitate was collected, washed with hexane and dried under vacuum to give {Cp(OC)$_3$W}(μ-C≡CC$_6$H$_4$C≡C){Ru(PPh$_3$)$_2$Cp} (**13**) (127 mg, 90%).

4.7.4. *With RhCl(CO)(PPh$_3$)$_2$*

Similarly, RhCl(CO)(PPh$_3$)$_2$ (85 mg, 0.123 mmol) was added to **3** (100 mg, 0.123 mmol) in a mixture of 3:1 NHEt$_2$–THF (20 ml) with a catalytic amount of CuI (ca. 5 mg). After stirring 2 h in the dark, the resulting solution was then chromatographed on an alumina column (3:7 acetone–hexane). An intense yellow band afforded {Cp(Ph$_3$P)$_2$Ru}(μ-C≡CC$_6$H$_4$C≡C)-{Rh(η-O$_2$)(CO)(PPh$_3$)$_2$} (**14**) as a yellow powder (42 mg, 23%).

4.7.5. *With IrCl(CO)(PPh$_3$)$_2$*

A similar reaction using IrCl(CO)(PPh$_3$)$_2$ (100 mg, 0.123 mmol) gave a yellow powder of {Cp(Ph$_3$P)$_2$Ru}-(μ-C≡CC$_6$H$_4$C≡C){Ir(η-O$_2$)(CO)(PPh$_3$)$_2$} (**15**) (112 mg, 57%).

4.7.6. *With PtCl$_2$(dppe)*

PtCl$_2$(dppe) (61 mg, 0.092 mmol) was added to a diethylamine (6 ml)–dmf (4 ml) solution containing **3** (150 mg, 0.184 mmol) and a catalytic amount of CuI (ca. 4 mg). A yellow precipitate formed in the solution after 10 min and after a further hour the solvent was partly removed. Addition of MeOH (10 ml) caused further precipitation. Filtration gave a yellow powder of Pt{C≡CC$_6$H$_4$C≡C[Ru(PPh$_3$)$_2$Cp}}$_2$(dppe) (**16**) (67 mg, 33%).

4.7.7. *With AuCl(PPh$_3$)*

Similarly, a mixture of AuCl(PPh$_3$) (61 mg, 0.123 mmol) with a catalytic amount of copper iodide (ca. 5 mg) in diethylamine (15 ml) was treated with **3** (100 mg, 0.123 mmol). There was immediate formation of a bright yellow precipitate, which was collected and dried to give {Cp(Ph$_3$P)$_2$Ru}(μ-C≡CC$_6$H$_4$C≡C){Au(PPh$_3$)} (**17**) (76 mg, 49%).

4.7.8. *With Hg(OAc)$_2$*

A mixture of **3** (100 mg, 0.123 mmol) and Hg(OAc)$_2$ (19 mg, 0.061 mmol) in THF (20 ml) was heated under reflux for 3 h. The yellow precipitate which formed was collected, washed with hexane and air dried to give Hg{C≡CC$_6$H$_4$C≡C[Ru(PPh$_3$)$_2$Cp]}$_2$ (**18**) (50 mg, 45%).

4.8. *Preparation of Ru(C≡CC$_6$H$_4$C≡CPh)(PPh$_3$)$_2$Cp* (**11**)

Iodobenzene (100 mg, 0.5 mmol) was added to a mixture of **3** (198 mg, 0.243 mmol), CuI (ca. 4 mg) and Pd(PPh$_3$)$_4$ (14 mg, 0.012 mmol) in NHEt$_2$ (30 ml). After 2 h stirring at r.t. in the dark, the solution was filtered into hexane (50 ml) to give a bright yellow precipitate of Ru(C≡CC$_6$H$_4$C≡CPh)(PPh$_3$)$_2$Cp (**11**) (212 mg, 98%).

4.9. *Oxidative coupling of* **3**

Addition of tmed (150 μl, 1.01 mmol) to a suspension of CuCl (100 mg, 1.01 mmol) in acetone (5 ml) gave a blue–green solution after 15 min. In a separate flask, dioxygen was passed into a solution of **3** (200 mg, 0.24 mmol) in acetone (40 ml) via a glass frit. The copper catalyst was added dropwise until **3** was no longer present (TLC). Evaporation and extraction of the residue with CH_2Cl_2 left a yellow insoluble material, tentatively identified as 1,4-{Ru(PPh$_3$)$_2$Cp(C≡C)}$_2$C$_6$H$_4$ (**12**) (61 mg, 31%).

4.10. *Conversion of* **3** *to* **1**

LiBu (61 μl of a 2 M solution in hexane, 0.122 mmol) was added to a cold (−78°C) solution of **3** (100 mg, 0.122 mmol) in THF (20 ml) and the mixture was stirred for 15 min. Addition of $SiClMe_3$ (15 μl, 0.122 mmol), warming to r.t. and separation of the product by chromatography on alumina gave **1** (105 mg, 89%).

4.11. Crystallography

A unique data set was measured at ca. 295 K to $2\theta_{max} = 50°$ using an Enraf–Nonius CAD4 diffractometer ($2\theta/\theta$ scan mode; monochromatic Mo–K_α radiation, $\lambda = 0.7107_3$ Å); 10123 (a hemisphere) reflections were measured, merging to 5712 unique ($R_{int} = 0.049$) after Gaussian absorption correction, 3747 with $I > 3\sigma(I)$ being considered 'observed' and used in the full-matrix least-squares refinement. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U_{iso})_H$ were included constrained at estimated values. Conventional residuals R, R_w on $|F|$ are 0.051, 0.047 respectively; statistical weights derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$ being used. Computation used the XTAL 3.4 program system [28] implemented by S.R. Hall; neutral atom complex scattering factors were employed. Pertinent results are given in the Figures and Tables.

4.12. Crystal and refinement data

(**7**) $Ru\{\eta^3\text{-}C(CN)_2C(C_6H_4C{\equiv}CH\text{-}4)C{=}C(CN)_2\}(PPh_3)Cp \equiv C_{39}H_{25}N_4PRu$, $M = 681.7$. Monoclinic, space group $P2_1/c$, $a = 12.351(3)$, $b = 14.173(5)$, $c = 20.049(5)$ Å, $\beta = 112.30(3)°$, $V = 3247$ Å^3, $Z = 4$, $\rho_c = 1.39_4$ g cm^{-3}, $F(000) = 1384$. Crystal dimensions: $0.25 \times 0.40 \times 0.15$ mm, $\mu(Mo\text{–}K_\alpha) = 5.7$ cm^{-1}, A^* (min, max) 1.06, 1.14.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC 127304 for compound **7**. Copies of the information can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

Support of this work by the Australian Research Council is gratefully acknowledged. B.C.H. and P.J.L. were the holders of Australian Post-graduate Awards. We thank Professor Brian Nicholson (University of Waikato, Hamilton, New Zealand) for some of the electrospray mass spectra. Johnson Matthey Technology plc, Reading, UK, generously loaned the $RuCl_3 \cdot nH_2O$.

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