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An efficient synthesis of polyynyl and polyynediyl complexes of ruthenium(II) †

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The fluoride-induced desilylation of trimethylsilyl-substituted alkynes and polyynes and subsequent reactions with $RuCl(PPh_3)_2Cp$ have been used to synthesize complexes containing unsaturated chains containing up to six carbons. Reactions with $Co_2(CO)_8$ or tetracyanoethene have been further used to characterise the products. Structural confirmation of $RuX(PPh_3)_2Cp$ [X = $C{\equiv}CC_6H_4C{\equiv}CSiMe_3$ **2**, $C{\equiv}CC{\equiv}CPh$ **4**, $C{\equiv}CC_2Ph\{Co_2(CO)_6\}$ **8**, $C{\equiv}CC_2H\{Co_2(\mu\text{-dppm})(CO)_4\}$ **9**, $C{\equiv}CC\{{=}C(CN)_2\}CPh{=}C(CN)_2$ **10** or $C{\equiv}CC\{{=}C(CN)_2\}C\{{=}C(CN)_2\}C{\equiv}CPh$ **11**] and $\{Ru(PPh_3)_2Cp\}_2(\mu\text{-}C_n)$ [$n = 4$ (**6**) or 6 (**7**)] is reported.

Introduction

Metal complexes containing long unsaturated carbon chains are currently the subject of intense international interest, attracting the attention of those concerned with the preparation of complexes with unusual electronic, magnetic and optical properties.[1] The metal acetylide linkage has proven to be especially popular in these respects, and consequently the chemistry of transition metal alkynyl, diynyl and higher polyynyl complexes has undergone something of a renaissance, with a view to the preparation of molecular wires and other nanoscale devices. Recent developments include the preparation of an extensive series of complexes which have been shown to have reasonable non-linear optical properties[2] and the synthesis of interesting luminescent complexes containing metal-capped carbon chains linked to clusters, such as $[Cu_3(\mu\text{-dppm})\{\mu_3\text{-}\eta^1\text{-}C{\equiv}CC_6H_4C{\equiv}C[Re(CO)_3(bpy)]\text{-}4\}_2]^+$ and related complexes.[3]

Some of our recent efforts have been directed towards overcoming the synthetic challenges associated with the preparation of organometallic compounds in which metal centres are linked by conjugated bridging ligands of well defined geometry. In particular, there is a need for synthetic methods which yield metal acetylide complexes, but do not require the isolation and manipulation of the parent terminal alkynes. We have recently described the use of buta-1,3-diyne as a reagent for the preparation of diynyl $\{ML_n\}C{\equiv}CC{\equiv}CH$ and both homo and hetero metallic diynediyl complexes $\{ML_m\}C{\equiv}CC{\equiv}C\{M'L'_n\}$ using a copper(I) catalyst.[4] While this has proven to be a versatile method for the preparation of $M(CO)_nCp$ derivatives, the reaction sequence failed when applied to more electron-rich metal centres such as $RuCl(PPh_3)_2Cp$ and $RuCl_2(dppm)_2$. This limitation, coupled with the obvious need for extreme caution when manipulating buta-1,3-diyne, prompted us to examine the use of acetylenic synthons bearing masked C≡CH functionalities.

Results

The reactions of $RuCl(PPh_3)_2Cp$ with the trimethylsilyl-protected alkynes $Me_3SiC{\equiv}CR$ (R = Ph, $C_6H_4C{\equiv}CSiMe_3$-4, C≡CPh, $C{\equiv}CSiMe_3$, C≡CC≡CPh or $C{\equiv}CC{\equiv}CSiMe_3$) and KF in methanol afforded the alkynyl, diynyl or diynediyl products in good to excellent yields as yellow or orange microcrystalline precipitates (Scheme 1). The complexes were readily purified by chromatography and crystallisation where necessary, and derivatives could be formed by reaction with $Co_2(CO)_8$ or tetracyanoethene (tcne). The new complexes were characterised by elemental microanalysis and the usual spectroscopic techniques, in addition to single crystal X-ray diffraction studies in selected cases (see below).

In the case of $Ru(C{\equiv}CPh)(PPh_3)_2Cp$ **1**, a mixture of $RuCl(PPh_3)_2Cp$, $PhC{\equiv}CSiMe_3$ and KF was heated in refluxing MeOH for a few minutes, when **1** precipitated and could be isolated by filtration in 84% yield. The product was readily identified by comparison of its spectral data with those obtained from an authentic sample.[5]

The related bright yellow $Ru(C{\equiv}CC_6H_4C{\equiv}CSiMe_3\text{-}4)(PPh_3)_2Cp$ **2** was similarly prepared from $1,4\text{-}(Me_3SiC{\equiv}C)_2C_6H_4$; it precipitated from the reaction solution before cleavage of the second ≡C–SiMe$_3$ bond could occur. Two ν(C≡C) bands were observed in the IR spectrum at 2155 and 2078 cm^{-1} (Table 1), the higher energy absorption probably arising from the $C{\equiv}CSiMe_3$ group. In the ^{1}H and ^{13}C NMR spectra singlet Cp resonances were found at δ 4.30 and 85.21 respectively, while the retention of an SiMe$_3$ group was evidenced by singlet resonances at δ_H 0.22 and δ_C 0.13. The acetylenic carbons were found at δ_C 123.46 (C_α, J_{CP} 25 Hz), 116.71, 115.10 and 106.48 while the ES mass spectrum contained the M$^+$ ion at *m*/*z* 888.

The remaining acetylenic SiMe$_3$ group in complex **2** was also amenable to metallation. Thus, subsequent treatment of **2** with $RuCl(PPh_3)_2Cp$ also in the presence of KF, carried out in a solvent mixture of thf–MeOH in which the solubility of **2** was improved, afforded the orange binuclear complex $1,4\text{-}\{Cp(PPh_3)_2Ru(C{\equiv}C)\}_2C_6H_4$ **3** in 43% yield. A single ν(C≡C) band was found in the IR spectrum at 2089 cm^{-1}, while the chemically equivalent Cp ligands gave rise to only one singlet resonance in each of the ^{1}H (δ_H 4.34) and ^{13}C (δ_C 85.15) NMR spectra. The acetylenic carbons were found at δ_C 115.10 and 106.40. Owing to the relatively poor solubility of **3** in common solvents, the signal-to-noise ratio in the ^{13}C spectrum was low, and the expected coupling to phosphorus could not be resolved. The ES mass spectrum contained M$^+$ at *m*/*z* 1506, and a fragment ion at *m*/*z* 720 representing the loss of three PPh$_3$ ligands was also present.

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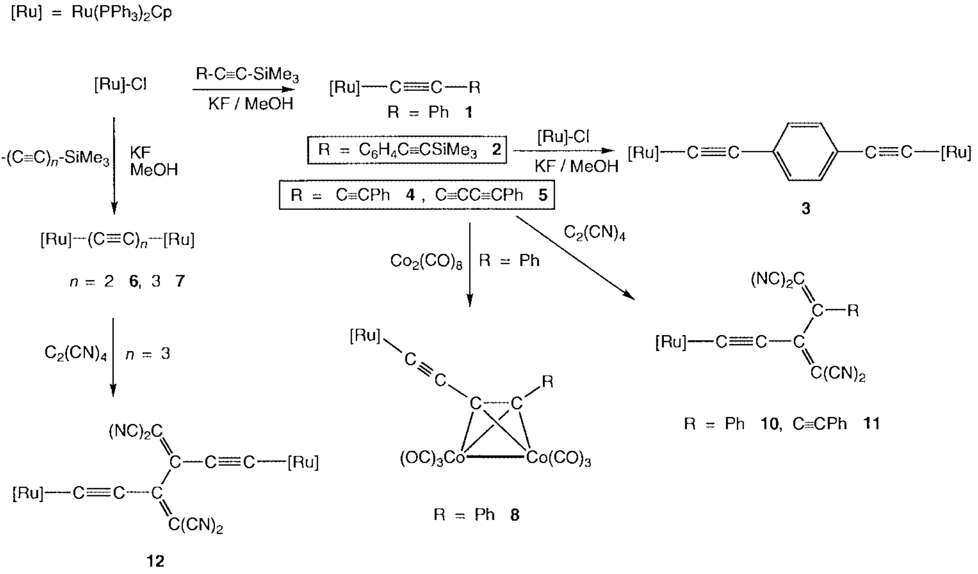
† *Supplementary data available*: rotatable 3-D crystal structure diagram in CHIME format. See http//www.rsc.org/suppdata/dt/1999/3719/

Table 1 Analytical and spectroscopic data

Complex/analysis	IR/cm^{-1}	NMR	ES MS *m*/*z*
2 $Ru(C\equiv CC_6H_4C\equiv CSiMe_3)(PPh_3)_2Cp$ Found: C, 72.43; H, 5.39. Calc. for $C_{54}H_{48}P_2RuSi$: C, 72.20; H, 5.59% *M* 888	(Nujol): ν(CC) 2155s, 2078s	^{1}H NMR ($CDCl_3$): δ 0.22 ($SiMe_3$, s, 9 H), 4.30 (Cp, s, 5 H), 7.0–7.50 (aryl H, m, 30 H) ^{13}C NMR ($CDCl_3$): δ 0.13 (s, $SiMe_3$), 85.21 (s, Cp), 106.48, 115.10, 116.71 (3 × s, C≡C), 123.46 (t, J_{CP} 25 Hz, Ru–C), 127.54–138.96 (m, Ph)	(MeOH): 888, M$^+$
3 1,4-$\{Cp(PPh_3)_2Ru(C\equiv C)\}_2C_6H_4$ Found: C, 72.56; H, 5.49. Calc. for $C_{92}H_{74}P_4Ru_2\cdot MeOH$: C, 72.64; H, 5.11% *M* 1506	(Nujol): ν(CC) 2089s	^{1}H NMR ($CDCl_3$): δ 4.34 (Cp, s, 10 H), 6.97–7.50 (Ph, m, 64 H) ^{13}C NMR ($CDCl_3$): δ 85.15 (s, Cp), 106.40 (s, C), 115.10 (s, C), 127.15–138.98 (m, Ph)	(MeOH): 1506, M$^+$; 720, $[M - 3PPh_3]^+$; 690, $[Ru(PPh_3)_2Cp]^+$
4 $Ru(C\equiv CC\equiv CPh)(PPh_3)_2Cp$ Found: C, 74.59; H, 4.87. Calc. for $C_{51}H_{40}P_2Ru$: C, 75.07; H, 4.94% *M* 816	(CH_2Cl_2): ν(C≡C) 2162s, 2025s	^{1}H NMR ($CDCl_3$): δ 4.35 (s, 5 H, Cp), 7.11–7.46 (m, 35 H, Ph) ^{13}C NMR ($CDCl_3$): δ 62.87 (C_γ, C_δ), 80.47 (t, J_{CP} 11.0, C_α), 85.71 (t, J_{CP} 8.4 Hz, Cp), 95.64, 102.40 (C_β, C_γ or C_δ), 126.00–138.78 (m, Ph)	(MeOH + NaOMe): 839, $[M + Na]^+$
5 $Ru(C\equiv CC\equiv CC\equiv CPh)(PPh_3)_2Cp$	(CH_2Cl_2): ν(C≡C) 1996s, 2108s, 2151m	^{1}H NMR ($CDCl_3$): δ 4.36 (s, 5 H, Cp), 7.10–7.43 (m, 35 H, Ph)	
7 $\{Ru(PPh_3)_2Cp\}_2(\mu\text{-}C\equiv CC\equiv CC\equiv C)$ Found: C, 69.63; H, 4.78. Calc. for $C_{88}H_{70}P_4Ru_2\cdot CH_2Cl_2$: C, 69.47; H, 4.72% *M* 1454	($CHCl_3$): ν(C≡C) 2135w, 2066s, 1965w	^{1}H NMR ($CDCl_3$): δ 4.29 (s, 10 H, Cp), 7.07–7.46 (m, 60 H, Ph)	(MeOH): 1454, $[M]^+$; 1192, $[M - PPh_3]^+$; 930, $[M - 2PPh_3]^+$
8 $Ru\{C\equiv CC_2Ph[Co_2(CO)_6]\}(PPh_3)_2Cp$ Found: C, 58.07; H, 3.63. Calc. for $C_{57}H_{40}Co_2O_6P_2Ru\cdot CH_2Cl_2$: C, 58.70; H, 3.57% *M* 1102	(cyclohexane): ν(C≡C) 2079w, ν(CO) 2040s, 2012 (br) s, 1996w	^{1}H NMR ($CDCl_3$): δ 4.34 (s, 5 H, Cp), 7.04–7.65 (m, 35 H, Ph)	(MeOH + NaOMe): 1133, $[M + OMe]^-$
10 $Ru\{C\equiv CC[=C(CN)_2]CPh{=}C(CN)_2\}(PPh_3)_2Cp$ Found: C, 68.08; H, 4.64; N, 5.20. Calc. for $C_{57}H_{40}N_4P_2Ru\cdot CH_2Cl_2$: C, 67.70; H, 4.11; N, 5.44% *M* 944	(CH_2Cl_2): ν(CN) 2214m, ν(C≡C) 1980s (br)	^{1}H NMR ($CDCl_3$): δ 4.62 (s, 5 H, Cp), 7.09–7.37 (m, 35 H, Ph) ^{13}C NMR ($CDCl_3$): δ 80.47 [t, *J*(CP) 11.0 Hz, C_α], 83.48, 88.94 (2 × Cp), 112.21, 112.88, 114.84, 116.16 (4 × CN), 127.79–146.45 (m, Ph)	(MeOH): 945, $[M + H]^+$
11 $Ru\{C\equiv CC[=C(CN)_2]C[=C(CN)_2]C\equiv CPh\}(PPh_3)_2Cp$ Found: C, 72.92; H, 4.78; N, 5.29. Calc. for $C_{59}H_{40}N_4P_2Ru$: C, 73.20; H, 4.16; N, 5.79% *M* 968	(CH_2Cl_2): ν(CN) 2214w, 2183m; ν(C≡C) 1984s (br)	^{1}H NMR ($CDCl_3$): δ 4.61 (s, 5 H, Cp), 7.14–7.32 (m, 35 H, Ph)	(MeOH + NaOMe): 991, $[M + Na]^+$
12 $\{Ru(PPh_3)_2Cp\}_2\{\mu\text{-}C\equiv CC[=C(CN)_2]_2\}$ Found: C, 68.58; H, 4.42; N, 3.40. Calc. for $C_{94}H_{70}N_4P_4Ru_2\cdot CH_2Cl_2$: C, 68.45; H, 4.35; N, 3.36% *M* 1582	(Nujol): ν(CN) 2213m, ν(C≡C) 1987s, 1967s, 1714m	^{1}H NMR ($CDCl_3$): δ 4.35 (s, 10 H, Cp), 5.32 (s, 2 H, CH_2Cl_2), 7.12–7.35 (m, 60 H, Ph)	(CH_2Cl_2–MeOH): 1583 $[M]^+$



Scheme 1 [Ru] = $Ru(PPh_3)_2Cp$.

The reaction of $Me_3SiC\equiv CC\equiv CPh$ with $RuCl(PPh_3)_2Cp$ and KF in methanol yielded a pale green-yellow precipitate from which the yellow diynyl complex $Ru(C\equiv CC\equiv CPh)(PPh_3)_2Cp$ **4** was isolated in good yield (75%). The ^{1}H and ^{13}C NMR spectra contained the expected resonances, with the diynyl carbons giving rise to resonances at δ_C 80.47 (C_α, J_{CP} 11 Hz), 81.42 (C_β), 95.64 and 102.40 (C_γ and C_δ). The IR spectrum contained two discrete ν(C≡C) absorptions at 2025 and 2162 cm^{-1}. The electrospray (ES) mass spectrum collected from solutions containing NaOMe, or KF, showed formation of aggregates with the alkali metal cations, the ions $[M + Na]^+$ and $[M + K]^+$, respectively, being observed.[6]

The triyne $Me_3SiC{\equiv}CC{\equiv}CC{\equiv}CPh$ was prepared by Sonogashira coupling[7] of $Me_3SiC{\equiv}CC{\equiv}CH$ with $IC{\equiv}CPh$ in moderate (29%) yield. The $SiMe_3$ protecting group gave rise to a high field singlet at δ 0.22 in the ^1H NMR spectrum, while the IR spectrum contained three $\nu(C{\equiv}C)$ bands at 2075, 2174 and 2195 cm^{-1}. The reaction between $RuCl(PPh_3)_2Cp$ and $Me_3SiC{\equiv}CC{\equiv}CC{\equiv}CPh$ with KF in methanol afforded a dark coloured solution, which was shown to contain the triynyl complex $Ru(C{\equiv}CC{\equiv}CC{\equiv}CPh)(PPh_3)_2Cp$ **5** by ^1H NMR and IR spectroscopy. The presence of *ca.* 10% unchanged $RuCl(PPh_3)_2Cp$ was established by the presence of the characteristic Cp resonance at δ_H 4.10 in the NMR spectrum. Purification of the complex was complicated by its ready decomposition on both Al_2O_3 and silica gel; mass spectroscopic characterisation could not be achieved, despite the use of various chemical ionisation aids.

The reaction between the bis(trimethylsilyl)diyne $Me_3SiC{\equiv}CC{\equiv}CSiMe_3$, two equivalents of $RuCl(PPh_3)_2Cp$ and KF in methanol gave the bis(ruthenium) diynediyl complex $\{Ru(PPh_3)_2Cp\}_2(\mu\text{-}C{\equiv}CC{\equiv}C)$ **6** as a microcrystalline orange material in good overall yield (*ca.* 70%). We noted an increased yield of **6** when the reaction mixture contained an additional amount of a base, such as $NEtCy_2$. The complex was characterised by comparison of the spectral data with those previously reported,[8] including the $\nu(C{\equiv}C)$ band at 1970 cm^{-1}, a single Cp resonance at δ_H 4.17 and the observation of both M^+ (*m*/*z* 1430) and M^{2+} (*m*/*z* 715) ions in the ES mass spectrum. Adjusting the stoichiometry of the reaction had no effect on the nature of the product and attempts to prepare the diynyl complexes $Ru(C{\equiv}CC{\equiv}CR)(PPh_3)_2Cp$ (R = H or $SiMe_3$) from reactions of $RuCl(PPh_3)_2Cp$ with an excess of $Me_3SiC{\equiv}CC{\equiv}CSiMe_3$ resulted only in the isolation of **6**.

Our previous study described the synthesis of complex **6** from the reaction of $Ru(thf)(PPh_3)_2Cp$ with one half equivalent of the dilithiodiacetylide $LiC{\equiv}CC{\equiv}CLi$.[8] At that time, we identified two rotamers of this complex in which the Cp rings were disposed in either *cis* (**6-cis**) or *trans* (**6-trans**) fashion about the $C{\equiv}CC{\equiv}C$ ligand, although we were then unable to establish selective preparations of these structural isomers, the details of their interconversion, or any distinguishing spectral properties.

Crystallisation of complex **6** by either slow evaporation of a concentrated CH_2Cl_2 solution or by vapour diffusion of diethyl ether into a thf solution afforded orange crystals of the *cis* isomer **6-cis** which is characterised by a single $\nu(C{\equiv}C)$ band in the IR spectrum (Nujol) at 1970 cm^{-1}. A single crystal structure determination using crystals obtained from dichloromethane was of the *cis* form;[8] that study is augmented by the two further studies recorded herein (see below).

When a thf solution of complex **6-cis** prepared as above was allowed to stand undisturbed large crystals of the second isomer, shown previously to be **6-trans**,[8] were deposited from solution. This isomer is characterised by the presence of two $\nu(C{\equiv}C)$ bands in the IR spectrum (Nujol) at 1990w and 1976m cm^{-1}. As might be expected, the structural isomers readily and reproducibly interconvert with no loss of material. Thus, a sample of **6-cis** could be taken up in hot thf and allowed to crystallise thereby yielding **6-trans**. Conversely, recrystallisation of **6-trans** from CH_2Cl_2 afforded **6-cis**. The solution IR spectra of both isomers in CH_2Cl_2 were identical, with a single $\nu(C{\equiv}C)$ band at 1969 cm^{-1}. Likewise, NMR spectra in $CDCl_3$ were indistinguishable and only one Cp environment was detected at room temperature.

The analogous triynediyl complex $\{Ru(PPh_3)_2Cp\}_2(\mu\text{-}C{\equiv}CC{\equiv}CC{\equiv}C)$ **7** was prepared in a similar fashion to **6** from $RuCl(PPh_3)_2Cp$ and $Me_3SiC{\equiv}CC{\equiv}CC{\equiv}CSiMe_3$. The structural determination described below showed it to have the *trans* conformation. Complex **7** was characterised by $\nu(C{\equiv}C)$ bands between 1965 and 2135 cm^{-1}, a sharp δ_H resonance at 4.29, and the observation of the molecular ion at *m*/*z* 1454 in the ES mass spectrum. Fragment ions consistent with the sequential loss of two PPh_3 ligands were also present at *m*/*z* 1192 and 930.

We have shown previously that complexation of one or more $C{\equiv}C$ triple bonds in polyynylmetal complexes with $Co_2(CO)_6$ or $Co_2(\mu\text{-dppm})(CO)_4$ fragments affords derivatives which often crystallise more readily than the parent compounds and enable structural confirmation of the presence of the C_n chain to be obtained.[9] Treatment of complex **4** with $Co_2(CO)_8$ afforded black crystals of $Ru\{C{\equiv}CC_2Ph[Co_2(CO)_6]\}(PPh_3)_2Cp$ **8**, in which the dicobalt fragment was shown to be attached to the C_2 fragment adjacent to the Ph group by a single-crystal X-ray determination (see below). A similar complex had been obtained previously from the reaction of $HC{\equiv}CC_2H[Co_2(\mu\text{-dppm})(CO)_4]$ with $RuCl(PPh_3)_2Cp$ in the presence of 1,8-diazabicyclo[5,4,0]undec-7-ene(dbu),[10] but until the recent acqusition of a CCD area detector facility the product had defied structural characterisation. This complex has now been identified as $Ru\{C{\equiv}CC_2H[Co_2(\mu\text{-dppm})(CO)_4]\}(PPh_3)_2Cp$ **9**. Since **9** exhibits structural elements similar to the other compounds described herein its structure is described below for comparative purposes.

Tetracyanoethene (tcne) is known to undergo rapid reactions with many acetylide complexes of transition metals, to give stable crystalline derivatives.[11] These derivatives are occasionally more suitable for structural analysis than the parent complex. The reaction of **4** with tcne afforded deep red crystals of $Ru\{C{\equiv}CC[{=}C(CN)_2]CPh{=}C(CN)_2\}(PPh_3)_2Cp$ **10**, which was characterised as the mono adduct by elemental analyses and the electrospray (ES) mass spectrum, which gave $[M + H]^+$ at *m*/*z* 945, while the site of addition was confirmed as the $C{\equiv}C$ triple bond adjacent to the Ph group by an X-ray determination.

Similar reactions of complexes **5** and **7** with an excess of tcne afforded $Ru\{C{\equiv}CC[{=}C(CN)_2]C[{=}C(CN)_2]C{\equiv}CPh\}(PPh_3)_2Cp$ **11** and $\{Ru(PPh_3)_2Cp\}_2\{\mu\text{-}C{\equiv}CC[{=}C(CN)_2]C[{=}C(CN)_2]C{\equiv}C\}$ **12**, respectively, the structure of the former being unequivocally characterised by an X-ray determination. In the case of the reaction with **7** the initial orange solution deepened to dark red over 30 min. Purification of the reaction mixtures by preparative TLC afforded green-black and dark red bands which yielded **11** and **12**, respectively, following crystallisation from dichloromethane–methanol mixtures.

The IR spectrum of complex **11** contained two $\nu(CN)$ bands at 2214 and 2183 cm^{-1}, as well as a strong $\nu(C{\equiv}C)$ or $\nu(C{=}C{=}C)$ band at 1984 cm^{-1}. The Cp ligand gave rise to a sharp singlet at δ_H 4.61. The addition reaction was shown to have occurred at the central $C{\equiv}C$ moiety by a single crystal X-ray diffraction study (see below). A degree of symmetry in complex **12** was evidenced by the presence of a singlet Cp resonance in the ^1H NMR spectrum (δ_H 4.35) and only a single $\nu(CN)$ band in the IR spectrum. The ES mass spectrum contained the $[M]^+$ ion *m*/*z* 1583, and the $[M - PPh_3]^+$ fragment ion at *m*/*z* 1321.

Molecular structures

The molecular structures of several of the complexes described above have been determined by single crystal X-ray studies and are best described by comparison of the main structural features present in each molecule with those of related alkynyl and diynyl compounds and derivatives. In all cases the geometries of the $Ru(PPh_3)_2Cp$ fragments are closely similar to those of the many other examples in the literature,[12] the structural parameters (Table 2) being within the ranges: Ru–P 2.283(3)–2.333(1); Ru–C(cp) 2.202(6)–2.273(4) (av. 2.22–2.25) Å; P–Ru–P 99.02(5)–102.94(4), P–Ru–C 85.8(4)–95.1(2)°, consistent with a slightly distorted octahedral geometry about ruthenium, considering the Cp ligand to be occupying three coordination sites. One molecule comprises the asymmetric unit

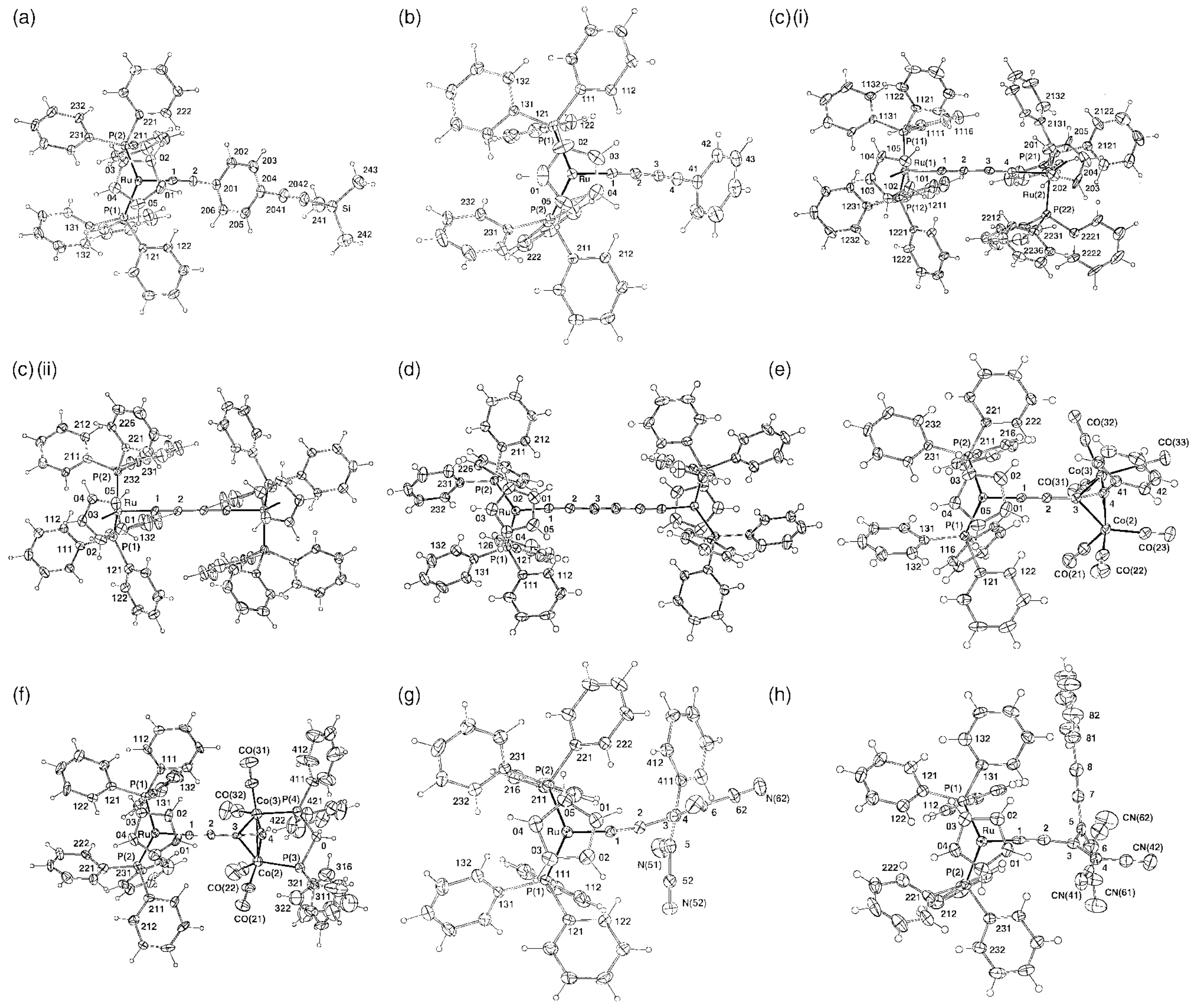


Fig. 1 Projections of single molecules of complexes (a) **2**, (b) **4**, (c) **6-cis** [(i) thf and (ii) MeOH solvates], (d)–(h) **7–11** respectively. Ellipsoids are shown at the 20 (room temperature) and 50% (low temperature) levels, as appropriate. For **11**, only molecule 1 is depicted.

in all cases, except **6**·MeOH and **7** (where a half molecule, disposed about a crystallographic *2* axis or inversion centre, respectively) and **11** (two molecules).

(a) Ru(C≡CC$_6$H$_4$C≡CSiMe$_3$-4)(PPh$_3$)$_2$Cp 2. A molecule of complex **2** is shown in Fig. 1(a). It is appropriate to compare the structure with that of Ru(C≡CPh)(PPh$_3$)$_2$Cp **1**,[5] from which there is little significant difference. Thus the Ru–C(1) and C(1)–C(2) distances are respectively 2.021(6), 1.173(9), and 2.017(5), 1.214(7) Å for the two complexes, with angles at C(1) and C(2) of 177.5(7), 171.8(8) and 177.4(4), 170.6(5)°. In the C≡CSiMe$_3$ fragment of **2** the C≡C and Si–C bond lengths are 1.21(1) and 1.817(8) Å, with angles at C(2041) and C(2042) of 177(1) and 174.2(9)°, respectively. These parameters are within previously measured ranges, the most notable difference being the barely significant shortening of the C(1)–C(2) bond compared with that in the phenylethynyl complex.

(b) Ru(C≡CC≡CPh)(PPh$_3$)$_2$Cp 4, Ru{C≡CC$_2$Ph[Co$_2$(CO)$_6$]}(PPh$_3$)$_2$Cp 8 and Ru{C≡CC$_2$H[Co$_2$(μ-dppm)(CO)$_4$]}(PPh$_3$)$_2$Cp 9. Figs. 1(b), 1(e) and 1(f) contain plots of molecules of **4**, **8** and **9**, respectively. In **4** atom separations along the RuC$_4$ chain are 1.994(4), 1.206(5), 1.389(6) and 1.200(6) Å, the two C≡C bonds being essentially identical. Angles at carbons C(1), C(2), C(3) and C(4) are 178.3(3), 169.5(4), 175.9(4) and 176.9(4)°, so that the chain shows marked non-linearity. In the cobalt derivatives **8** and **9** the dicobalt fragment is attached to the C≡C triple bond furthest from the ruthenium, perhaps as a result of steric constraints imposed by the two PPh$_3$ ligands. The Ru–C(1) separations are 1.985(4) (**8**) and 2.01(2) Å (**9**), the former perhaps being slightly shorter than that found in precursor **4**. The uncomplexed C≡C triple bond in **8** [1.227(5) Å] is slightly longer than in **4**, but that in **9** [1.19(3) Å] appears normal. Angles at C(1) and C(2) are 171.3(2) and 176.7(2)° in **8**, 168(2) and 177(2)° in **9**, the former values showing two of the largest distortions observed in a σ-bonded C≡C unit. The usual lengthening of the complexed C(3)–C(4) moiety [to 1.354(5) in **8**, 1.32(3) Å in **9**] results from the back bonding from the Co$_2$ fragment; associated bend-back angles at C(3) and C(4) are 140.0(3) and 135.1(3)° (**8**) and 145(2)° [at C(3) in **9**].

(c) {Ru(PPh$_3$)$_2$Cp}$_2$(μ-C≡CC≡C) 6 and {Ru(PPh$_3$)$_2$Cp}$_2$(μ-C≡CC≡CC≡C) 7. Comparison of the *cis* forms of complex **6**, here and as described earlier, shows that the lengths of comparable bonds are experimentally identical, with the possible exception of C(2)–C(2′), which is 1.39(1) in the present MeOH solvate, 1.370(6) Å in the *trans* isomer. There are small differences in angles at the ruthenium atom in the two isomers, with the C$_4$ chain being somewhat more linear in the *trans* isomer.

In complex **7**, containing the longer carbon chain, steric interference between PPh$_3$ ligands on the two metal centres is further diminished and the molecule adopts a *trans* conformation. Structural parameters are similar to those of **6**, the central C≡C triple bond being identical with the two outer ones.

Table 2 Selected structural data

(a) The ruthenium environments

Compound (molecule)	Distance/Å				Angles (subtending atoms)/°					
	Ru–C(0)	Ru–C(1)	Ru–P(1)	Ru–P(2)	C(0)···P(1)	C(0)···P(2)	C(0)···C	C···P(1)	C···P(2)	P···P
2	1.88_0	2.021(6)	2.299(2)	2.287(2)	$122._6$	$123._8$	$122._6$	89.4(2)	87.0(2)	101.77(8)
4	1.89_6	1.994(4)	2.296(1)	2.333(1)	$121._2$	$121._2$	$127._0$	87.3(1)	88.7(1)	102.94(4)
6/thf(1)	1.89	2.00(1)	2.304(3)	2.276(5)	$123._7$	$121._8$	$124._6$	86.7(1)	89.0(5)	101.7(1)
(2)	1.87	2.01(1)	2.289(4)	2.284(4)	$120._6$	$124._4$	$123._3$	90.8(3)	85.8(4)	102.7(1)
/MeOH(1)	1.88	2.00(1)	2.283(3)	2.296(4)	$121._7$	$123._7$	$123._2$	90.0(3)	86.5(3)	102.4(1)
7	1.88_3	2.001(6)	2.297(2)	2.301(1)	$123._0$	$122._7$	$121._1$	87.8(2)	95.1(2)	99.02(5)
8	1.89	1.985(4)	2.2947(7)	2.2873(8)	$124._0$	$122._2$	$121._0$	90.63(8)	89.42(9)	100.82(2)
9	1.88	2.01(2)	2.292(6)	2.289(5)	$122._0$	$123._7$	$119._5$	88.6(5)	92.3(5)	102.3(2)
10	1.90_1	1.947(8)	2.305(2)	2.299(2)	$121._5$	$124._0$	$122._4$	91.8(2)	87.8(2)	100.86(8)
11(1)	1.90_2	1.935(5)	2.308(1)	2.306(1)	$123._0$	$120._6$	$123._2$	88.7(1)	90.4(1)	102.67(4)
(2)	1.90_4	1.927(5)	2.315(1)	2.310(1)	$123._4$	$123._6$	$121._0$	89.7(1)	90.3(1)	99.76(5)

(b) The alkynyl string; carbon atoms are denoted by number only

	1–2	2–3(X)	3–4	4–5/X	1	2	3	4
2	1.173(9)	(1.463(9))			177.5(7)	171.8(8)		
4	1.206(5)	1.389(6)	1.200(6)	1.416(6)	178.3(3)	169.5(4)	175.9(4)	176.9(4)
6/thf	1.20(2)	1.38(2)	1.25(2)		177(1)	178(2)	175(1)	170(1)
/MeOH	1.22(1)	1.39(1)			175(1)	177(1)		
7	1.210(8)	1.382(8)	1.212(8)		172.2(4)	178.8(6)	177.3(6)	
8	1.227(5)	1.394(5)	1.354(5)	1.460(3)	171.3(2)	176.7(2)	140.0(3)	135.1(3)
9	1.19(3)	1.43(3)	1.32(3)		168(2)	177(2)	145(2)	
10	1.21(1)	1.40(1)	1.51(1)	1.35(1)	169.4(7)	170.5(9)	116.9(6)	118.4(7)
11(1)	1.237(6)	1.372(6)	1.384(6)		173.1(4)	170.5(5)	123.7(4)	
(2)	1.227(7)	1.377(7)	1.378(7)		170.5(4)	168.6(4)	124.0(4)	

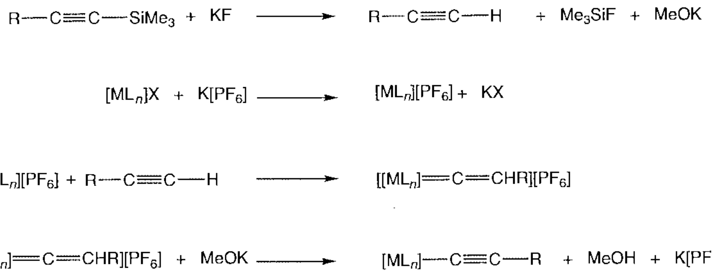
Also: **2**, C(2041)–C(204,2042) 1.44(1), 1.21(1); Si–C(2042), 1.817(8) Å; angles at C(2041,2042): 177(1), 174.2(9)°; **8**, C(3)–Co(2,3) 2.001(4), 1.993(4); C(4)–Co(2,3) 1.942(3), 1.956(3); Co(2)–Co(3) 2.4758(7) Å; Co(2)–C(3,4)–Co(3) 76.6(1), 78.85(9); C(3)–Co(2,3)–C(4) 40.1(1), 40.1(1); C(3)–Co(2,3)–Co(3,2) 51.6(1), 51.8(1); C(4)–Co(2,3)–Co(3,2) 50.83(9), 50.33(9)°; **9**, C(3)–Co(2,3) 1.96(2), 2.00(2); C(4)–Co(2,3) 1.93(2), 1.98(2); Co(2)–Co(3) 2.451(5) Å; Co(2)–C(3,4)–Co(3) 76.4(8), 77.7(8); C(3)–Co(2,3)–C(4) 39.6(9), 39(1); C(3)–Co(2,3)–Co(3,2) 52.6(9), 51.0(5); C(4)–Co(2,3)–Co(3,2) 51.9(7), 50.4(6)°; Co(2)–P(3) 2.213(7); Co(3)–P(4) 2.212(8) Å; P(3)–C(0)–P(4) 110(1); C(0)–P(3)–Co(2) 109.4(6); C(0)–P(4)–Co(3) 110.1(8); P(3)–Co(2)–C(3,4), Co(3) 132.8(7), 93.5(7), 99.5(2); P(4)–Co(3)–C(3,4), Co(2) 134.2(7), 97.7(7), 94.0(2)°; **10**, C(4)–C(411) 1.46(1); C(5)–C(51,52) 1.45(1), 1.45(1); C(3)–C(6) 1.386(9); C(6)–C(61,62) 1.41(1) (×2); C≡N(51,52,61,62) 1.15(1), 1.12(1), 1.15(1), 1.11(1) Å; angles at C(51,52,61,62) 176.6(9), 178(1), 179(1), 177(1), C(411)–C(4)–C(3,5) 116.4(7), 125.0(8); C(4)–C(5)–C(51,52) 122.1(8), 123.0(8); C(3)–C(6)–C(61,62) 118.0(7), 123.3(8); C(6)–C(3)–C(2,4) 123.8(8), 119.2(7)°; **11**, molecules 1(2), C(4)–C(41,42) 1.423(7), 1.418(6) (1.438(6), 1.432(7)); C(3)–C(5) 1.521(7) (1.511(6)); C(5)–C(6,7) 1.332(6), 1.430(6) (1.369(7), 1.409(6)); C(6)–C(61,62) 1.427(7), 1.455(8), (1.426(6), 1.444(7)); C(7)–C(8) 1.170(7) (1.177(6)); C(8)–C(81) 1.452(7) (1.462(9)); C≡N(41,42,61,62) 1.150(7), 1.152(6), 1.152(7), 1.136(8), (1.136(6), 1.141(7), 1.142(6), 1.139(7)) Å; angles at C(41,42,61,62) 176.3(5), 176.8(5), 177.3(6), 178.9(6) (178.0(6), 178.4(5), 179.3(6), 179.2(6)); at C(7,8) 176.2(5), 173.8(5) (173.7(5), 172.2(6)); C(3)–C(4)–C(41,42) 119.3(4), 121.4(4) (119.6(4), 123.6(4)); C(41)–C(4)–C(42) 119.3(4) (116.7(4)); C(6)–C(5)–C(7) 121.0(5) (122.4(4)); C(3)–C(5)–C(6,7) 122.1(4), 116.9(4) (120.3(4), 116.9(4)); C(5)–C(6)–C(61,62) 123.6(5), 119.9(5) (122.0(4), 121.4(4)); C(61)–C(6)–C(62) 116.5(4) (116.6(4))°.

There is a more pronounced bending of the C_6 chain at C(1) [172.2(4)°] and, somewhat surprisingly, one of the P–Ru–C angles has opened to 95.1(2)°, with a concomitant but lesser contraction of the P–Ru–P angle to 99.02(5)°. These minor changes (compared with **6**) probably result from intermolecular interactions. Whereas **7**, disposed about a crystallographic inversion centre, is obligate *trans*, **6** is found in two distinct phases, as different solvates, both *cis*; in the more precisely determined structure the molecule is disposed about a crystallographic *2* axis. These complement the previous study[8] which presented **6** in both *cis* and *trans* forms, the present MeOH solvate being an improved definition of the *cis* phase.

(d) Ru{C≡CC[=C(CN)$_2$]CPh=C(CN)$_2$}(PPh$_3$)$_2$Cp 10 and Ru{C≡CC[=C(CN)$_2$]C[=C(CN)$_2$]C≡CPh(PPh$_3$)$_2$Cp 11. Figs. 1(g) and 1(h) contain plots of molecules of complexes **10** and **11**. These complexes are formed by cycloaddition of the electron-deficient olefin to the second C≡C triple bond out from the ruthenium, followed by ring opening of the cyclobutene to give the *trans*-buta-1,3-dienyl derivatives described here. The latter group has been described on several previous occasions, the closest analogue being Ru{C[=C(CN)$_2$]CPh=C(CN)$_2$}(dppe)Cp.[11] Comparable structural parameters in the latter are similar to those found in **10** and **11**. Within the RuC≡C moieties the Ru–C bonds are significantly shorter than those found in the other complexes above [1.947(8), 1.935(5) and 1.927(5) Å, respectively], while the C(1)–C(2) bonds are either similar or longer [1.21(1) Å in **10**, 1.237(6), 1.227 Å in **11**]. In **11**, C(7)–C(8) are 1.170(7), 1.177(6) Å, at the short end of the C≡C triple bond length range. Angles at C(1) and C(2) are between 169.4 and 173.1(4) (molecule 1), 173.7(5), 172.2(6)° (molecule 2), because of the steric interactions between the PPh$_3$ ligands and the cyanocarbon substituents whereas at C(7) and C(8) values of 176.2, 173.7 and 173.8(5)°, 172.2, respectively, are found. Overall, angles within the dicyanomethylene groups are less than 120° as a result of some delocalisation of electron density within these groups, while angles at C(3) involving other carbon chain atoms are between 115.4(4) and 120.5(4)°. In **10** the dihedral angle between the planes defined by C(2,3,4)CN(61,62) and C(3,4,411,5)CN(51,52) is 66.4(2)°, the associated phenyl C_6 dihedral to the latter being 39.7(3)°; in **11** the dihedral angle between the planes defined by C(3,5–7)-CN(61,62) and C(2–5)CN(41,42) is 63.2(1) (molecule 1), 75.0(1)° (molecule 2).

Discussion

Many metal acetylide complexes may be prepared by deprotonation of the corresponding mono-substituted vinylidene complexes [{ML$_n$}=C=CHR]$^+$. In turn, the vinylidene complexes are conveniently obtained from the reactions of terminal alkynes with metal complexes containing a labile ligand *via* a 1,2-H



$$R{-}C{\equiv}C{-}SiMe_3 + KF \longrightarrow R{-}C{\equiv}C{-}H + Me_3SiF + MeOK$$

$$[ML_n]X + K[PF_6] \longrightarrow [ML_n][PF_6] + KX$$

$$[ML_n][PF_6] + R{-}C{\equiv}C{-}H \longrightarrow [[ML_n]{=}C{=}CHR][PF_6]$$

$$[[ML_n]{=}C{=}CHR][PF_6] + MeOK \longrightarrow [ML_n]{-}C{\equiv}C{-}R + MeOH + K[PF_6]$$

Scheme 2

shift.[13] However, attempts to prepare polyynyl complexes $\{ML_n\}(C{\equiv}C)_nR$ *via* similar reactions are hampered by the formation of highly reactive complexes containing cumulated ligands from reactions between various metal species and terminal polyynes $H(C{\equiv}C)_nR$,[14] and consequently this approach has met with only limited success.[14b,15]

Alkynyl and dialkynyl carbanions are sufficiently nucleophilic to displace labile ligands, such as a halide, from a variety of transition metal complexes to give metal acetylide or diacetylide complexes.[16] The reactions of 1-alkynes with an appropriate metal substrate in the presence of a copper(I) catalyst is widely recognised as a useful procedure for the formation of metal acetylide complexes,[17] and these conditions have been applied with some success to the preparation of higher polyynyl complexes and polyynediyl polymers.[18]

Several successful synthetic schemes incorporating the use of trialkylstannyl-protected diyne reagents have been described, including the preparations of $Fe(C{\equiv}CC{\equiv}CH)(CO)_2Cp$ and $\{Fe(CO)_2Cp\}_2(\mu\text{-}C{\equiv}CC{\equiv}C)$,[19] *trans*-$Rh(C{\equiv}CC{\equiv}CSiMe_3)(CO)(PPr^i{}_3)_2$,[20] *trans*-$RuCl\{C{\equiv}CC{\equiv}CCPh_2(OSiMe_3)\}(dppm)_2$[15a] and the high molecular weight polymers of general form $\{Pt(EBu_3)_2(C{\equiv}C)_m\}_n$ (E = P or As).[21]

While the introduction of the terminal trialkyltin group results in the formation of diynyl reagents of greatly increased thermal stability when compared to the parent terminal diynyl reagents, they still suffer from several drawbacks, not the least of these being the extreme deliquescence of these materials and their extreme toxicity. Furthermore, these organotin compounds are often prepared from the terminal polyyne reagent, either *via* a lithiation/derivatisation sequence,[22] or the reaction of $SnR_3(NR'_2)$ with the terminal polyyne.[23] These successful applications of the trialkyltin-protected polyynes for the synthesis of metal complexes prompted us and others to consider the use of trialkylsilyl-protected polyynes directly in the preparation of metal alkynyl and polyynyl complexes. The silicon-protected compounds offer several synthetic advantages over the corresponding tin compounds in that the silylated compounds are both thermally stable and chemically robust. Indeed, trialkylsilyl moieties lend such stability to alkynyl and polyynyl compounds that they are widely used as protecting groups in conventional organic acetylene and polyacetylene syntheses and as such they are also readily available.

In 1993 the formation of $Ru\{C{\equiv}CC(O)CHMe_2\}(PPh_3)_2Cp$ from the reaction of $RuCl(PPh_3)_2Cp$, $Me_3SiC{\equiv}CC(O)CHMe_2$ and KF in methanol was briefly described, although, to the best of our knowlege, no subsequent reports have described this synthesis in detail.[24] More recently, Lapinte and co-workers[25] have described the formation of the iron(II) acetylide complexes 1,3-$\{Cp^*(dppe)FeC{\equiv}C\}_2C_6H_4$ and 1,3,5-$\{Cp^*(dppe)FeC{\equiv}C\}_3C_6H_3$ from methanolic solutions of $FeCl(dppe)Cp^*$ and $C_6(C{\equiv}CSiMe_3)_nH_{6-n}$ in the presence of KF and KPF_6 salts, while we have mentioned the use of $Me_3SiC{\equiv}CC{\equiv}CSiMe_3$/KF in the synthesis of $\{Ru(PPh_3)_2Cp\}_2(\mu\text{-}C{\equiv}CC{\equiv}C)$.[26] The Dixneuf group have obtained the diynyl complex $Ru\{C{\equiv}CC{\equiv}CCPh_2(OSiMe_3)\}Cl(PMe_3)(\eta^6\text{-}C_6Me_6)$ from the reaction of $RuCl_2(PMe_3)(\eta^6\text{-}C_6Me_6)$ with $Me_3SiC{\equiv}CC{\equiv}CCPh_2(OSiMe_3)$ in the presence of both $NHPr^i{}_2$ and $NaPF_6$.[27]

The Lapinte group has proposed the mechanism shown in Scheme 2 to explain the formation of their complexes.[25] Initial desilylation of the trimethylsilyl-substituted acetylene by fluoride ion generates the terminal acetylene *in situ*, together with an equivalent amount of the strong base KOMe. The KPF_6 salt acts as a halide abstractor and helps promote co-ordination of the terminal alkyne to the metal centre leading to the formation of an intermediate vinylidene complex. Finally, the vinylidene cation is deprotonated by KOMe yielding the acetylide complex as the final product.

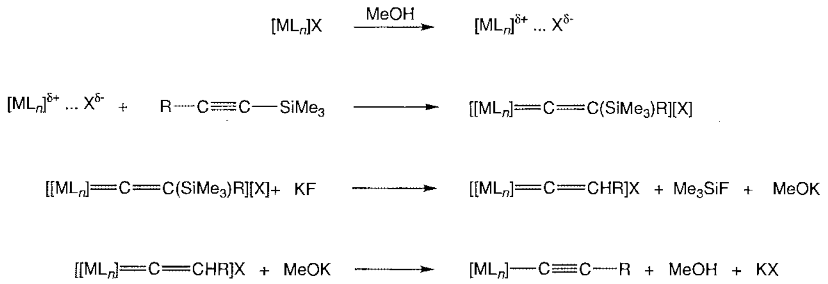
A similar mechanism may be invoked to explain the formation of $Ru(C{\equiv}CPh)(PPh_3)_2Cp$ from $Me_3SiC{\equiv}CPh$ and $\{Ru(PPh_3)_2Cp\}_2(\mu\text{-}C{\equiv}CC_6H_4C{\equiv}C\text{-}4)$ from $Ru(C{\equiv}CC_6H_4C{\equiv}CSiMe_3\text{-}4)(PPh_3)_2Cp$, as described above. However, the formation of the complexes $Ru\{(C{\equiv}C)_nPh\}(PPh_3)_2Cp$ from $Me_3Si(C{\equiv}C)_nPh$ ($n = 2$ or 3), $Ru(C{\equiv}CC_6H_4C{\equiv}CSiMe_3\text{-}4)(PPh_3)_2Cp$ from $Me_3SiC{\equiv}CC_6H_4C{\equiv}CSiMe_3\text{-}4$ and $[Ru(PPh_3)_2Cp]_2\{\mu\text{-}(C{\equiv}C)_n\}$ from $Me_3Si(C{\equiv}C)_nSiMe_3$ ($n = 2$ or 3) is more difficult to rationalise in this manner.

In the case of $Me_3SiC{\equiv}CC_6H_4C{\equiv}CSiMe_3\text{-}4$ it may reasonably be expected that both $SiMe_3$ groups would display similar reactivity towards fluoride-induced desilylation and consequently that the removal of both $SiMe_3$ groups would occur essentially concurrently. In order to account for the formation of $Ru(C{\equiv}CC_6H_4C{\equiv}CSiMe_3\text{-}4)(PPh_3)_2Cp$ *via* the Lapinte mechanism the initial, monodesilylation of $Me_3SiC{\equiv}CC_6H_4C{\equiv}CSiMe_3\text{-}4$ to give $HC{\equiv}CC_6H_4C{\equiv}CSiMe_3\text{-}4$ must be followed by the metallation sequence with a combined reaction rate several orders of magnitude faster than that of cleavage of the second ${\equiv}C\text{–}SiMe_3$ bond.

The high yield formation of the phenyl-substituted complexes $Ru\{(C{\equiv}C)_nPh\}(PPh_3)_2Cp$ and the bimetallic complexes $\{Ru(PPh_3)_2Cp\}_2\{\mu\text{-}(C{\equiv}C)_n\}$ also poses some problems for the reaction mechanism in Scheme 2 as the terminal diynes $HC{\equiv}CC{\equiv}CR$ (R = H, $SiMe_3$ or Ph) are all thermally unstable compounds which are prone to rapid polymerisation. In addition, as indicated above, 1,3-diynes have been shown to react with metal fragments, including $[Ru(PPh_3)_2Cp]^+$, to give highly reactive butatrienylidene cations $[\{M\}{=}C{=}C{=}C{=}CHR]^+$, rather than simple, stable vinylidene complexes.[14]

An alternative interpretation of these results is embodied in the reaction mechanism shown in Scheme 3. In methanol the Ru–Cl bond is significantly ionised, which offers a point of entry for the silyl-substituted alkyne into the metal co-ordination sphere, followed by, or possibly concomitant with, a 1,2-silyl shift to give a silylvinylidene. 1,2-Silyl shifts have been reported previously.[28] Nucleophilic attack by fluoride ion on the silicon centre then generates the alkynyl complexes which, in our systems, precipitate from the reaction mixture. In the case of the bis(silyl) alkynes precipitation of the product acetylides may occur either before (in the case of $Ru(C{\equiv}CC_6H_4C{\equiv}CSiMe_3\text{-}4)(PPh_3)_2Cp$) or after (as with $\{Ru(PPh_3)_2Cp\}_2\{\mu\text{-}(C{\equiv}C)_n\}$) the reaction of the second silyl group. Dixneuf and co-workers[27] have proposed a similar mechanism to explain the activation of 1-silyl-1,3-diynes by ruthenium(II) complexes.

The ease with which these compounds are obtained is noteworthy. For example, many complexes of bifunctional dialkynes



Scheme 3

such as 1,4-diethynylbenzene have been reported in recent times.[29] While the vast majority of these complexes are symmetrically metallated homobimetallic complexes, Dixneuf's group have been successful in the preparation of complexes of general form $\{ML_n\}C{\equiv}CC_6H_4C{\equiv}CSiR_3$,[30] which are more closely related to the $Ru(C{\equiv}CC_6H_4C{\equiv}CSiMe_3\text{-}4)(PPh_3)_2Cp$ described here. Dixneuf's compounds were prepared from $HC{\equiv}CC_6H_4C{\equiv}CSiPr^i_3$, which is obtained in four steps from 4-$IC_6H_4NH_2$ in 50% overall yield.[31] The isolation of the asymmetric derivative $Ru(C{\equiv}CC_6H_4C{\equiv}CSiMe_3\text{-}4)(PPh_3)_2Cp$ directly from the symmetrical reagent $Me_3SiC{\equiv}CC_6H_4C{\equiv}CSiMe_3$, which is readily available on a gram scale,[32] results from the low solubility of the monosubstituted complex in the reaction solvent, and has provided us with a useful point of entry to the chemistry of monometallated 1,4-diethynylbenzene complexes.[33]

The reaction between $Me_3SiC{\equiv}CC{\equiv}CSiMe_3$, two equivalents of $RuCl(PPh_3)_2Cp$, KF and $NEtCy_2$ in methanol gave the bis(ruthenium) diynediyl complex $\{Ru(PPh_3)_2Cp\}_2(\mu\text{-}C{\equiv}CC{\equiv}C)$, which precipitated from the reaction solution. This diynediyl compound has previously been obtained from the reaction of $LiC{\equiv}CC{\equiv}CLi$ and two equivalents of the lightly stabilised complex $[Ru(thf)(PPh_3)_2Cp][PF_6]$.[8] While the buta-1,3-diyne-1,4-diyl dianion may be prepared either by treatment of buta-1,3-diyne with two equivalents of BuLi,[34] or from $HC{\equiv}CCH{=}CH(OMe)$ and three equivalents of the same base,[35] the method described above allows multigram amounts of $\{Ru(PPh_3)_2Cp\}_2(\mu\text{-}C{\equiv}CC{\equiv}C)$ to be prepared from the stable bis-silyl reagent, and thereby avoids the use of the potentially hazardous buta-1,3-diyne and alkyllithium reagents.

Several complexes of phenylbuta-1,3-diyne are known. These include $W(C{\equiv}CC{\equiv}CPh)(CO)_3Cp^*$ [36] and $Rh(C{\equiv}CC{\equiv}CPh)(CO)(PPr^i_3)_2$ and $RhH(C{\equiv}CC{\equiv}CPh)(PPr^i_3)_2(L)$ (L = CO or py),[37] both of which were prepared by direct reaction of the unstable and polymerisation-prone reagent phenylbuta-1,3-diyne with a suitable metal complex. Alternatively, the phenyldiynyl ligand may be assembled in stepwise fashion by Sonogashira-type coupling of the butadiynyl ligand in $W(C{\equiv}CC{\equiv}CH)(CO)_3Cp$ with iodobenzene.[4] In contrast, $Me_3SiC{\equiv}CC{\equiv}CPh$ is a thermally stable material, readily prepared by coupling of $PhC{\equiv}CBr$ and $HC{\equiv}CSiMe_3$ in the presence of a mixed palladium(0)–copper(I) catalyst as described below, or by the more traditional Cadiot–Chodkiewicz coupling of $Me_3SiC{\equiv}CBr$ with $HC{\equiv}CPh$.[38] The trialkylsilyl-protected diyne may be purified by distillation or chromatography in air. The reaction of $RuCl(PPh_3)_2Cp$ with $Me_3SiC{\equiv}CC{\equiv}CPh$ in the presence of a fluoride ion source is a very convenient route to the diynyl complex $Ru(C{\equiv}CC{\equiv}CPh)(PPh_3)_2Cp$ **4**.

The preparation of longer chain polyynyl $\{ML_n\}(C{\equiv}C)_nR$ and polyynediyl $\{ML_n\}(C{\equiv}C)_n\{M'L'_m\}$ complexes has become a field of endeavour for many in recent times. Gladysz's group has elegantly demonstrated that a terminal ynyl ligand may be readily extended by linking the ligand with acetylenic building blocks, such as $Me_3SiC{\equiv}CBr$, using the traditional Cadiot–Chodkiewicz alkyne cross-coupling protocol.[39] Gladysz and others have reported the preparation of long chain polyynediyl complexes by oxidative coupling of two terminal diynyl complexes. The family of symmetrical octatetraynediyl compounds $\{ML_n\}(C{\equiv}C)_4\{ML_n\}$ ($\{ML_n\}$ = $Re(NO)(PPh_3)Cp^*$,[40] $Fe(dppe)Cp^*$,[41] $Fe(CO)_2Cp^*$ [42] or $W(CO)_3Cp$[4]) have all been prepared using this approach. The Lewis–Johnson group has used 1,6-bis(trimethylstannyl)hexa-1,3,5-triyne in the preparation of platinum-containing triacetylenic polymers.[21,43] We have found that it is also possible to use the preassembled triyne compounds $Me_3SiC{\equiv}CC{\equiv}CC{\equiv}CPh$ and $Me_3SiC{\equiv}CC{\equiv}CC{\equiv}CSiMe_3$ as a source of the polyyn-yl and -diyl fragments. These compounds are highly reactive, and derivatives such as the dicobalt and tcne adducts are easily obtained.

Conclusion

The use of fluoride ion as base has allowed the syntheses of some ruthenium acetylide, diynyl and diynediyl complexes simply and in high yield, from trimethylsilyl-protected alkynes or polyynes, thereby avoiding the use of unstable reagents, such as 1,3-diynes or the corresponding lithiated or stannyl derivatives. In their reactions with cobalt carbonyls or tetracyanoethene, it is the second C≡C triple bond out from the ruthenium centre which is attacked as a result of the steric protection afforded by the two bulky PPh_3 ligands to the C≡C triple bond adjacent to the ruthenium. Further studies are directed towards extending the scope of this reaction and establishing its versatility.

Experimental

General conditions

All reactions were carried out under dry, high purity nitrogen unless otherwise stated, using standard Schlenk techniques. Methanol was BDH AnalaR grade used as received. Light petroleum refers to a fraction of bp 60–80 °C. Elemental analyses were preformed by the Canadian Microanalytical Service, Delta, B.C. Column chromatography was carried out on alumina (Brockman Grade 1 from Merck, used as received). Preparative TLC was carried out on glass plates (20 × 20 cm) coated with silica gel (Merck 60 GF_{254}, 0.5 mm thick).

Instrumentation

Infrared spectra were obtained on Perkin-Elmer 1700 or 1720X FT IR spectrometers, NMR spectra of $CDCl_3$ solutions 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 were obtained from MeOH solutions unless otherwise indicated. Solutions were directly infused into a Finnegan LCQ instrument. Nitrogen was used as the drying and nebulising gas. Chemical aids to ionisation are indicated where used.[6]

Reagents

The compounds $RuCl(PPh_3)_2Cp$,[44] $Pd(PPh_3)_4$,[45] $PhC{\equiv}CBr$,[46] $PhC{\equiv}CI$,[47] $Me_3SiC{\equiv}CPh$,[48] 1,4-$(C{\equiv}C)_2C_6H_4$ and 1,4-$(SiMe_3\text{-}C{\equiv}C)_2C_6H_4$,[32] $PhC{\equiv}CC{\equiv}CSiMe_3$,[49] $Me_3SiC{\equiv}CC{\equiv}CSiMe_3$,[50]

$Me_3SiC{\equiv}CC{\equiv}CC{\equiv}CSiMe_3$,[51] $HC{\equiv}CSiMe_3$[52] and $HC{\equiv}CC{\equiv}CSiMe_3$[53] were prepared by the literature methods. Methanol (BDH AR grade), CuI (Ajax), 1,4-dibromobenzene (Aldrich), KF (BDH), dbu (Aldrich) and $NEtCy_2$ (Aldrich) were used as received. Triethylamine was dried and distilled from KOH prior to use.

$Me_3SiC{\equiv}CC{\equiv}CC{\equiv}CPh$. A flame-dried Schlenk tube containing triethylamine (20 ml) was rigorously degassed using a freeze/pump/thaw sequence. To the amine was then added $PhC{\equiv}CI$ (280 mg, 1.23 mmol), $HC{\equiv}CC{\equiv}CSiMe_3$ (150 mg, 1.23 mmol), $Pd(PPh_3)_4$ (71 mg, 0.06 mmol) and CuI (23 mg, 0.12 mmol) and the resulting mixture left to stir at r.t. overnight. The mixture was filtered to remove a suspension of light brown solids, which were then washed with hexane. The filtrate was then concentrated, and the residue purified by TLC (silica gel; hexane, R_f 0.7) to give $PhC{\equiv}CC{\equiv}CC{\equiv}CSiMe_3$ as a light yellow oil (78 mg, 29%). ^1H NMR ($CDCl_3$): δ 0.22 (s, 9 H, $SiMe_3$) and 7.32–7.52 (m, 5 H, Ph). IR (CH_2Cl_2): $\nu(C{\equiv}C)$ 2195m, 2174m and 2075s cm^{-1}.

Preparation of ruthenium alkynyl and polyynyl complexes

(a) $Ru(C{\equiv}CPh)(PPh_3)_2Cp$ 1. A mixture of $RuCl(PPh_3)_2Cp$ (200 mg, 0.276 mmol), $PhC{\equiv}CSiMe_3$ (60 mg, 0.34 mmol) and KF (16 mg, 0.28 mmol) was heated in refluxing MeOH (20 ml) for 2.5 h. After cooling in ice, the precipitated $Ru(C{\equiv}CPh)(PPh_3)_2Cp$ (182 mg, 84%) was filtered off and washed with cold MeOH and Et_2O. It was identified by comparison with an authentic sample.[5]

(b) $Ru(C{\equiv}CC_6H_4C{\equiv}CSiMe_3)(PPh_3)_2Cp$ 2. A mixture of 1,4-bis(trimethylsilylethynyl)benzene (450 mg, 1.66 mmol), $RuCl(PPh_3)_2Cp$ (1210 mg, 1.66 mmol) and KF (98 mg, 1.66 mmol) was stirred in refluxing MeOH (80 ml) overnight. After this time the orange suspension had become bright yellow. The solvent was filtered off to give a yellow powder (1280 mg, 87%). The crude product was then chromatographed on an alumina column eluting with acetone–hexane (3:7). Concentration of the yellow fraction, filtration and washing the solid with hexane gave $Ru(C{\equiv}CC_6H_4C{\equiv}CSiMe_3)(PPh_3)_2Cp$ **2** as a yellow powder (960 mg, 64%).

(c) 1,4-$\{Cp(PPh_3)_2Ru(C{\equiv}C)\}_2C_6H_4$ 3. A mixture of $RuCl(PPh_3)_2Cp$ (262 mg, 0.37 mmol), 1,4-bis(trimethylsilylethynyl)benzene (50 mg, 0.185 mmol) and KF (21 mg, 0.37 mmol) was heated in a refluxing mixture of thf–MeOH (1:1, 40 ml) for 16 h. An orange precipitate formed which was collected and washed with hexane and recrystallised (CH_2Cl_2–MeOH) to give 1,4-$\{Cp(PPh_3)_2Ru(C{\equiv}C)\}_2C_6H_4$ **3** (120 mg, 43%).

(d) $Ru(C{\equiv}CC{\equiv}CPh)(PPh_3)_2Cp$ 4. To a methanolic (30 ml) suspension of $RuCl(PPh_3)_2Cp$ (810 mg, 1.12 mmol) was added $PhC{\equiv}CC{\equiv}CSiMe_3$ (221 mg, 1.12 mmol) and KF (65 mg, 1.12 mmol). The mixture was refluxed for 1 h when all the orange $RuCl(PPh_3)_2Cp$ had been replaced by a pale green precipitate. The solution was then allowed to cool, and the precipitate filtered off and washed with cold MeOH. The product was then purified by passage through basic alumina, eluting with CH_2Cl_2, to give $Ru(C{\equiv}CC{\equiv}CPh)(PPh_3)_2Cp$ **4** (680 mg, 75%). Crystals suitable for X-ray study were obtained from toluene–hexane.

(e) $Ru(C{\equiv}CC{\equiv}CC{\equiv}CPh)(PPh_3)_2Cp$ 5. The compounds $RuCl(PPh_3)_2Cp$ (327 mg, 0.45 mmol) and KF (26 mg, 0.45 mmol) were added to a solution of $PhC{\equiv}CC{\equiv}CC{\equiv}CSiMe_3$ (*ca.* 100 mg, 0.45 mmol, freshly purified by TLC and extracted with MeOH (30 ml)). The resulting mixture was refluxed for 4 h, allowed to cool, then filtered to remove unchanged $RuCl(PPh_3)_2Cp$. The filtrate was then concentrated to give $Ru(C{\equiv}CC{\equiv}CC{\equiv}CPh)(PPh_3)_2Cp$ **5** (150 mg, 40%) as a brown solid. (The product was contaminated with *ca.* 8–10% $RuCl(PPh_3)_2Cp$ as shown by its ^1H NMR Cp resonance at δ 4.10.) No ES mass spectrum could be obtained.

(f) $\{Ru(PPh_3)_2Cp\}_2(\mu\text{-}C{\equiv}CC{\equiv}C)$ 6. A suspension of $RuCl(PPh_3)_2Cp$ (2.0 g, 2.76 mmol) in methanol (150 ml) was treated with $Me_3SiC{\equiv}CC{\equiv}CSiMe_3$ (0.268 g, 1.38 mmol), KF (0.16 g, 2.76 mmol) and $NEtCy_2$ (600 μl, 3.3 mmol). The reaction mixture was heated at reflux point for 18 h. After this time the solution was deep blue over a pale yellow-orange precipitate. The precipitate was collected by filtration, and washed with several portions of cold methanol. The solid was purified by flash chromatography on an alumina column (30 × 200 mm) using light petroleum–acetone (7:3) as the eluting solvent. Concentration of the orange fraction gave $\{Ru(PPh_3)_2Cp\}_2(\mu\text{-}C{\equiv}CC{\equiv}C)$ **6a** as a pale orange microcrystalline powder (1.3 g, 66%). IR (Nujol): $\nu(C{\equiv}C)$ 1970m cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.17 (s, 10 H, Cp) and 7.03–7.64 (m, 60 H, Ph). ES mass spectrum (MeOH): *m/z* 1430, $[M]^+$; 715, $[M]^{2+}$ and 692, $[Ru(PPh_3)_2Cp]^+$. Recrystallisation of **6a** from hot thf afforded isomer **6b** quantitatively. IR (Nujol): $\nu(C{\equiv}C)$ 1990w and 1976m cm^{-1}. ^1H NMR ($CDCl_3$): δ 4.17 (s, 10 H, Cp) and 7.03–7.64 (m, 60 H, Ph). ES MS (MeOH): *m/z* 1430, $[M]^+$; 715, $[M]^{2+}$ and 692, $[Ru(PPh_3)_2Cp]^+$.

(g) $\{Ru(PPh_3)_2Cp\}_2(\mu\text{-}C{\equiv}CC{\equiv}CC{\equiv}C)$ 7. To a methanolic (30 ml) suspension of $RuCl(PPh_3)_2Cp$ (200 mg, 0.28 mmol) was added $Me_3SiC{\equiv}CC{\equiv}CC{\equiv}CSiMe_3$ (60 mg, 0.28 mmol) and KF (20 mg, 0.35 mmol). The resulting mixture was refluxed for 1 h until all the orange $RuCl(PPh_3)_2Cp$ had been replaced by a pale green precipitate. The solution was then allowed to cool, and the precipitate filtered off and washed with cold MeOH to give $\{Ru(PPh_3)_2Cp\}_2(\mu\text{-}C{\equiv}CC{\equiv}CC{\equiv}C)$ **7** (173 mg, 87%). Crystals suitable for X-ray study were obtained from $CHCl_3$–pentane.

Reaction of $Ru(C{\equiv}CC{\equiv}CPh)(PPh_3)_2Cp$ with $Co_2(CO)_8$. A mixture of $Ru(C{\equiv}CC{\equiv}CPh)(PPh_3)_2Cp$ (80 mg, 0.10 mmol) and $Co_2(CO)_8$ (74 mg, 0.22 mmol) in benzene (10 ml) was stirred at r.t. for 1 h. The solvent was removed, and the residue purified by TLC (silica gel; acetone–hexane 1:4, R_f 0.6, black band) giving $Ru\{C{\equiv}CC_2Ph[Co_2(CO)_6]\}(PPh_3)_2Cp$ **8** (70 mg, 65%). Crystals suitable for X-ray study were obtained from CH_2Cl_2–MeOH.

Reactions with tetracyanoethene (tcne). *(a) $Ru(C{\equiv}CC{\equiv}CPh)(PPh_3)_2Cp$.* A mixture of $Ru(C{\equiv}CC{\equiv}CPh)(PPh_3)_2Cp$ (80 mg, 0.10 mmol) and tcne (40 mg, 0.30 mmol) in CH_2Cl_2 (10 ml) was stirred at r.t. for 1 h. The solvent was removed, and the residue purified by TLC (silica gel; CH_2Cl_2–hexane 1:2, R_f 0.5, deep red band) to give $Ru\{C{\equiv}CC[{=}C(CN)_2]CPh{=}C(CN)_2\}(PPh_3)_2Cp$ **10** (80 mg, 90%). Crystals suitable for X-ray study were obtained from CH_2Cl_2–hexane.

(b) $Ru(C{\equiv}CC{\equiv}CC{\equiv}CPh)(PPh_3)_2Cp$. A mixture of $Ru(C{\equiv}CC{\equiv}CC{\equiv}CPh)(PPh_3)_2Cp$ (50 mg, 0.059 mmol) and tcne (23 mg, 0.180 mmol) in CH_2Cl_2 was stirred at r.t. for 30 min. The mixture was concentrated, and the residue purified by TLC (silica gel; hexane–acetone 7:3). A green-black band (R_f 0.8) contained $Ru\{C{\equiv}CC[{=}C(CN)_2]C[{=}C(CN)_2]C{\equiv}CPh\}(PPh_3)_2Cp$ **11** (17 mg, 30%). Crystals suitable for X-ray study were obtained from CH_2Cl_2–MeOH.

(c) $\{Ru(PPh_3)_2Cp\}_2(\mu\text{-}C{\equiv}CC{\equiv}CC{\equiv}C)$. A mixture of $\{Ru(PPh_3)_2Cp\}_2(\mu\text{-}C{\equiv}CC{\equiv}CC{\equiv}C)$ (100 mg, 0.063 mmol) and tcne (50 mg, 0.39 mmol) in thf (10 ml) was stirred at r.t. for 30 min. The mixture was concentrated, and the residue purified by TLC (silica gel; hexane–acetone 7:3). The red band (R_f 0.5) gave $\{Ru(PPh_3)_2Cp\}_2\{\mu\text{-}(C{\equiv}CC[{=}C(CN)_2])_2\}$ **12** (75 mg, 70%). Crystals suitable for X-ray study were obtained from $CHCl_3$–hexane.

Crystallography

Full spheres of data were measured at the specified temperatures to $2\theta_{max} = 58°$ using a Bruker AXS CCD instrument (monochromatic Mo-Kα radiation, λ 0.7107$_3$ Å); N_{total} data were measured and reduced to N independent reflections, N_o with $F > 4\sigma(F)$ being considered 'observed' and used in the full matrix least squares refinement after absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U_{iso})_H$ were included constrained at estimated values. Computation used the XTAL 3.4 program system[54] implemented by S. R. Hall; neutral atom complex scattering factors were employed. Individual variations in procedure/difficulties/idiosyncrasies are noted below.

Crystal/refinement data. $Ru(C\equiv CC_6H_4C\equiv CSiMe_3\text{-}4)(PPh_3)_2Cp$ **2** $\equiv C_{54}H_{48}P_2RuSi$. $M = 888.1$, monoclinic, space group $P2_1/c$ (no. 14), $a = 19.420(1)$, $b = 14.889(1)$, $c = 17.173(2)$ Å, $\beta = 112.851(1)°$, $V = 4575._9$ Å^3, $Z = 4$, $\mu_{Mo} = 4.7$ cm^{-1}, $N_t = 50803$, $N = 8031$ ($R_{int} = 0.040$), $N_o = 5328$; $R = 0.058$, $R' = 0.072$, $n_v = 523$, T *ca.* 300 K. The specimen was a feebly diffracting flake, data being limited to $2\theta_{max} = 50°$.

$Ru(C\equiv CC\equiv CPh)(PPh_3)_2Cp$ **4**. $\equiv C_{51}H_{40}P_2Ru$. $M = 815.9$, monoclinic, space group $P2_1/c$, $a = 14.825(3)$, $b = 14.561(3)$, $c = 18.613(4)$ Å, $\beta = 100.446(3)°$, $V = 3952$ Å^3, $Z = 4$, $\mu_{Mo} = 5.1$ cm^{-1}, $N_t = 46126$, $N = 10005$ ($R_{int} = 0.027$), $N_o = 5644$, $R = 0.044$, $R' = 0.043$, $n_v = 487$, T *ca.* 300 K.

$\{Ru(PPh_3)_2Cp\}_2(\mu\text{-}C\equiv CC\equiv C)\cdot 2thf$ **6**$\cdot$2thf $\equiv C_{94}H_{86}O_2P_4Ru_2$. $M = 1573.8$, monoclinic, space group $P2_1/c$, $a = 23.51(1)$, $b = 14.710(9)$, $c = 25.874(9)$ Å, $\beta = 118.11(3)°$, $V = 7894$ Å^3, $Z = 4$, $\mu_{Mo} = 5.1$ cm^{-1}, $N = 14092$, $N_o = 6675$, $R = 0.083$, $R' = 0.083$, $n_v = 896$.

For this compound and its 0.8 MeOH solvated counterpart, data were measured using a single-counter/sequential instrument to $2\theta_{max} = 50°$ at *ca.* 295 K; gaussian absorption corrections were applied. In this compound specifically, thf solvent residues were refined with constrained geometries, and in the case of thf isotropic thermal parameter forms. Linewidths were rather large throughout, perhaps a consequence of rather facile desolvation. In the methanol solvate residues modelled as C, O were refined with isotropic thermal parameters forms and site occupancies set at 0.8 after trial refinement; this latter form, for which samples are also difficult, has been previously recorded in ref. 8, described as unsolvated ($R = 0.11$); the present study, in standard space group setting, represents an improvement on the previous effort. The cell volume of the previous (nicely precise) definition of a 2thf solvate as a triclinic form was 2015 Å^3, larger than the present asymmetric unit ascribed as a 2thf solvate also, in the monoclinic form. Asymmetric unit volumes of the studies recorded for previous and the present unsolvated and solvated orthorhombic forms are identical.

$\{Ru(PPh_3)_2Cp\}_2(\mu\text{-}C\equiv CC\equiv C)\cdot 0.8CH_3OH$ **6**$\cdot$*MeOH* $\equiv C_{86}H_{70}P_4Ru_2\cdot 0.8CH_3OH$. $M = 1455.2$, orthorhombic, space group *Pcca* (no. 54), $a = 21.542(6)$, $b = 11.463(3)$, $c = 29.377(15)$ Å, $V = 7254$ Å^3, $Z = 4$, $\mu_{Mo} = 5.5$ cm^{-1}, $N = 6402$, $N_o = 2457$, $R = 0.058$, $R' = 0.053$, $n_v = 424$.

$\{Ru(PPh_3)_2Cp\}_2(\mu\text{-}C\equiv CC\equiv CC\equiv C)\cdot 4CH_2Cl_2$ *7* $\equiv C_{92}H_{78}Cl_8P_4Ru_2$. $M = 1793.3$, monoclinic, space group $P2_1/n$ [no. 14 (variant)], $a = 12.408(1)$, $b = 15.398(2)$, $c = 21.246(3)$ Å, $\beta = 97.833(2)°$, $V = 4021$ Å^3, $Z = 2$, $\mu_{Mo} = 7.7$ cm^{-1}, $N_t = 48326$, $N = 9240$ ($R_{int} = 0.044$), $N_o = 5146$, $R = 0.054$, $R' = 0.054$, $n_v = 489$, T *ca.* 153 K.

$Ru\{C\equiv CC_2Ph[Co_2(CO)_6]\}(PPh_3)_2Cp\cdot CH_2Cl_2$ **8** $\equiv C_{58}H_{42}Cl_2Co_2O_6P_2Ru$. $M = 1186.8$, triclinic, space group $P\bar{1}$ (no. 2), $a = 11.831(1)$, $b = 14.195(1)$, $c = 17.632(2)$ Å, $\alpha = 95.453(1)$, $\beta = 104.238(1)$, $\gamma = 112.847(1)°$, $V = 2584$ Å^3, $Z = 2$, $\mu_{Mo} = 11.4$ cm^{-1}, $N_t = 30223$, $N = 16225$ ($R_{int} = 0.026$), $N_o = 9742$, $R = 0.038$, $R' = 0.046$, $n_v = 641$, T *ca.* 300 K. Solvent site occupancy was set at unity after trial refinement.

$Ru\{C\equiv CC_2H[Co_2(\mu\text{-}dppm)(CO)_4]\}(PPh_3)_2Cp$ **9** $\equiv C_{74}H_{58}Co_2O_4P_4Ru$. $M = 1354.1$, monoclinic, space group $P2_1/n$, $a = 17.474(3)$, $b = 17.164(3)$, $c = 22.453(4)$ Å, $\beta = 111.223(5)°$, $V = 6277$ Å^3, $Z = 4$, $\mu_{Mo} = 9.1$ cm^{-1}, $N_t = 55791$, $N = 11195$ ($R_{int} = 0.092$), $N_o = 3240$, $R = 0.082$, $R' = 0.071$, $n_v = 731$, T *ca.* 300 K. In consequence of weak and limited data/high 'thermal motion' (poor crystal quality?) ring 132 was modelled with isotropic thermal parameter forms.

$Ru\{C\equiv CC[=C(CN)_2]CPh=C(CN)_2\}(PPh_3)_2Cp\cdot C_2H_5Me\cdot C_6H_{14}$ **10** $\equiv C_{70}H_{62}N_4P_2Ru$. $M = 1122.3$, monoclinic, space group $C2/c$ (no. 15), $a = 26.078(3)$, $b = 12.559(1)$, $c = 37.015(4)$ Å, $\beta = 110.218(1)°$, $V = 11375$ Å^3, $Z = 8$, $\mu_{Mo} = 3.8$ cm^{-1}, $N_t = 67495$, $N = 9976$ ($R_{int} = 0.058$), $N_o = 6359$, $R = 0.068$, $R' = 0.092$, $n_v = 609$, T *ca.* 300 K. Data were weak and limited, $2\theta_{max} = 50°$, high thermal motion on the solvent moieties, modelled as above, presumably being a contributing factor. Site occupancy of the latter was set at unity after trial refinement.

$Ru\{C\equiv CC[=C(CN)_2]C[=C(CN)_2]C\equiv CPh\}(PPh_3)_2Cp$ **11** $\equiv C_{59}H_{40}N_4P_2Ru$. $M = 968.0$, monoclinic, space group $P2_1/c$, $a = 26.229(3)$, $b = 16.301(2)$, $c = 23.696(3)$ Å, $\beta = 105.880(2)°$, $V = 9745$ Å^3, $Z = 8$, $\mu_{Mo} = 4.3$ cm^{-1}, $N_t = 109545$, $N = 25078$ ($R_{int} = 0.022$), $N_o = 13808$, $R = 0.058$, $R' = 0.054$; $n_v = 1160$. Phenyl ring 28 in molecule 2 was modelled as disordered over two sets of sites, occupancies set at 0.5 after trial refinement, both rings were refined as rigid bodies with isotropic thermal parameter forms.

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See http://www.rsc.org/suppdata/dt/1999/3719/ for crystallographic files in .cif format.

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