

σ -Acetylide complexes of ruthenium and osmium containing alkynylsilane ligands

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Abstract

The use of the ligands, diethynyldiphenylsilane and 1,3-diethynyltetramethyldisiloxane, in the synthesis of Group 8 metal σ -acetylide mononuclear complexes is demonstrated. New complexes *trans*-[(dppm)₂ClM≡CSi(Ph)₂C≡CH] (M = Ru **1**; Os **2**) and *trans*-[(dppm)₂ClM≡CSi(Me)₂–O–Si(Me)₂C≡CH] (M = Ru, **3**; Os, **4**) featuring different silyl units were prepared from a mixture of *cis*-[M(dppm)₂Cl₂] and HC≡CSi(Ph)₂C≡CH or HC≡CSi(Me)₂–O–Si(Me)₂C≡CH in the presence of NaPF₆ followed by deprotonation with 1,8-diazabicyclo[5.4.0]undec-7-ene. All the new complexes have been fully characterized by FTIR and NMR spectroscopies and fast atom bombardment mass spectrometry. Single-crystal X-ray structures of **1** and **2** confirm that the two diphosphines adopt a *trans* geometry at the metal centre and one of the terminal ethynyl groups remains intact. Complexes **1–4** show reversible redox chemistry and their half-wave potentials due to the metal centres are less anodic than those for the starting precursors *cis*-[M(dppm)₂Cl₂] (M = Ru, Os).

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1. Introduction

The development of synthetic methodologies towards transition metal–acetylide oligomers and polymers has shown tremendous progress following the initial reports on Group 10 metal–acetylide polymers [1]. Since then, various synthetic routes have been devised by a number of research groups to afford organometallic acetylide molecules of other metal groups and there has been a burgeoning range of ligands and metals incorporated into these π -conjugated systems [2]. Rigid-rod conjugated organometallic systems of the form $[-M(L)_x C \equiv C - R - C \equiv C -]_n$ containing transition metal sites linked via organic moieties impart interesting electronic and optical properties with potential technological applications [2]. A detailed understanding of structure-property relationships in these compounds is essential for full exploitation of these materials. One general approach to

gain insight in this area has been to investigate the factors that contribute to the extent of π -electron delocalization in the main chain by varying the metal centre, the auxiliary ligands and the connecting organic functionalities [2]. While much research effort has been devoted to the use of aromatic [3], heteroaromatic [4] or oligoacetylenic spacers [5], very few reports were known for the silicon-linked system and related studies on organometallic alkynylsilanes are very scarce [6]. Although sp^3 -silicon unit is generally not as good as sp - or sp^2 -carbon structural motif in facilitating electronic conjugation, recent studies demonstrate that deliberate inclusion of conjugation-interrupting units shows good potential in improving the resulting optical and photophysical properties of these conjugated compounds [3d,7]. As part of our continuing study into the properties of organometallic alkynyls [2h,2i,3c,3d,8], a comprehensive program was therefore launched recently in our laboratory to develop synthetic pathways to a new class of organic and metalloorganic conjugated materials containing alkynylsilane units [9]. Here, we present the results on the first synthesis, characterization

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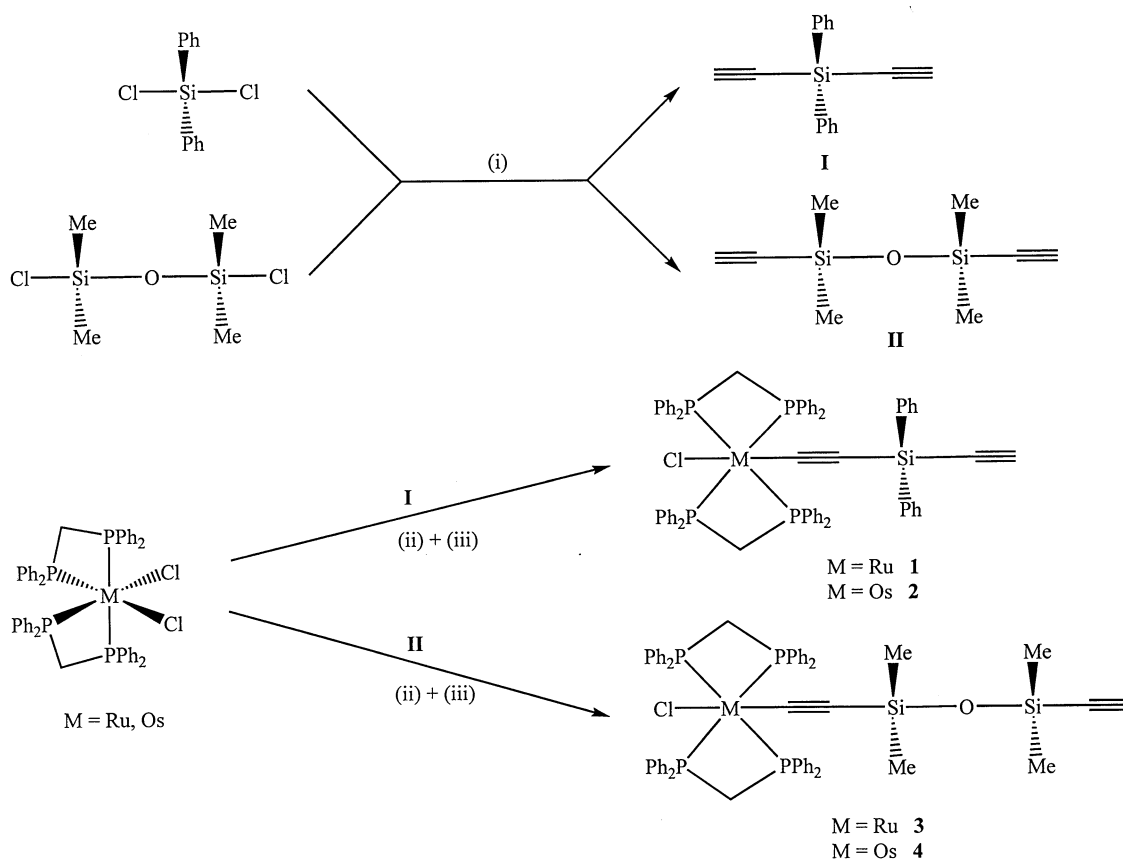
and electrochemistry of a series of soluble Group 8 metal-containing alkynylsilanes and alkynylsiloxanes. The crystal structures of *trans*-[(dppm)₂ClM≡CSi(Ph)₂C≡CH] (M = Ru, Os) are presented which represent the first structurally characterized examples of ruthenium(II) and osmium(II) acetylide complexes linked by a SiPh₂ group.

2. Results and discussion

2.1. Synthesis

The synthesis of the ligands, diethynyldiphenylsilane (**I**) and 1,3-diethynyltetramethyldisiloxane (**II**), was carried out by modifications of the literature procedures (Scheme 1) [10]. Reaction of the Grignard reagent HC≡CMgCl with Ph₂SiCl₂ or ClSi(Me)₂–O–Si(Me)₂Cl in THF afforded crude products **I** and **II**, respectively. Compound **I** was purified by column chromatography on silica to give an off-white solid whereas **II** was collected by vacuum distillation to furnish a colorless volatile liquid which should cautiously be stored below 4 °C. The reactions leading to the new σ-acetylide complexes of ruthenium(II) and osmium(II) containing alkynylsilane ligands are also shown in Scheme 1. New

terminal acetylide complexes of ruthenium and osmium, *trans*-[(dppm)₂ClM≡CSi(Ph)₂C≡CH] (M = Ru **1**; Os **2**) and *trans*-[(dppm)₂ClM≡CSi(Me)₂–O–Si(Me)₂C≡CH] (M = Ru, **3**; Os, **4**), were made using the established method through the formation of vinylidene intermediates followed by deprotonation [11]. The reactions of *cis*-[M(dppm)₂Cl₂] (M = Ru, Os) with one equivalent of **I** and two equivalents of NaPF₆ produced vinylidene complexes which were not isolated but instead, were deprotonated in situ by one equivalent of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) to give complexes **1** and **2**. In a similar manner, compounds **3** and **4** have been prepared via the NaPF₆–DBU route involving *cis*-[M(dppm)₂Cl₂] (M = Ru, Os) and **II** in a 1:1 stoichiometry. Efforts to synthesize the homometallic dinuclear di-yne complexes using two molar equivalents of *cis*-[M(dppm)₂Cl₂] under ambient conditions were unsuccessful, presumably due to the steric bulk between the terminal metal groups with bulky phosphine rings. All these newly synthesized Group 8 metal complexes were purified by passage of the respective crude product through a short alumina column and isolated as air-stable light yellow fine powders in reasonably good yields. They show good solubility in chlorinated solvents and have been characterized by IR, ¹H- and ³¹P{¹H}-NMR spectroscopies and positive FAB-mass spectra.



Scheme 1. (i) $\text{HC}\equiv\text{CMgCl}$, THF; (ii) NaPF_6 , CH_2Cl_2 ; (iii) DBU, CH_2Cl_2 .

2.2. Spectroscopic properties

The starting precursors **I** and **II** both show IR absorptions assignable to the C≡C and C≡CH stretching vibrations. The ¹H-NMR resonances arising from the phenyl (for **I**) and methyl (for **II**) protons are clearly identified and each of them shows two strong ¹³C-NMR signals for the two distinct sp carbons, in accordance with their formulations. For **1–4**, characteristic ν(C≡C) bands are observed in their IR spectra in the range 1983–2035 cm^{−1}. The presence of an uncoordinated acetylenic group is discernible from the IR spectral peaks at ca. 3284 cm^{−1} due to ν(≡CH) in all cases. In their ¹H-NMR spectra, the proton signal stemming from the terminal acetylene appears as a sharp peak within the short range δ 2.3–2.5 and resonances characteristic of the CH₂ group in the bridging phosphines are apparent. Two well-defined methyl signals which are separated by about 0.6 ppm are evident in the ¹H-NMR spectra of **3** and **4** and each of them is integrated as six protons. Complexes **1–4** show room-temperature ³¹P{¹H}-NMR spectra consistent with the *trans* geometry of the two dppm ligands and the spectral data fully agree with the solid state structures (vide infra). The ³¹P{¹H} chemical shifts for **1–4** compare well with those reported for other mononuclear ruthenium and osmium σ-acetylide complexes [11] and they are rather insensitive to the variation of the central organic linker groups. The FAB-mass spectra of compounds **1–4** all exhibit small molecular ion peaks and comparatively more intense peaks attributable to the daughter ions [M(dppm)₂]⁺ (M = Ru, Os). Fragmentation by the loss of Ph group was also observed in each case. Rupture of the metal–phosphorus bond (for **1–4**) and the silicon–oxygen bond (for **3** and **4**) is not a major fragmentation pattern for these complexes under the experimental conditions.

2.3. Electrochemistry

The electrochemical properties of complexes **1–4** were studied in CH₂Cl₂ at room temperature by means of cyclic voltammetry and the redox data are collected in Table 1 together with those for the starting metal precursors *cis*-[M(dppm)₂Cl₂] (M = Ru, Os). For **1–4**, each shows a quasi-reversible oxidation event due to the M(II) → M(III) process (M = Ru, Os). The half-wave potentials of ruthenium in **1** and **3** and osmium in **2** and **4** are considerably less anodic than those of the metal centres in *cis*-[M(dppm)₂Cl₂] (M = Ru, Os). This can be attributed to the increased electron density in the metal vicinity induced by the unsaturation of the ethynyl bridge, which renders the oxidation easier. The presence of an electron-rich oxygen atom in the disiloxane bridge in **3** and **4** lowers the electrode potential values by ca. 0.10 V as compared to **1** and **2**, respectively. Our results

Table 1

Electrochemical data for complexes **1–4** and *cis*-[M(dppm)₂Cl₂] (M = Ru, Os) in CH₂Cl₂

Complex	<i>E</i> _{1/2} (V) ^a
1	0.11
2	−0.11
3	0.01
4	−0.21
<i>cis</i> -[Ru(dppm) ₂ Cl ₂]	0.41
<i>cis</i> -[Os(dppm) ₂ Cl ₂]	0.27

^a Scan rate = 100 mV s^{−1}, half-wave potential values *E*_{1/2} = (*E*_{pa} + *E*_{pc})/2 for reversible oxidation, where *E*_{pa} and *E*_{pc} are the anodic and cathodic peak potentials, respectively.

also indicate that the ruthenium centre acts as a better acceptor than the osmium counterpart, probably owing to better stabilization of the +3 state by osmium and this phenomenon was also observed for the complexes [(η⁵-C₅H₅)Fe(η⁵-C₅H₄)C≡CM(dppm)₂Cl] (M = Ru, Os) [12].

2.4. Molecular structures

Yellow block-shaped crystals of good quality for **1** and **2** were obtained by allowing their respective solutions in CH₂Cl₂–hexane to stand in crystallization vials for 1 day. Both compounds **1** and **2** are isostructural and conform to the same space group with two crystallographically independent molecules per asymmetric unit. The structures of one molecule of **1** and **2** are depicted in Figs. 1 and 2, respectively, and the important molecular dimensions are listed in Table 2. To our knowledge, complexes **1** and **2** are the first structurally characterized examples of Group 8 metal mono-acetylide compounds bearing an inorganic sp³-silicon bridging unit. Each molecule possesses an overall C_s symmetry with the mirror plane passing through the metal atom and bisecting each dppm ligand. Both the chlorine atom and the alkynyl unit lie within the mirror plane.

The crystal structures of **1** and **2** consist of discrete monomer molecules with the corresponding metal atom coordinated in a *trans* disposition to two chelating dppm ligands and the coordination sphere around the metal is completed by one chlorine and one alkynylsilane ligands in a *trans* arrangement. The coordination at the ruthenium (or osmium) is distorted octahedral, with angles between *cis* donor atoms in the range 69.41(4)–111.06(5)° (69.08(6)–111.58(6)°) and those between *trans* atoms in the range 176.53(5)–178.16(14)° (176.04(7)–177.84(19)°). The principal contractions from 90° are due to the ‘bite’ of the chelating dppm groups. The metal–phosphorus bonds are typical at 2.3271(14)–2.3768(13) (for **1**) and 2.3353(19)–2.3723(17) (for **2**), while the metal–chlorine distances

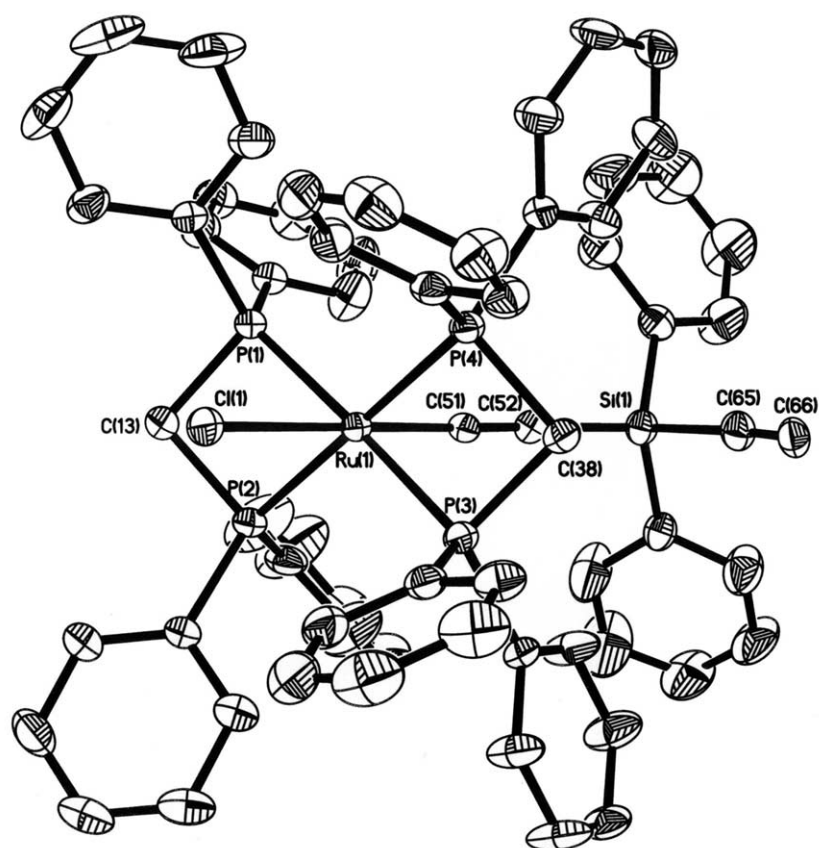


Fig. 1. A perspective view of one molecule of **1**, with thermal ellipsoids shown at the 25% probability level. Hydrogen atoms and all labels on phenyl carbon atoms were omitted for clarity.

at 2.5034(14)–2.5041(13) (for **1**) and 2.5070(18)–2.5119(17) (for **2**) are in good agreement with those found in other structurally characterized ruthenium and osmium mono-chloro acetylide complexes [11c,12,13]. In both cases, the metal-coordinated C≡C bond lengths (C(51)–C(52) 1.225(7), 1.213(6) Å in **1** and 1.225(9), 1.229(9) Å in **2**) are a common feature of metal-acetylide σ -bonding and the C≡CH bond (C(65)–C(66) 1.129(7), 1.105(7) Å in **1** and 1.167(10), 1.160(9) Å in **2**) appears slightly shorter because of the libration effect frequently observed in terminal acetylene unit [8a,9a,14]. The Si(1)–C(52) single bond lengths (average 1.790 Å in **1**, 1.780 Å in **2**) are notably shorter than the other Si(1)–C(65) bond (average 1.847 Å in **1**, 1.848 Å in **2**), suggesting that the sp^3 -silicon atom partially breaks π -conjugation along the chain. The Cl(1)–M(1)–C(51)–C(52) and Si(1)–C(65)–C(66) fragments are essentially linear in both complexes. There are no apparent short intermolecular contacts between adjacent molecules in these crystals. All of the remaining structural parameters are comparable to those observed for other crystal

structures of the type *trans*-[(dppm)₂ClMC≡CArC≡CR] [11c,12,13].

3. Concluding remarks

In summary, we have widened our scope to form a new series of rigid-rod σ -acetylide complexes of ruthenium(II) and osmium(II) containing functionalized silyl moieties as the linking unit and have structurally characterized the first examples of such complexes. These complexes exhibit reversible redox couple attributable to the M^{II}/M^{III} oxidation. We are currently attempting to develop new synthetic methodologies in the quest for a novel class of silyl-bridged heterometallic alkynyl complexes starting from compounds **1–4** or alike. Analysis of the physical and optical properties of the resulting complexes to assess the extent of conjugation in the main chain and a comparison with those for the corresponding complexes of Group 10 metals and other complexes of Group 8 having (hetero)aromatic

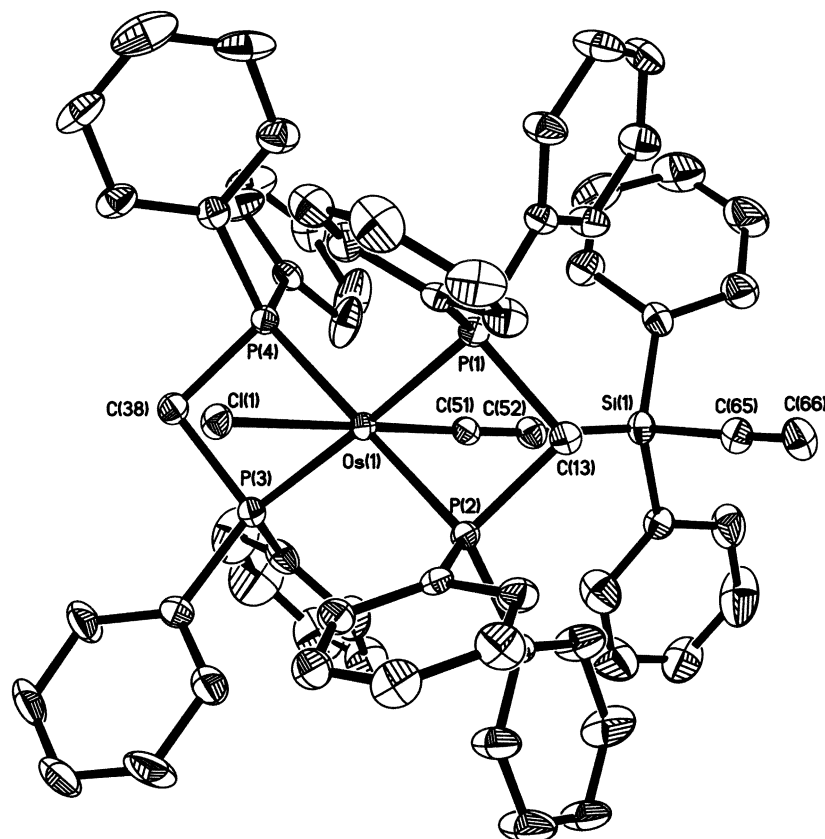


Fig. 2. A perspective view of one molecule of **2**, with thermal ellipsoids shown at the 25% probability level. Hydrogen atoms and all labels on phenyl carbon atoms were omitted for clarity.

spacers are also worthy of study and will be pursued in our laboratory.

Table 2
Selected bond lengths (Å) and bond angles (°) for complexes **1** and **2**

	1		2	
	Molecule 1	Molecule 2	Molecule 1	Molecule 2
<i>Bond lengths</i>				
M(1)–P(1)	2.3531(13)	2.3480(13)	2.3628(18)	2.3662(18)
M(1)–P(2)	2.3271(14)	2.3439(13)	2.3723(17)	2.3719(18)
M(1)–P(3)	2.3634(14)	2.3661(13)	2.3463(19)	2.3528(18)
M(1)–P(4)	2.3768(13)	2.3706(13)	2.3473(18)	2.3353(19)
M(1)–Cl(1)	2.5034(14)	2.5041(13)	2.5119(17)	2.5070(18)
M(1)–C(51)	1.990(5)	2.003(5)	2.001(7)	2.010(7)
C(51)–C(52)	1.225(7)	1.213(6)	1.225(9)	1.229(9)
Si(1)–C(52)	1.791(5)	1.788(5)	1.786(8)	1.774(8)
Si(1)–C(65)	1.847(7)	1.846(6)	1.846(8)	1.849(9)
C(65)–C(66)	1.129(7)	1.105(7)	1.167(10)	1.160(9)
<i>Bond angles</i>				
P(1)–M(1)–P(4)	110.56(5)	111.06(5)	108.71(6)	109.32(6)
P(2)–M(1)–P(3)	108.82(5)	108.60(5)	111.58(6)	111.03(6)
Cl(1)–M(1)–C(51)	178.16(14)	177.46(13)	177.37(19)	177.84(19)
M(1)–C(51)–C(52)	177.5(4)	174.4(4)	175.5(6)	177.9(6)
Si(1)–C(52)–C(51)	165.6(5)	166.4(5)	163.8(7)	163.4(6)
C(52)–Si(1)–C(65)	106.4(2)	109.0(2)	109.5(3)	107.5(3)
Si(1)–C(65)–C(66)	173.4(6)	175.5(6)	178.4(8)	172.8(8)

4. Experimental

4.1. General procedures

All reactions were carried out under a nitrogen atmosphere with the use of standard inert atmosphere and Schlenk techniques, but no special precautions were taken to exclude oxygen during work-up. Solvents were predried and distilled from appropriate drying agents [15]. All chemicals, unless otherwise stated, were obtained from commercial sources and used as received. The compounds *cis*-[M(dppm)₂Cl₂] were prepared by the reported procedures [16]. Infrared spectra were recorded as CH₂Cl₂ solutions in a CaF₂ cell (0.5 mm path length) on a Perkin Elmer Paragon 1000 PC or Nicolet Magna 550 Series II FTIR spectrometer. NMR spectra were measured in CDCl₃ on a JEOL EX270 or a Varian Inova 400 MHz FT NMR spectrometer, with ¹H NMR chemical shifts quoted relative to SiMe₄ and ³¹P{¹H} chemical shifts relative to an 85% H₃PO₄ external standard. Fast atom bombardment mass spectra were recorded on a Finnigan MAT SSQ710 mass spectrometer. Cyclic voltammetry experiments were done with a Princeton Applied Research (PAR) model 273A potentiostat. A conventional three-electrode configuration consisting of a glassy-carbon working elec-

trode, a Pt-wire counter electrode and a Ag/AgNO₃ reference electrode (0.1 M in acetonitrile) was used. The solvent in all measurements was deoxygenated CH₂Cl₂ and the supporting electrolyte was 0.1 M [Bu₄N]PF₆. Ferrocene was added as a calibrant after each set of measurements and all potentials reported were quoted with reference to the ferrocene-ferrocenium couple (taken as $E_{1/2} = +0.17$ V relative to Ag/AgNO₃).

4.2. Preparations of compounds

4.2.1. Synthesis of HC≡CSi(Ph)₂C≡CH (**I**)

A 0.5 M THF solution of HC≡CMgCl (50 cm³, 25.0 mmol, Aldrich) was added dropwise into a solution of Ph₂SiCl₂ (2.5 g, 10.0 mmol) in the same solvent (5 cm³) at room temperature (r.t.) under nitrogen. The mixture was heated to 30–40 °C and stirred for 3 h before all the volatile components were removed under reduced pressure. The residue was taken up in Et₂O and filtered through a pad of Celite. The filtrate was concentrated and subjected to column separation on silica using a mixture of Et₂O and hexane (1:9, v/v) as eluent. From the major band, the title compound was collected as an off-white solid in 97% yield (2.3 g). IR (CH₂Cl₂): 3263 $\nu(\equiv\text{CH})$, 2032 $\nu(\text{C}\equiv\text{C})$ cm⁻¹. ¹H-NMR (CDCl₃): δ 2.75 (s, 2H, C≡CH), 7.39–7.48 (m, 6H, Ph) and 7.74–7.79 (m, 4H, Ph). ¹³C-NMR (CDCl₃): δ 83.37 (C≡C), 97.36 (C≡CH), 128.19, 130.60, 131.25, 134.74 (Ph). FABMS: m/z 232 [M⁺]. Anal. Found: C, 82.60; H, 5.02. Calc. for C₁₆H₁₂Si: C, 82.71; H, 5.21%.

4.2.2. Synthesis of HC≡CSi(Me)₂-O-Si(Me)₂C≡CH (**II**)

To a solution of ClSi(Me)₂-O-Si(Me)₂Cl (1.0 g, 5.0 mmol) in pre-dried THF (5 cm³), 0.5 M THF solution of HC≡CMgCl (25 cm³, 12.5 mmol) was added dropwise at r.t. under nitrogen. The mixture was heated to 40–50 °C and stirred for a period of 3 h. The solution was gently concentrated to about 10 cm³ under reduced pressure and then filtered through a short layer of silica to remove the Mg residue using pentane–Et₂O (1:1, v/v) as eluent. The filtrate was concentrated in vacuo gently without heating to give a volatile and colorless liquid in 94% yield (0.86 g) which should be stored below 4 °C. IR (CH₂Cl₂): 3284 $\nu(\equiv\text{CH})$ 2037 $\nu(\text{C}\equiv\text{C})$ cm⁻¹. ¹H-NMR (CDCl₃): δ 0.31 (s, 12H, Me) and 2.42 (s, 2H, C≡CH). ¹³C-NMR (CDCl₃): δ 1.89 (Me), 88.96 (C≡C) and 92.33 (C≡CH). FABMS: m/z 182 [M⁺]. Anal. Found: C, 52.26; H, 7.48. Calc. for C₈H₁₄OSi₂: C, 52.69; H, 7.74%.

4.2.3. Synthesis of trans-[(dppm)₂ClRuC≡CSi(Ph)₂C≡CH] (**I**)

A mixture of *cis*-[Ru(dppm)₂Cl₂] (47.0 mg, 0.05 mmol), HC≡CSi(Ph)₂C≡CH (**I**, 11.6 mg, 0.05 mmol) and NaPF₆ (16.8 mg, 0.10 mmol) in CH₂Cl₂ (40 cm³)

were stirred for 6 h at r.t. The resulting light yellow solution was filtered through a pad of Celite to remove any excess NaPF₆ and NaCl by-product, and DBU (7.60 mg, 0.05 mmol) was added. After stirring for 3 h, the solvent was removed in vacuo. The residue was dissolved in Et₂O and filtration through a short alumina column using pure Et₂O as eluent afforded complex **1** as a pale yellow solid in 74% yield (42.0 mg). Recrystallization of **1** was achieved from an evaporated hexane–CH₂Cl₂ solution at r.t., giving light yellow crystals in a pure form. IR (CH₂Cl₂): 3284 $\nu(\equiv\text{CH})$, 2032, 1989 $\nu(\text{C}\equiv\text{C})$ cm⁻¹. ¹H-NMR (CDCl₃): δ 2.48 (s, 1H, C≡CH), 4.75 (m, 2H, CH₂), 4.92 (m, 2H, CH₂) and 6.96–7.57 (m, 50H, Ph). ³¹P{¹H}-NMR (CDCl₃): δ -4.61. FABMS: m/z 1137 [M⁺], 1102 ([M-Cl]⁺), 1060 ([M-Ph]⁺) and 871 ([M-Cl-C≡CSi(Ph)₂C≡CH]⁺). UV-vis (CH₂Cl₂): λ_{max} ($\epsilon \times 10^{-4}$ dm³ mol⁻¹ cm⁻¹) 230 (7.4) and 266 (5.0). Anal. Found: C, 69.50; H, 4.68. Calc. for C₆₆H₅₅ClP₄RuSi: C, 69.74; H, 4.88%.

4.2.4. Synthesis of trans-[(dppm)₂ClOsC≡CSi(Ph)₂C≡CH] (**2**)

To a solution of *cis*-[Os(dppm)₂Cl₂] (103 mg, 0.10 mmol) in 80 cm³ of CH₂Cl₂, compound **I** (23.2 mg, 0.10 mmol) and NaPF₆ (33.6 mg, 0.20 mmol) were added. The reaction mixture was allowed to react for 6 h at ambient temperature. The solution which changed from yellow to greenish-yellow was filtered through Celite. After the addition of DBU (15.2 mg, 0.10 mmol), the solution turned light yellow at once and the mixture was allowed to stir for an additional 3 h. The solvent was evaporated to dryness and the residue was taken up in Et₂O and then chromatographed on a short alumina column eluting with Et₂O, resulting in the isolation of bright yellow product **2** (80.0 mg, 65%). Similar to **1**, this compound can be purified by recrystallizing from a hexane–CH₂Cl₂ solution at r.t. IR (CH₂Cl₂): 3284 $\nu(\equiv\text{CH})$, 2031, 1983 $\nu(\text{C}\equiv\text{C})$ cm⁻¹. ¹H-NMR (CDCl₃): δ 2.46 (s, 1H, C≡CH), 5.27 (m, 2H, CH₂), 5.46 (m, 2H, CH₂) and 6.97–7.52 (m, 50H, Ph). ³¹P{¹H}-NMR (CDCl₃): δ -46.21. FABMS: m/z 1226 [M⁺], 1149 ([M-Ph]⁺), 1037 ([M-Cl-2Ph]⁺) and 960 ([M-Cl-C≡CSi(Ph)₂C≡CH]⁺). UV-vis (CH₂Cl₂): λ_{max} ($\epsilon \times 10^{-4}$ dm³ mol⁻¹ cm⁻¹) 230 (6.7) and 254 sh (3.8). Anal. Found: C, 64.44; H, 4.39. Calc. for C₆₆H₅₅ClP₄OsSi: C, 64.67; H, 4.52%.

4.2.5. Synthesis of trans-[(dppm)₂ClRuC≡CSi(Me)₂-O-Si(Me)₂C≡CH] (**3**)

cis-[Ru(dppm)₂Cl₂] (47.0 mg, 0.05 mmol) was added to HC≡CSi(Me)₂-O-Si(Me)₂C≡CH (**II**, 9.10 mg, 0.05 mmol) in CH₂Cl₂ (40 cm³) in the presence of NaPF₆ (16.8 mg, 0.10 mmol) and the mixture was stirred for 24 h. The resultant faintly yellow vinylidene solution was filtered and DBU (7.60 mg, 0.05 mmol) was added. After the solution was stirred for a further 3 h, the

solvent was removed and the residue dissolved in Et₂O was subjected to a short silica column using the same solvent as eluent. A light yellow solid of **3** was collected in 49% yield (26.6 mg). IR (CH₂Cl₂): 3284 $\nu(\equiv\text{CH})$, 2034, 1993 $\nu(\text{C}\equiv\text{C})$ cm⁻¹. ¹H-NMR (CDCl₃): δ -0.51 (s, 6H, Me), 0.11 (s, 6H, Me), 2.35 (s, 1H, C $\equiv$ CH), 4.91 (m, 4H, CH₂) and 7.13–7.54 (m, 40H, Ph). ³¹P{¹H}-NMR (CDCl₃): δ -4.71. FABMS: m/z 1085 [M⁺], 1008 ([M–Ph]⁺) and 869 ([M–Cl–C $\equiv$ CSi(Me)₂–O–Si(Me)₂C $\equiv$ CH]⁺). UV–vis (CH₂Cl₂): λ_{max} ($\epsilon \times 10^{-4}$ dm³ mol⁻¹ cm⁻¹) 230 (6.5) and 269 (3.8). Anal. Found: C, 63.98; H, 5.18. Calc. for C₅₈H₅₇ClOP₄RuSi₂: C, 64.11; H, 5.29%.

4.2.6. Synthesis of *trans*-[(*dppm*)₂ClOsC $\equiv$ CSi(Me)₂–O–Si(Me)₂C $\equiv$ CH] (**4**)

Following the same procedures as for **3** above, the desired product **4** was obtained as a bright yellow powder in 51% yield (30.0 mg) from *cis*-[Os(*dppm*)₂Cl₂] (51.5 mg, 0.05 mmol) and **II** (9.10 mg, 0.05 mmol) instead. IR (CH₂Cl₂): 3284 $\nu(\equiv\text{CH})$, 2035, 2001 $\nu(\text{C}\equiv\text{C})$ cm⁻¹. ¹H-NMR (CDCl₃): δ -0.51 (s, 6H, Me), 0.09 (s, 6H, Me), 2.33 (s, 1H, C $\equiv$ CH), 5.42 (m, 4H, CH₂) and 7.13–7.48 (m, 40H, Ph). ³¹P{¹H}-NMR (CDCl₃): δ -46.64. FABMS: m/z 1175 [M⁺], 1098 ([M–Ph]⁺) and 961 ([M–Cl–C $\equiv$ CSi(Me)₂–O–Si(Me)₂C $\equiv$ CH]⁺). UV–vis (CH₂Cl₂): λ_{max} ($\epsilon \times 10^{-4}$ dm³ mol⁻¹ cm⁻¹) 230 (1.2) and 255 sh (7.0). Anal. Found: C, 59.01; H, 5.08. Calc. for C₅₈H₅₇ClOOSi₂P₄: C, 59.25; H, 4.89%.

5. Crystallography

Single crystals of **1** and **2** suitable for X-ray crystallographic analyses were chosen and mounted on a glass fiber using epoxy resin. Crystal data and other experimental details are summarized in Table 3. The diffraction experiments were carried out at 293 K on a Bruker AXS SMART 1000 CCD area-detector diffractometer using graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å). At the end of data collection, no crystal decay was observed. The collected frames were processed with the software SAINT [17a], and an absorption correction was applied (SADABS) [17b] to the collected reflections. The structures were solved by direct methods and expanded by difference Fourier syntheses using the software SHELXTL [18]. Structure refinements were made on F^2 by the full-matrix least-squares technique. In each case, all the non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed in their ideal positions and not refined.

Table 3
Summary of crystal structure data for complexes **1** and **2**

	1	2
Empirical formula	C ₆₆ H ₅₅ ClP ₄ RuSi	C ₆₆ H ₅₅ ClOsP ₄ Si
Molecular weight	1136.59	1225.72
Crystal size (mm ³)	0.28 × 0.18 × 0.16	0.32 × 0.23 × 0.18
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>
Unit cell dimensions		
<i>a</i> (Å)	11.9173(15)	11.9087(6)
<i>b</i> (Å)	22.976(3)	22.9827(11)
<i>c</i> (Å)	41.205(5)	41.113(2)
α (°)		
β (°)	98.228(2)	98.2440(10)
γ (°)		
<i>U</i> (Å ³)	11166(2)	11136.1(10)
<i>D</i> _{calc} (g cm ⁻³)	1.352	1.462
<i>Z</i>	8	8
μ (Mo–K α) (mm ⁻¹)	0.506	2.516
<i>F</i> (000)	4688	4944
θ Range (°)	1.34–27.51	1.34–27.51
Reflections collected	65778	65816
Unique reflections	25145	25173
<i>R</i> _{int}	0.0636	0.0896
Observed reflections [<i>I</i> > 2 σ (<i>I</i>)]	12491	12071
No. of parameters	1316	1316
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0560, 0.1471	0.0463, 0.0852
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.1275, 0.1913	0.1294, 0.1139
Goodness-of-fit on <i>F</i> ²	0.718	0.763
Residual extrema in final difference map (e Å ⁻³)	0.826 to -0.799	0.867 to -1.071

6. Supplementary material

Crystallographic data (comprising hydrogen atom coordinates, thermal parameters and full tables of bond lengths and angles) for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 197039 and 197040. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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