Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Organometallic Chemistry 671 (2003) 27–34

Journal of Organo metallic Chemistry

www.elsevier.com/locate/jorganchem

σ-Acetylide complexes of ruthenium and osmium containing alkynylsilane ligands

Wai-Yeung Wong*, Chun-Kin Wong, Guo-Liang Lu

Department of Chemistry, Hong Kong Baptist University, Waterloo Road, Kowloon Tong, Hong Kong

Received 25 November 2002; received in revised form 2 January 2003; accepted 2 January 2003

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*-[$(dppm)_2ClMC{\equiv}CSi(Ph)_2C{\equiv}CH$] (M = Ru **1**; Os **2**) and *trans*-[$(dppm)_2ClMC{\equiv}CSi(Me)_2{-}O{-}Si(Me)_2C{\equiv}CH$] (M = Ru, **3**; Os, **4**) featuring different silyl units were prepared from a mixture of *cis*-[$M(dppm)_2Cl_2$] and $HC{\equiv}CSi(Ph)_2C{\equiv}CH$ or $HC{\equiv}CSi(Me)_2{-}O{-}Si(Me)_2C{\equiv}CH$ in the presence of $NaPF_6$ 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*-[$M(dppm)_2Cl_2$] (M = Ru, Os).

Keywords: Alkynyl complexes; Ruthenium; Osmium; Silane; Siloxane

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 incoporated into these π-conjugated systems [2]. Rigid-rod conjugated organometallic systems of the form $[-M(L)_xC{\equiv}C{-}R{-}C{\equiv}C-]_n$ 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

---

* Corresponding author. Tel.: +852-3411-7074; fax: +852-3411-7348.

E-mail address: rwywong@hkbu.edu.hk (W.-Y. Wong).

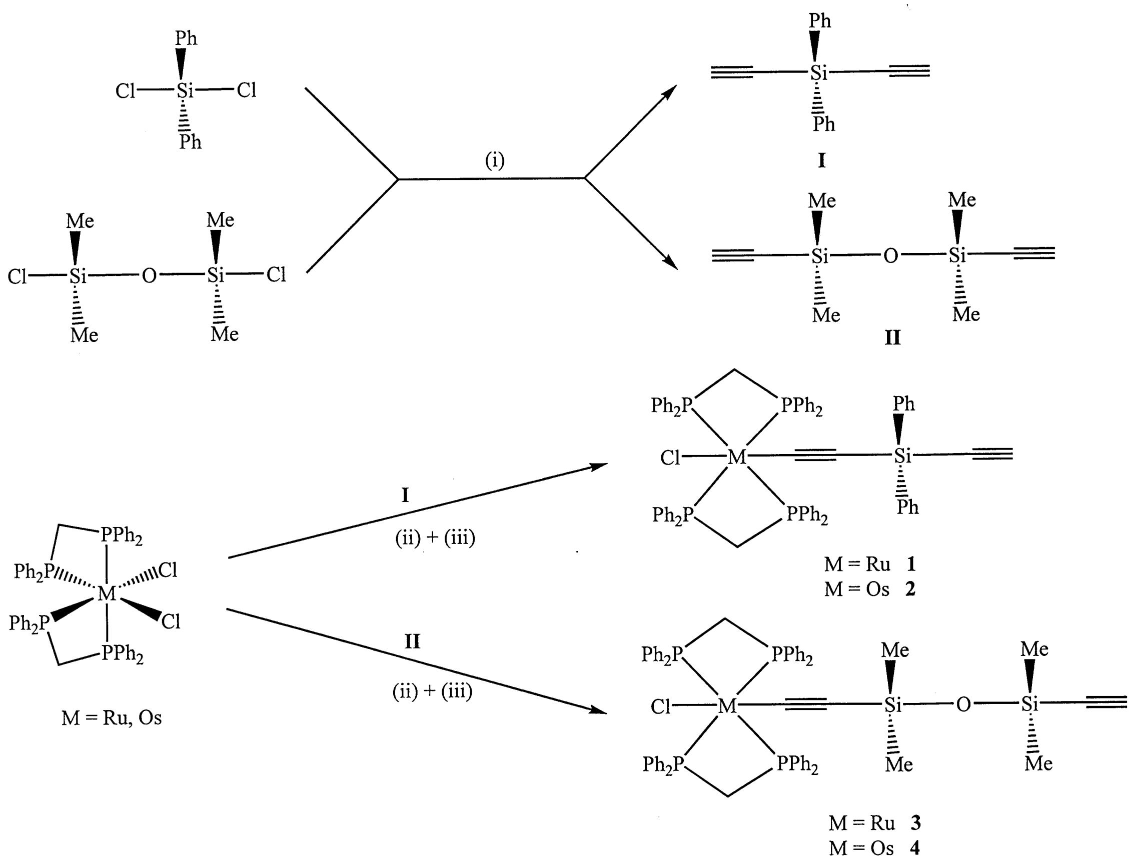
0022-328X/03/$ - see front matter © 2003 Elsevier Science B.V. All rights reserved.
doi:10.1016/S0022-328X(03)00003-2

and electrochemistry of a series of soluble Group 8 metal-containing alkynylsilanes and alkynyldisiloxanes. The crystal structures of *trans*-[$(dppm)_2ClMC{\equiv}CSi(Ph)_2C{\equiv}CH$] (M = Ru, Os) are presented which represent the first structurally characterized examples of ruthenium(II) and osmium(II) acetylide complexes linked by a $SiPh_2$ 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 $HC{\equiv}CMgCl$ with Ph_2SiCl_2 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*-[$(dppm)_2ClMC{\equiv}CSi(Ph)_2C{\equiv}CH$] (M = Ru **1**; Os **2**) and *trans*-[$(dppm)_2ClMC{\equiv}CSi(Me)_2{-}O{-}Si(Me)_2C{\equiv}CH$] (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*-[$M(dppm)_2Cl_2$] (M = Ru, Os) with one equivalent of **I** and two equivalents of $NaPF_6$ 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 $NaPF_6$–DBU route involving *cis*-[$M(dppm)_2Cl_2$] (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*-[$M(dppm)_2Cl_2$] 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 $^{31}P\{^1H\}$-NMR spectroscopies and positive FAB-mass spectra.



Scheme 1. (i) $HC{\equiv}CMgCl$, 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 ^{1}H-NMR resonances arising from the phenyl (for **I**) and methyl (for **II**) protons are clearly identified and each of them shows two strong ^{13}C-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 ^{1}H-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 CH_2 group in the bridging phosphines are apparent. Two well-defined methyl signals which are separated by about 0.6 ppm are evident in the ^{1}H-NMR spectra of **3** and **4** and each of them is integrated as six protons. Complexes **1**–**4** show room-temperature $^{31}P\{^1H\}$-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 $^{31}P\{^1H\}$ 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 CH_2Cl_2 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*-$[M(dppm)_2Cl_2]$ (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*-$[M(dppm)_2Cl_2]$ (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 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 $[(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)C{\equiv}CM(dppm)_2Cl]$ (M = Ru, Os) [12].

Table 1
Electrochemical data for complexes **1**–**4** and *cis*-$[M(dppm)_2Cl_2]$ (M = Ru, Os) in CH_2Cl_2

Complex	$E_{1/2}$ (V) [a]
1	0.11
2	−0.11
3	0.01
4	−0.21
cis-$[Ru(dppm)_2Cl_2]$	0.41
cis-$[Os(dppm)_2Cl_2]$	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.

2.4. Molecular structures

Yellow block-shaped crystals of good quality for **1** and **2** were obtained by allowing their respective solutions in CH_2Cl_2–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 sp^3-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* deposition 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

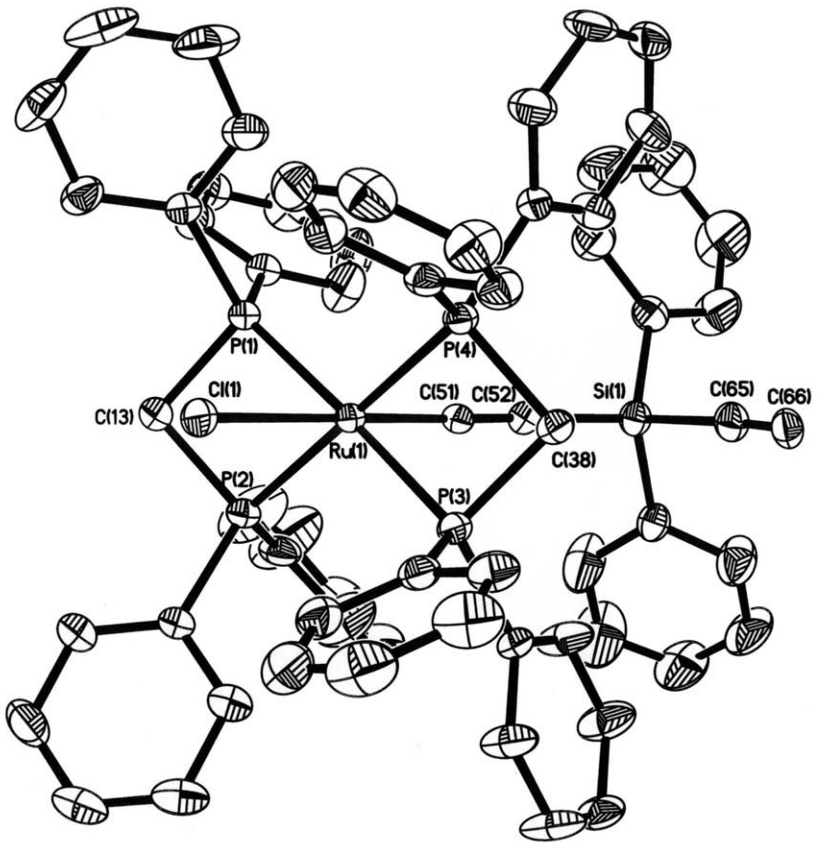


Fig. 1. A perspective view of one molecule of **1**, with thermal ellipsoids shown at the 25% probability level. Hydrogen atoms and all labels on phenyl carbon atoms were omitted for clarity.

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)$_2$ClMC≡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

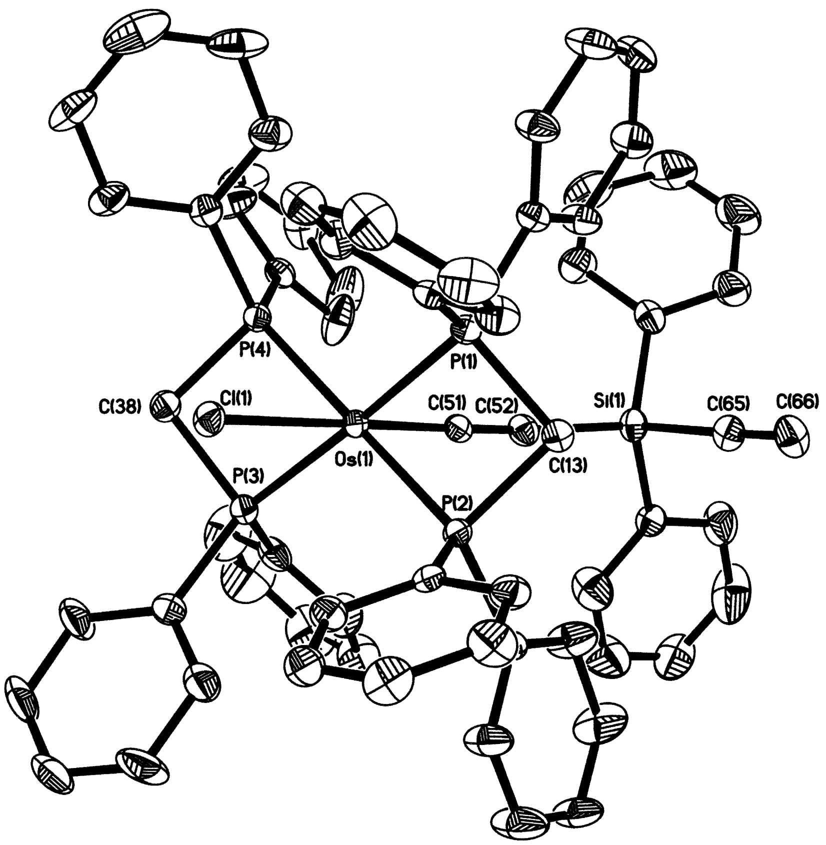


Fig. 2. A perspective view of one molecule of **2**, with thermal ellipsoids shown at the 25% probability level. Hydrogen atoms and all labels on phenyl carbon atoms were omitted for clarity.

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
Bond lengths				
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)
Bond angles				
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)$_2$Cl$_2$] were prepared by the reported procedures [16]. Infrared spectra were recorded as CH_2Cl_2 solutions in a CaF_2 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 $CDCl_3$ on a JEOL EX270 or a Varian Inova 400 MHz FT NMR spectrometer, with ^{1}H NMR chemical shifts quoted relative to $SiMe_4$ and $^{31}P\{^1H\}$ chemical shifts relative to an 85% H_3PO_4 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 electrode, a Pt-wire counter electrode and a Ag/AgNO$_3$ reference electrode (0.1 M in acetonitrile) was used. The solvent in all measurements was deoxygenated CH$_2$Cl$_2$ and the supporting electrolyte was 0.1 M [Bu$_4$N]PF$_6$. 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/AgNO$_3$).

4.2. Preparations of compounds

4.2.1. Synthesis of HC≡CSi(Ph)$_2$C≡CH (**I**)

A 0.5 M THF solution of HC≡CMgCl (50 cm^3, 25.0 mmol, Aldrich) was added dropwise into a solution of Ph$_2$SiCl$_2$ (2.5 g, 10.0 mmol) in the same solvent (5 cm^3) 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 Et$_2$O and filtered through a pad of Celite. The filtrate was concentrated and subjected to column separation on silica using a mixture of Et$_2$O 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 (CH$_2$Cl$_2$): 3263 ν(≡CH), 2032 ν(C≡C) cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ 2.75 (s, 2H, C≡CH), 7.39–7.48 (m, 6H, Ph) and 7.74–7.79 (m, 4H, Ph). ^{13}C-NMR (CDCl$_3$): δ 83.37 (C≡C), 97.36 (C≡*C*H), 128.19, 130.60, 131.25, 134.74 (Ph). FABMS: *m/z* 232 [M$^+$]. Anal. Found: C, 82.60; H, 5.02. Calc. for C$_{16}$H$_{12}$Si: C, 82.71; H, 5.21%.

4.2.2. Synthesis of HC≡CSi(Me)$_2$–O–Si(Me)$_2$C≡CH (**II**)

To a solution of ClSi(Me)$_2$–O–Si(Me)$_2$Cl (1.0 g, 5.0 mmol) in pre-dried THF (5 cm^3), 0.5 M THF solution of HC≡CMgCl (25 cm^3, 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 cm^3 under reduced pressure and then filtered through a short layer of silica to remove the Mg residue using pentane–Et$_2$O (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 (CH$_2$Cl$_2$): 3284 ν(≡CH) 2037 ν(C≡C) cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ 0.31 (s, 12H, Me) and 2.42 (s, 2H, C≡CH). ^{13}C-NMR (CDCl$_3$): δ 1.89 (Me), 88.96 (C≡C) and 92.33 (C≡*C*H). FABMS: *m/z* 182 [M$^+$]. Anal. Found: C, 52.26; H, 7.48. Calc. for C$_8$H$_{14}$OSi$_2$: C, 52.69; H, 7.74%.

4.2.3. Synthesis of *trans*-[(dppm)$_2$ClRuC≡CSi(Ph)$_2$C≡CH] (**1**)

A mixture of *cis*-[Ru(dppm)$_2$Cl$_2$] (47.0 mg, 0.05 mmol), HC≡CSi(Ph)$_2$C≡CH (**I**, 11.6 mg, 0.05 mmol) and NaPF$_6$ (16.8 mg, 0.10 mmol) in CH$_2$Cl$_2$ (40 cm^3) were stirred for 6 h at r.t. The resulting light yellow solution was filtered through a pad of Celite to remove any excess NaPF$_6$ 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 Et$_2$O and filtration through a short alumina column using pure Et$_2$O 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–CH$_2$Cl$_2$ solution at r.t., giving light yellow crystals in a pure form. IR (CH$_2$Cl$_2$): 3284 ν(≡CH), 2032, 1989 ν(C≡C) cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ 2.48 (s, 1H, C≡CH), 4.75 (m, 2H, CH$_2$), 4.92 (m, 2H, CH$_2$) and 6.96–7.57 (m, 50H, Ph). ^{31}P{^{1}H}-NMR (CDCl$_3$): δ −4.61. FABMS: *m/z* 1137 [M$^+$], 1102 ([M−Cl]$^+$), 1060 ([M−Ph]$^+$) and 871 ([M−Cl−C≡CSi(Ph)$_2$C≡CH]$^+$). UV–vis (CH$_2$Cl$_2$): λ_{max} ($\varepsilon \times 10^{-4}$ dm^3 mol^{-1} cm^{-1}) 230 (7.4) and 266 (5.0). Anal. Found: C, 69.50; H, 4.68. Calc. for C$_{66}$H$_{55}$ClP$_4$RuSi: C, 69.74; H, 4.88%.

4.2.4. Synthesis of *trans*-[(dppm)$_2$ClOsC≡CSi(Ph)$_2$C≡CH] (**2**)

To a solution of *cis*-[Os(dppm)$_2$Cl$_2$] (103 mg, 0.10 mmol) in 80 cm^3 of CH$_2$Cl$_2$, compound **I** (23.2 mg, 0.10 mmol) and NaPF$_6$ (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 Et$_2$O and then chromatographed on a short alumina column eluting with Et$_2$O, 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–CH$_2$Cl$_2$ solution at r.t. IR (CH$_2$Cl$_2$): 3284 ν(≡CH), 2031, 1983 ν(C≡C) cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ 2.46 (s, 1H, C≡CH), 5.27 (m, 2H, CH$_2$), 5.46 (m, 2H, CH$_2$) and 6.97–7.52 (m, 50H, Ph). ^{31}P{^{1}H}-NMR (CDCl$_3$): δ −46.21. FABMS: *m/z* 1226 [M$^+$], 1149 ([M−Ph]$^+$), 1037 ([M−Cl−2Ph]$^+$) and 960 ([M−Cl−C≡CSi(Ph)$_2$C≡CH]$^+$). UV–vis (CH$_2$Cl$_2$): λ_{max} ($\varepsilon \times 10^{-4}$ dm^3 mol^{-1} cm^{-1}) 230 (6.7) and 254 sh (3.8). Anal. Found: C, 64.44; H, 4.39. Calc. for C$_{66}$H$_{55}$ClP$_4$OsSi: C, 64.67; H, 4.52%.

4.2.5. Synthesis of *trans*-[(dppm)$_2$ClRuC≡CSi(Me)$_2$-O–Si(Me)$_2$C≡CH] (**3**)

cis-[Ru(dppm)$_2$Cl$_2$] (47.0 mg, 0.05 mmol) was added to HC≡CSi(Me)$_2$–O–Si(Me)$_2$C≡CH (**II**, 9.10 mg, 0.05 mmol) in CH$_2$Cl$_2$ (40 cm^3) in the presence of NaPF$_6$ (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 Et_2O 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 (CH_2Cl_2): 3284 ν(≡CH), 2034, 1993 ν(C≡C) cm^{-1}. ^1H-NMR ($CDCl_3$): δ −0.51 (s, 6H, Me), 0.11 (s, 6H, Me), 2.35 (s, 1H, C≡CH), 4.91 (m, 4H, CH_2) and 7.13–7.54 (m, 40H, Ph). $^{31}P\{^1H\}$-NMR ($CDCl_3$): 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 ($CH_2Cl_2$): λ_{max} ($\varepsilon \times 10^{-4}$ dm^3 mol^{-1} cm^{-1}) 230 (6.5) and 269 (3.8). Anal. Found: C, 63.98; H, 5.18. Calc. for $C_{58}H_{57}ClOP_4RuSi_2$: C, 64.11; H, 5.29%.

4.2.6. Synthesis of trans-[(dppm)$_2$ClOsC≡CSi(Me)$_2$–O–Si(Me)$_2$C≡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*-[$Os(dppm)_2Cl_2$] (51.5 mg, 0.05 mmol) and **II** (9.10 mg, 0.05 mmol) instead. IR (CH_2Cl_2): 3284 ν(≡CH), 2035, 2001 ν(C≡C) cm^{-1}. ^1H-NMR ($CDCl_3$): δ −0.51 (s, 6H, Me), 0.09 (s, 6H, Me), 2.33 (s, 1H, C≡CH), 5.42 (m, 4H, CH_2) and 7.13–7.48 (m, 40H, Ph). $^{31}P\{^1H\}$-NMR ($CDCl_3$): 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 ($CH_2Cl_2$): λ_{max} ($\varepsilon \times 10^{-4}$ dm^3 mol^{-1} cm^{-1}) 230 (1.2) and 255 sh (7.0). Anal. Found: C, 59.01; H, 5.08. Calc. for $C_{58}H_{57}ClOOsP_4Si_2$: 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 (λ = 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 SHELTXL [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	$C_{66}H_{55}ClP_4RuSi$	$C_{66}H_{55}ClOsP_4Si$
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	$P2_1/n$	$P2_1/c$
Unit cell dimensions		
a (Å)	11.9173(15)	11.9087(6)
b (Å)	22.976(3)	22.9827(11)
c (Å)	41.205(5)	41.113(2)
α (°)		
β (°)	98.228(2)	98.2440(10)
γ (°)		
U (Å^3)	11166(2)	11136.1(10)
D_{calc} (g cm^{-3})	1.352	1.462
Z	8	8
μ (Mo-K_α) (mm^{-1})	0.506	2.516
F(000)	4688	4944
θ Range (°)	1.34–27.51	1.34–27.51
Reflections collected	65778	65816
Unique reflections	25145	25173
R_{int}	0.0636	0.0896
Observed reflections $[I > 2\sigma(I)]$	12491	12071
No. of parameters	1316	1316
R_1, wR_2 $[I > 2\sigma(I)]$	0.0560, 0.1471	0.0463, 0.0852
R_1, wR_2 (all data)	0.1275, 0.1913	0.1294, 0.1139
Goodness-of-fit on F^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).

Acknowledgements

Financial support from the Hong Kong Research Grants Council (HKBU 2054/02P) is gratefully acknowledged.

References

[1] (a) N. Hagihara, K. Sonogashira, S. Takahashi, Adv. Polym. Sci. 41 (1981) 149;

(b) S. Takahashi, N. Hagihara, K. Sonogashira, Macromolecules 11 (1978) 1063.

[2] (a) P. Nguyen, P. Gómez-Elipe, I. Manners, Chem. Rev. 99 (1999) 1515 (and references therein);
(b) R.P. Kingsborough, T.M. Swager, Prog. Inorg. Chem. 48 (1999) 123 (and references therein);
(c) R.J. Puddephatt, Chem. Commun. (1998) 1055 and references therein;
(d) V.W.-W. Yam, Chem. Commun. (2001) 789 and references therein;
(e) N.J. Long, A.J. Martin, R. Vilar, A.J.P. White, D.J. Williams, M. Younus, Organometallics 18 (1999) 4261;
(f) M. Younus, A. Köhler, S. Cron, N. Chawdhury, M.R.A. Al-Mandhary, M.S. Khan, J. Lewis, N.J. Long, R.H. Friend, P.R. Raithby, Angew. Chem. Int. Ed. Engl. 37 (1998) 3036;
(g) C.J. Adams, S.L. James, P.R. Raithby, Chem. Commun. (1997) 2155;
(h) W.-Y. Wong, K.-H. Choi, G.-L. Lu, Z. Lin, Organometallics 21 (2002) 4475;
(i) W.-Y. Wong, K.-H. Choi, G.-L. Lu, J.-X. Shi, P.-Y. Lai, S.-M. Chan, Z. Lin, Organometallics 20 (2001) 5446.

[3] (a) M.S. Khan, A.K. Kakkar, N.J. Long, J. Lewis, P. Raithby, P. Nguyen, T.B. Marder, F. Wittmann, R.H. Friend, J. Mater. Chem. 4 (1994) 1227;
(b) K. Onitsuka, Y. Harada, F. Takei, S. Takahashi, Chem. Commun. (1998) 643;
(c) W.-Y. Wong, K.-H. Choi, G.-L. Lu, J.-X. Shi, Macromol. Rapid Commun. 22 (2001) 461;
(d) W.-Y. Wong, G.-L. Lu, K.-H. Choi, J.-X. Shi, Macromolecules 35 (2002) 3506.

[4] (a) N. Chawdhury, A. Köhler, R.H. Friend, M. Younus, N.J. Long, P.R. Raithby, J. Lewis, Macromolecules 31 (1998) 722;
(b) J.S. Wilson, N. Chawdhury, M.R.A. Al-Mandhary, M. Younus, M.S. Khan, P.R. Raithby, A. Köhler, R.H. Friend, J. Am. Chem. Soc. 123 (2001) 9412;
(c) M.S. Khan, M.R.A. Al-Mandhary, M.K. Al-Suti, A.K. Hisahm, P.R. Raithby, B. Ahrens, M.F. Mahon, L. Male, E.A. Marseglia, E. Tedesco, R.H. Friend, A. Köhler, N. Feeder, S.J. Teat, J. Chem. Soc. Dalton Trans. (2002) 1358;
(d) W.-Y. Wong, S.-M. Chan, K.-H. Choi, K.-W. Cheah, W.-K. Chan, Macromol. Rapid Commun. 21 (2000) 453;
(e) N. Chawdhury, A. Köhler, R.H. Friend, W.-Y. Wong, M. Younus, P.R. Raithby, J. Lewis, T.C. Corcoran, M.R.A. Al-Mandhury, M.S. Khan, J. Chem. Phys. 110 (1999) 4963.

[5] (a) B.F.G. Johnson, A.K. Kakkar, M.S. Khan, J. Lewis, A.E. Dray, R.H. Friend, F. Wittmann, J. Mater. Chem. 1 (1991) 485;
(b) T.B. Peters, J.C. Bohling, A.M. Arif, J.A. Gladysz, Organometallics 18 (1999) 3261;
(c) W. Mohr, J. Stahl, F. Hampel, J.A. Gladysz, Inorg. Chem. 40 (2001) 3263;
(d) R. Dembinski, T. Bartik, M. Jeager, J.A. Gladysz, J. Am. Chem. Soc. 122 (2000) 810;
(e) M.I. Bruce, B.C. Hall, B.D. Kelly, P.J. Low, B.W. Skelton, A.H. White, J. Chem. Soc. Dalton Trans. (1999) 3719;
(f) W. Lu, H.-F. Xiang, N. Zhu, C.-M. Che, Organometallics 21 (2002) 2343;
(g) S. Kheradmandan, K. Heinze, H.W. Schmalle, H. Berke, Angew. Chem. Int. Ed. 38 (1999) 2270;
(h) K.-T. Wong, J.-M. Lehn, S.-M. Peng, G.-H. Lee, Chem. Commun. (2000) 2259.

[6] (a) T. Kuhnen, M. Stradiotto, R. Ruffolo, D. Ulbrich, M. McGlinchey, M.A. Brook, Organometallics 16 (1997) 5048;
(b) R.J.P. Corriu, N. Devylder, C. Guérin, B. Henner, A. Jean, Organometallics 13 (1994) 3194;
(c) H. Lang, S. Weinmann, I.Y. Wu, T. Stein, A. Jacobi, G. Huttner, J. Organomet. Chem. 575 (1999) 133.

[7] (a) R. Fáber, A. Stasko, O. Nuyken, Macromol. Chem. Phys. 201 (2000) 2257;
(b) G.G. Malliaras, J.K. Herrema, J. Wildeman, R.H. Wieringa, R.E. Gill, S.S. Lampoura, G. Hadziioannou, Adv. Mater. 5 (1993) 721;
(c) A. Hilberer, P.F. van Hutten, J. Wildeman, G. Hadziioannou, Macromol. Chem. Phys. 198 (1997) 2211;
(d) M. Remmers, M. Schulze, G. Wegner, Macromol. Rapid Commun. 17 (1996) 239;
(e) A.G. Martínez, J.O. Barcina, A.de F. Cerezo, A.-D. Schlüter, J. Frahn, Adv. Mater. 7 (1995) 1568;
(f) Q. Pei, Y. Yang, Chem. Mater. 7 (1995) 1568.

[8] (a) W.-Y. Wong, G.-L. Lu, K.-F. Ng, K.-H. Choi, Z. Lin, J. Chem. Soc. Dalton Trans. (2001) 3250;
(b) P. Li, B. Ahrens, K.-H. Choi, M.S. Khan, P.R. Raithby, P.J. Wilson, W.-Y. Wong, Cryst. Eng. Comm. 4 (2002) 405;
(c) W.-Y. Wong, G.-L. Lu, K.-F. Ng, C.-K. Wong, K.-H. Choi, J. Organomet. Chem. 637–639 (2001) 159;
(d) H. Zhang, A.W.M. Lee, W.-Y. Wong, M.S.M. Yuen, J. Chem. Soc. Dalton Trans. (2000) 3675;
(e) A.W.M. Lee, A.B.W. Yeung, M.S.M. Yuen, H. Zhang, X. Zhao, W.-Y. Wong, Chem. Commun. (2000) 75.

[9] (a) W.-Y. Wong, A.W.M. Lee, C.-K. Wong, G.-L. Lu, H. Zhang, T. Mo, K.T. Lam, New J. Chem. (2002) 354;
(b) W.-Y. Wong, C.-K. Wong, G.-L. Lu, K.-W. Cheah, J.-X. Shi, Z. Lin, J. Chem. Soc. Dalton Trans. (2002) 4578.

[10] W.E. Davidsohn, M.C. Henry, J. Organomet. Chem. 5 (1966) 29.

[11] (a) P. Haquette, N. Pirio, D. Touchard, L. Toupet, P.H. Dixneuf, J. Chem. Soc. Chem. Commun. (1993) 163;
(b) D. Touchard, C. Morice, V. Cadierno, P. Haquette, L. Toupet, P.H. Dixneuf, J. Chem. Soc. Chem. Commun. (1994) 859;
(c) A.J. Hodge, S.L. Ingham, A.K. Kakkar, M.S. Khan, J. Lewis, N.J. Long, D.G. Parker, P.R. Raithby, J. Organomet. Chem. 488 (1995) 205;
(d) M. Younus, N.J. Long, P.R. Raithby, J. Lewis, J. Organomet. Chem. 570 (1998) 55;
(e) J. Lewis, P.R. Raithby, W.-Y. Wong, J. Organomet. Chem. 556 (1998) 219.

[12] M.C.B. Colbert, S.L. Ingham, J. Lewis, N.J. Long, P.R. Raithby, J. Chem. Soc. Dalton Trans. (1994) 2215.

[13] N.J. Long, A.J. Martin, A.J.P. White, D.J. Williams, M. Fontani, F. Laschi, P. Zanello, J. Chem. Soc. Dalton Trans. (2000) 3387.

[14] J.P. Glusker, M. Lewis, M. Rossi, Crystal Structure Analysis for Chemists and Biologists, Ch. 13, VCH, New York, 1994, p. 548.

[15] W.L.F. Armarego, D.D. Perrin, Purification of Laboratory Chemicals, 4th ed., Butterworth-Heinemann, Guildford, UK, 1996.

[16] B.P. Sullivan, T.J. Meyer, Inorg. Chem. 21 (1982) 1037.

[17] (a) SAINT, Reference Manual, Siemens Energy and Automation, Madison, WI, 1994–1996;
(b) G.M. Sheldrick, SADABS, Empirical Absorption Correction Program, University of Göttingen, Göttingen, Germany, 1997.

[18] G.M. Sheldrick, SHELXTL™, Reference Manual, ver. 5.1, Madison, WI, 1997.