ELSEVIER

Journal of Organometallic Chemistry 629 (2001) 7–18

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Synthesis, structure and redox behaviour of tethered arene–ruthenium(II) complexes

Martin A. Bennett [a,*], Alison J. Edwards [a], Joanne R. Harper [a,b], Tetyana Khimyak [b], Anthony C. Willis [a]

[a] *Research School of Chemistry, Australian National University, Canberra ACT 0200, Australia*
[b] *Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK*

Received 11 January 2001; accepted 5 March 2001

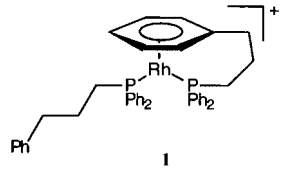
Abstract

Tethered arene–ruthenium complexes $[RuCl_2\{\eta^1{:}\eta^6\text{-}Me_2P(CH_2)_3C_6H_5\}]$, $[RuCl_2\{\eta^1{:}\eta^6\text{-}Ph_2PCH_2SiMe_2C_6H_5\}]$ and $[RuCl_2\{\eta^1{:}\eta^6\text{-}Ph_2P(CH_2)_3(aryl)\}]$ (aryl = 2,4,6-$C_6H_2Me_3$, C_6Me_5) have been prepared by thermal displacement of methyl *o*-toluate from the appropriate P-donor derivatives of $[RuCl_2(\eta^6\text{-}1,2\text{-}MeC_6H_4CO_2Me)]_2$ and their structures determined by X-ray studies. The tethered complexes undergo reversible one-electron oxidation by cyclic voltammetry; the half-wave potentials are in the range 1.10–1.34 V versus Ag | AgCl and decrease with increasing methyl substitution on the arene.

Keywords: Arene; Phosphine; Chelating ligand; Ruthenium; Electrochemistry

1. Introduction

Much attention has been devoted to the chemistry of tethered or strapped cyclopentadienyl complexes in which one or more hydrogen atoms of the ring are replaced by a connecting group to a pendant donor atom that is capable of binding to the metal atom [1–3]. Metal–arene complexes are less numerous and, in general, less stable than their metal-cyclopentadienyl counterparts, in part because the neutral arene is more readily lost from the coordination sphere. Thus, tethered arene ligands offer the possibility of stabilising arene complexes for a range of metals and oxidation states. Mirkin et al. [4–6] showed that the ligands $Ph_2PCH_2CH_2XPh$ (X = CH_2, O) form tethered arene–rhodium(I) cations such as **1**, which undergo reversible electrochemical one-electron oxidation, presumably to the corresponding arene–rhodium(II) dications; the latter are stabilised kinetically compared to their unstrapped counterparts.

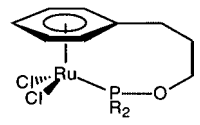


1

We are interested in extending these studies to strapped arene–ruthenium(II) complexes, from which it might be possible to generate, by one-electron oxidation, paramagnetic arene–ruthenium(III) ($4d^5$) cations analogous to the chelation-stabilised alkene- and alkyne-complexes of bis(acetylacetonato)ruthenium(III), such as $[Ru(acac)_2(o\text{-}CH_2{=}CHC_6H_4NMe_2)]^+$ [7] and $[Ru(acac)_2(PhC{\equiv}CC_6H_4NMe_2)]^+$ [8]. During the progress of our work, a number of reports on tethered arene–ruthenium complexes have appeared in which a variety of preparative methods have been used. Smith and Wright [9] reported that thermal displacement of *p*-cymene (cym, 1,4-$MeC_6H_4CHMe_2$) from the P-coordinated derivative $[RuCl_2\{Ph_2P(CH_2)_3C_6H_5\}(\eta^6\text{-cym})]$ occurred in chlorobenzene at 130°C to give the tethered complex $[RuCl_2\{\eta^1{:}\eta^6\text{-}Ph_2P(CH_2)_3C_6H_5\}]$ in 50% yield; a higher yield (75%) was achieved at the cost of preparative convenience by carrying out exhaustive bulk anodic oxidation of the starting P-complex. Subsequently,

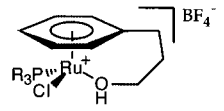
* Corresponding author. Tel.: +61-2-61253639; fax: +61-2-61253216.
E-mail address: bennett@rsc.anu.edu.au (M.A. Bennett).

0022-328X/01/$ - see front matter
PII: S0022-328X(01)00801-4



R = Ph, *i*-Pr

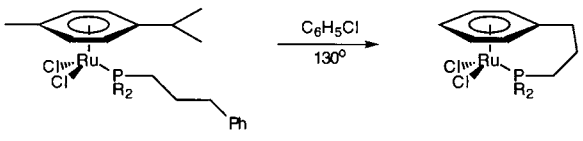
2



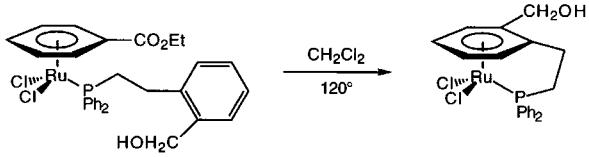
R = Ph, Et

3

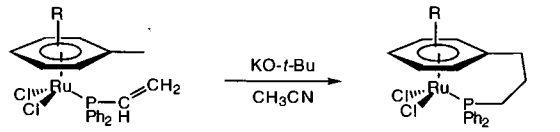
Noels et al. [10,11] and Fürstner et al. [12] independently have obtained tethered complexes such as $[RuCl_2\{\eta^1{:}\eta^6\text{-}Cy_2P(CH_2)_3C_6H_5\}]$ in 80–90% yield by heating the *p*-cymene P-donor complex in chlorobenzene (Eq. (1)). Therrien, Ward and co-workers have prepared tethered complexes containing the benzyl alcohols 1,2- or 1,3-$C_6H_4(CH_2OH)(CH_2CH_2PPh_2)$ by displacement of ethyl benzoate from its ruthenium(II) complex $[RuCl_2(\eta^6\text{-}C_6H_5CO_2Et)]_2$ [13] (Eq. (2)) and have used the same methodology to prepare tethered arene complexes of ruthenium(II) that are configurationally stable at the metal centre [14,15]. Rieger et al. have also employed the ethyl benzoate complex as a precursor to tethered arene–ruthenium(II) complexes such as $[RuCl_2\{\eta^1{:}\eta^6\text{-}R_2P(CH_2)_2C_6H_5\}]$ (R = Ph, Cy) [16]. Silver ion-promoted abstraction of chloride ion from ligand derivatives of the dimer $[RuCl_2\{\eta^6\text{-}C_6H_5(CH_2)_3OH\}]_2$ has been used to prepare tethered complexes such as **2** and **3** [17]. Finally, in a recently reported general method for preparing $(CH_2)_3$-strapped arene complexes of ruthenium(II), the diphenylvinylphosphine adduct of a methyl-substituted arene–ruthenium(II) complex undergoes a base-promoted Michael addition or hydroalkylation reaction (Eq. (3)) [18]. A preliminary report of our work in this field was presented at the most recent International Conference on Coordination Chemistry [19].



R = Ph, Cy (1)



(2)



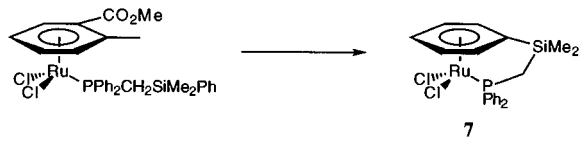
R = H, *p*-Me, *p*-CHMe$_2$, 3,5-Me$_2$, Me$_5$ (3)

2. Results and discussion

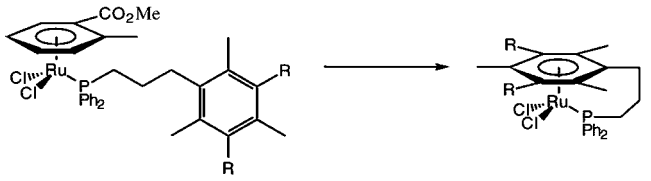
The compound $C_6H_5(CH_2)_3PPh_2$ has been made previously by the reaction of 1-chloro-3-phenylpropane with $KPPh_2$ [4,5] or of 1-bromo-3-phenylpropane with $LiPPh_2$ [9]. We employed the alternative reaction of Ph_2PCl with the Grignard reagent derived from 1-bromo-3-phenylpropane and extended this procedure to prepare $C_6H_5(CH_2)_3PMe_2$ by use of Me_2PCl in place of Ph_2PCl. Similarly, we synthesised the compounds $C_6Me_5(CH_2)_3PPh_2$, 2,4,6-$Me_3C_6H_2(CH_2)_3PPh_2$ and $C_6H_5SiMe_2CH_2PPh_2$ from the reactions of Ph_2PCl with THF solutions of the Grignard reagents derived from $C_6Me_5(CH_2)_3Br$, 2,4,6-$Me_3C_6H_2(CH_2)_3Br$ and $C_6H_5SiMe_2CH_2Cl$, respectively. Yields were generally between 40 and 80%; in the last case, some diphenylmethylphosphine was formed as a results of Si–CH_2 bond cleavage and was separated from $C_6H_5SiMe_2CH_2PPh_2$ by vacuum sublimation.

In agreement with Therrien, Ward et al. [13–15], we find that the $RuCl_2$ complex of an aromatic ester, in our case the methyl *o*-toluate complex $[RuCl_2(\eta^6\text{-}1,2\text{-}MeC_6H_4CO_2Me)]_2$ (**4**) [20], is a suitably labile precursor to tethered arene complexes. It reacts with the ligands mentioned above in a 1:2 mole ratio in dichloromethane at room temperature to give quantitatively the corresponding P-bonded adducts $[RuCl_2(\eta^6\text{-}1,2\text{-}MeC_6H_4CO_2Me)(L)]$, which lose the methyl *o*-toluate on heating in dichloromethane or dichloromethane-THF at 120°C for 24–72 h (Eqs. (4–6)). The tethered complexes can be isolated after chromatography of the crude reaction mixtures in yields ranging from 60 to 80% for $C_6H_5(CH_2)_3PR_2$ (R = Ph (**5**), Me (**6**)) and $C_6H_5SiMe_2CH_2PPh_2$ (**7**), through ca. 18% for 2,4,6-$Me_2C_6H_3(CH_2)_3PPh_2$ (**8**), to ca. 7% for $C_6Me_5(CH_2)_3PPh_2$ (**9**). In the cases of **5**–**7** it is not necessary to isolate the initially formed P-donor adducts; they can be generated in situ from complex **4** and the ligand at room temperature.

R = Ph (**5**), Me (**6**) (4)



7 (5)



R = H (**8**), Me (**9**)

(6)

The formation of the tethered complex $[RuCl_2\{\eta^1:\eta^6\text{-}Ph_2P(CH_2)_3C_6H_5\}]$ (**5**) seems to be favoured by the presence of a small amount of THF, which slightly increases the yield and shortens the reaction time from 72 to 36 h. In the case of $C_6Me_5(CH_2)_3PPh_2$, the yield of **9** can be increased to 35% by the use of di-*n*-butyl ether in place of dichloromethane. This behaviour is reminiscent of the effect of ether solvents in the synthesis of (η^6-arene) chromium tricarbonyls [21,22]. Attempts to form the tethered complexes **5** and **6** by UV-irradiation of solutions of the η^6-methyl *o*-toluate complexes at room temperature led only to decomposition, with loss of the aromatic ester and formation of the phosphine oxide.

We were unable to reproduce Smith and Wright's preparation of **5** from the *p*-cymene complex $[RuCl_2(\eta^6\text{-}1,4\text{-}MeC_6H_4CHMe_2)\{Ph_2P(CH_2)_3C_6H_5\}]$ in chlorobenzene at 130°C [9], and use of dichloromethane containing THF at 120°C was also unsuccessful. When the adduct was heated in an NMR tube at 130°C in C_6D_5Cl, displacement of the *p*-cymene was observed but the ^{31}P-NMR singlet of the tethered complex at δ 22.2 was not present. There was a broad ^{31}P-NMR singlet at δ 29.6 and the ^2H-NMR spectrum showed a doublet at δ 5.33 ($J = 6.5$ Hz) and a multiplet at δ 6.46. These can be attributed to an intermediate $[RuCl_2(\eta^6\text{-}C_6D_5Cl)\{Ph_2P(CH_2)_3C_6H_5\}]$ which, however, decomposed on attempted isolation.

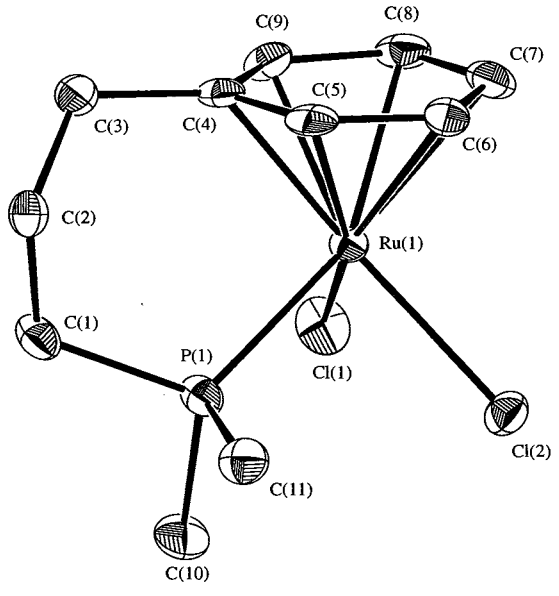


Fig. 1. ORTEP drawing of **6** with 30% probability thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

The NMR spectra of the methyl *o*-toluate complexes show, in addition to resonances characteristic of the CO_2Me group, resonances due to the four protons of the coordinated arene ring in the region δ 4.2–6.2 and corresponding resonances due to the aromatic carbon atoms in the region δ 76–115. The P-methyl groups in $[RuCl_2(\eta^6\text{-}1,2\text{-}MeC_6H_4CO_2Me)\{Me_2P(CH_2)_3C_6H_5\}]$ are inequivalent because of the planar chirality of the η^6-methyl *o*-toluate [20] and appear as two doublets in the $^{13}C\{^1H\}$- and ^1H-NMR spectra. The IR spectra of the complexes contain typical $\nu(CO_2)$ ester absorptions at ca. 1720 and 1260 cm^{-1}, and one strong, broad band centred at 280–290 cm^{-1}, which presumably contains the two expected ν(RuCl) absorptions.

The ^1H- and $^{13}C\{^1H\}$-NMR spectra of the tethered complexes provide clear evidence for the coordination of the arene group of the P-donor ligands. Thus, the ^1H spectra of **5**, **6** and **7** contain three resonances in a 2:2:1 intensity ratio due to the C_6H_5 protons in the region δ 4.9–6.3. The low frequency shifts are mirrored in the $^{13}C\{^1H\}$-NMR spectra, which show four arene resonances in the region δ 80–100. Similarly, in complex **8**, the equivalent mesityl aromatic protons appear as a singlet at δ 5.25, cf. δ 6.69 in the precursor methyl *o*-toluate complex. The far IR spectra of **5**, **6**, **7** and **9** show the expected two strong ν(RuCl) bands at ca. 300 and 280 cm^{-1}. The singlet in the $^{31}P\{^1H\}$-NMR spectra of each of the tethered complexes containing PPh_2 groups appears in the region δ 22–29, the chemical shift being similar to, though distinguishable from, that of the precursor methyl *o*-toluate complexes. The ^{31}P chemical shifts of the methyl *o*-toluate and tethered complexes of $C_6H_5(CH_2)_3PMe_2$ are also similar (δ 15.7 and 13.7, respectively).

An indication of the stability of the tethered complexes is that they all show parent ions in their electron-impact (EI) or fast-atom-bombardment (FAB) mass spectra. In contrast, for the methyl *o*-toluate complexes, the highest mass ion is usually $[M - Cl]^+$ or, in the case of $C_6H_5SiMe_2CH_2PPh_2$, $[M - \text{arene}]^+$.

The molecular structures of the tethered $RuCl_2$ complexes **6**–**9** have been determined by single crystal X-ray analysis and are shown with atom labelling in Figs. 1–4, respectively. Selected bond distances and angles are in Tables 1–4. The complexes show the expected half-sandwich geometry, the Ru–P, Ru–Cl and Ru–C(arene) distances being similar to those previously reported for related tethered complexes such as **5** [9,18] and $[RuCl_2\{\eta^1:\eta^6\text{-}Cy_2P(CH_2)_3C_6H_5\}]$ [12]. In all the complexes containing aryl$(CH_2)_3PR_2$, the

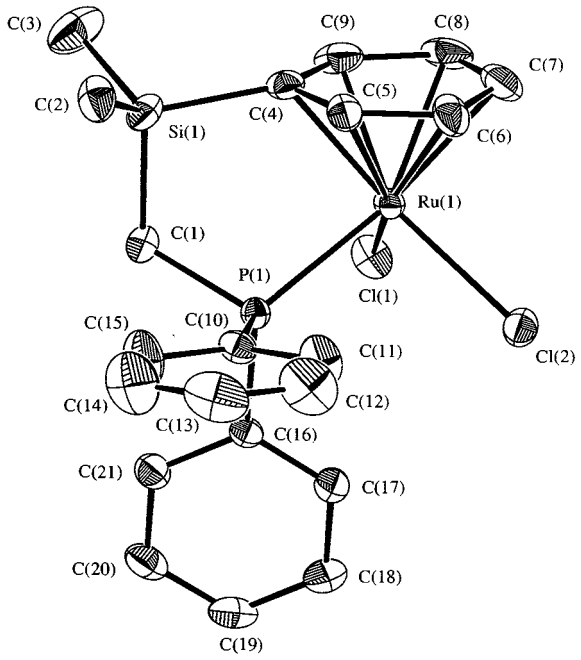


Fig. 2. ORTEP drawing of **7** with 30% probability thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

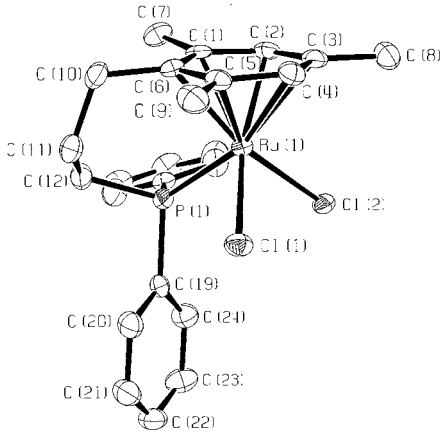


Fig. 3. ORTEP drawing of **8** with 50% probability thermal ellipsoids. Hydrogen atoms, labels C(13)–C(18) and the solvent molecule (CH_2Cl_2) have been omitted for clarity.

trimethylene strap allows simultaneously a close to regular trigonal geometry for the $RuCl_2P$ fragment and coplanarity of the benzylic carbon atom with the carbon atoms of the attached arene, without distortion of bond lengths or angles in the tether. In contrast, in **7** the presence of the two-atom strap causes a bending of the Si–C(C_6H_5) bond out of the aromatic plane by ca. 14°. In complexes **6**, **7** and **9**, the trigonal $RuCl_2P$ fragment adopts a staggered arrangement relative to the carbon atoms of the aromatic ring, whereas in complex **8** it lies about half-way between the eclipsed and staggered conformations. Although the complexed aromatic rings in **6**–**9** are almost planar, the Ru–C(arene) distances *trans* to the P-donor (2.24–2.28 Å) are significantly greater than those *trans* to the Ru–Cl bonds (2.16–2.21 Å), reflecting the relative *trans*-influences of Cl and PR_3; the same effect has been observed for the non-tethered complex [$RuCl_2(PMePh_2)(\eta^6$-$C_6H_6)$] [23].

All the tethered complexes show fully reversible, one-electron, $Ru^{II,III}$ redox couples in CH_2Cl_2 (Table 5). Our $E_{1/2}$ value for **5** (+ 1.32 V vs Ag | AgCl) seems to

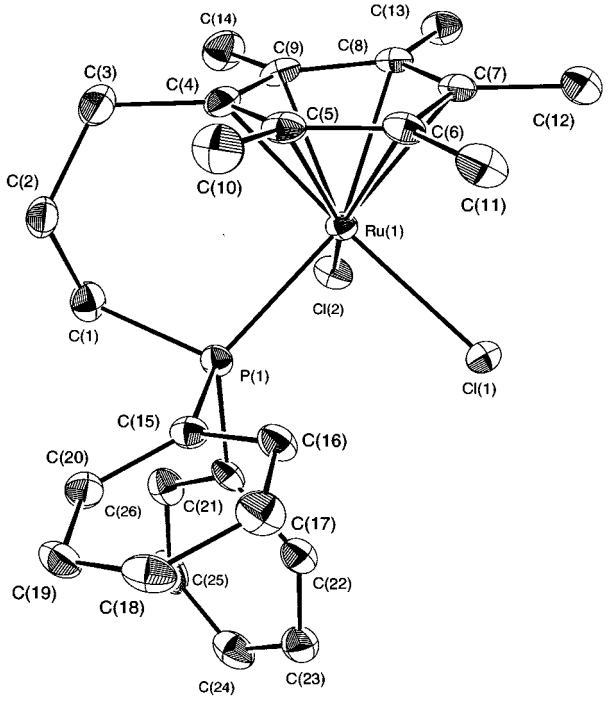


Fig. 4. ORTEP drawing of **9** with 50% probability thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

Table 1
Selected bond lengths (Å) and angles (°) for **6**

Molecule 1		Molecule 2	
Ru(1)–Cl(1)	2.405(2)	Ru(2)–Cl(3)	2.415(2)
Ru(1)–Cl(2)	2.421(2)	Ru(2)–Cl(4)	2.421(3)
Ru(1)–P(1)	2.322(3)	Ru(2)–P(2)	2.303(2)
Ru(1)–C(4)	2.193(8)	Ru(2)–C(15)	2.194(9)
Ru(1)–C(5)	2.185(9)	Ru(2)–C(16)	2.189(9)
Ru(1)–C(6)	2.181(9)	Ru(2)–C(17)	2.158(9)
Ru(1)–C(7)	2.257(9)	Ru(2)–C(18)	2.253(9)
Ru(1)–C(8)	2.257(9)	Ru(2)–C(19)	2.24(1)
Ru(1)–C(9)	2.170(9)	Ru(2)–C(20)	2.182(9)
P–C	1.79(1)–1.82(1)	P–C	1.79(1)–1.82(1)
C–C(arene)	1.36(1)–1.42(1)	C–C(arene)	1.36(2)–1.43(1)
Cl(1)–Ru(1)–Cl(2)	87.68(9)	Cl(3)–Ru(2)–Cl(4)	87.8(1)
Cl(1)–Ru(1)–P(1)	89.34(9)	Cl(3)–Ru(2)–P(2)	89.17(8)
Cl(2)–Ru(1)–P(1)	83.83(9)	Cl(4)–Ru(2)–P(2)	84.72(9)

Table 2
Selected bond lengths (Å) and angles (°) for **7**

Ru(1)–Cl(1)	2.4050(7)	Ru(1)–Cl(2)	2.4159(7)
Ru(1)–P(1)	2.3526(7)	Ru(1)–C(4)	2.180(2)
Ru(1)–C(5)	2.180(2)	Ru(1)–C(6)	2.193(3)
Ru(1)–C(7)	2.250(3)	Ru(1)–C(8)	2.246(3)
Ru(1)–C(9)	2.145(3)	P–C	1.818(2)
			–1.831(2)
Si–C	1.847(3)–1.902(3)	C–C(arene)	1.405(4)
			–1.436(4)
Cl(1)–Ru(1)–Cl(2)	89.90(3)	Cl(1)–Ru(1)–P(1)	84.26(2)
Cl(2)–Ru(1)–P(1)	94.29(3)		

Table 3
Selected bond lengths (Å) and angles (°) for **8**

Ru(1)–Cl(1)	2.4159(10)	Ru(1)–Cl(2)	2.4425(10)
Ru(1)–P(1)	2.3230(10)	Ru(1)–C(1)	2.212(4)
Ru(1)–C(2)	2.183(4)	Ru(1)–C(3)	2.282(4)
Ru(1)–C(4)	2.262(4)	Ru(1)–C(5)	2.203(4)
Ru(1)–C(6)	2.200(4)	P–C	1.828(4)–1.845(4)
C–C(arene)	1.393(6)–1.439(6)		
Cl(1)–Ru(1)–Cl(2)	87.52(4)	Cl(1)–Ru(1)–P(1)	86.35(4)
Cl(2)–Ru(1)–P(1)	90.34(4)		

Table 4
Selected bond lengths (Å) and angles (°) for **9**

Ru(1)–Cl(1)	2.4016(12)	Ru(1)–Cl(2)	2.4163(12)
Ru(1)–P(1)	2.2995(14)	Ru(1)–C(4)	2.203(5)
Ru(1)–C(5)	2.249(5)	Ru(1)–C(6)	2.201(5)
Ru(1)–C(7)	2.284(5)	Ru(1)–C(8)	2.285(5)
Ru(1)–C(9)	2.182(5)	P–C	1.822(5)–1.834(5)
C–C(arene)	1.394(7)–1.454(7)		
Cl(1)–Ru(1)–Cl(2)	88.58(4)	Cl(1)–Ru(1)–P(1)	88.83(5)
Cl(2)–Ru(1)–P(1)	82.29(4)		

be in fair agreement with the values reported by Smith and Wright [9] (+ 1.34 V vs SCE) and by Ghebreyessus and Nelson [18] (+ 0.74 V vs ferrocene/ferrocenium), though exact comparison is difficult because we used a non-aqueous Ag | AgCl reference electrode. The potentials are reduced by increasing methyl substitution in the arene ring, as observed also in tethered arene–rhodium and non-tethered arene–ruthenium systems [6,24], and by replacement of PPh_2 by the more electron-donating PMe_2. The potentials are significantly greater than those of analogous unstrapped complexes, e.g. we find $E_{1/2}$ versus Ag | AgCl for [$RuCl_2(\eta^6$-$C_6Me_6)(PMe_3)$] to be + 1.05 V (similar values for related complexes have been reported [24]), indicating that although the tether may inhibit arene dissociation it also tends to stabilise Ru^{II} relative to Ru^{III}. The potentials in our complexes are clearly too high to permit isolation of the derived arene–ruthenium(III) cations and we are currently investigating the preparation of more electron-rich derivatives, such as dimethylruthenium(II) complexes, containing tethered arenes.

3. Experimental

3.1. General considerations

All reactions were carried out under purified nitrogen or argon with use of standard Schlenk techniques and solvents were purified and deoxygenated before use. The compounds 1-bromo-3-phenylpropanol, bromomesitylene, chlorodiphenylphosphine, 1,3-dibromopropane, α-phellandrene, pentamethylbenzene, *o*-toluic acid, (chloromethyl)dimethylphenylsilane and hydrated ruthenium chloride were obtained from commercial suppliers. Bromopentamethylbenzene was obtained by bromination of pentamethylbenzene [25]. The salt [*n*-Bu_4N]PF_6 was obtained by neutralising commercial aqueous [*n*-Bu_4N]OH with HPF_6; it was recrystallised three times from MeOH–H_2O (4:1) and dried in vacuo for 8 h. Chlorodimethylphosphine was prepared in three steps from $PSCl_3$ [26–28]. The complex [$RuCl_2(\eta^6$-1,2-$MeC_6H_4CO_2Me)]_2$ (**4**) was prepared as described previously [20].

NMR spectra were recorded either on Varian XL-200E, Varian Gemini 300-BB or Varian VXR 300 spectrometers in Canberra or on Bruker DPX-400 or Bruker DRX-500 spectrometers in Cambridge. The chemical shifts (δ) for ^1H and ^{13}C were measured relative to residual signals of the solvents and to exter-

Table 5
Electrochemical data for the tethered complexes **5–9**

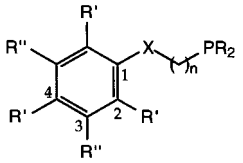
Compound	$E_{1/2}$ (V)	ΔEp (mV s^{-1})	Behaviour
5	+ 1.32 [a]	60	Reversible
6	+ 1.26 [a]	70	Reversible
7	+ 1.34 [a]	60	Reversible
8	+ 1.20 [b]	80	Reversible
9	+ 1.10 [b]	80	Reversible

All electrode potentials were referenced to an Ag | AgCl reference electrode.

[a] Experiments were recorded at 100 mV s^{-1} in 0.5 M [Bu_4NPF_6]/CH_2Cl_2 solution at 293 K.

[b] Experiments were recorded at 100 mV s^{-1} in 0.2 M [Bu_4NPF_6]/CH_2Cl_2 solution at 253 K.

nal 85% H_3PO_4 for ^{31}P-NMR. The $^{31}P\{^1H\}$-NMR resonances of all the compounds described here were singlets. Carbon atoms and the attached hydrogen atoms are numbered as shown below.



Fast Atom Bombardment (FAB) mass spectra were measured either on a VG ZAB2-SEQ spectrometer in Canberra or on a MSI Concept IH spectrometer in Cambridge, using either 3-nitrobenzyl alcohol or 3-nitro-octylphenylether as a matrix. Electron Impact (EI) mass spectra were measured either on a VG Micromass 7070 spectrometer in Canberra or on a Kratos Concept IH spectrometer in Cambridge. Gas chromatograph–mass spectra (GC–MS) were obtained on a 5970 MSD Hewlett–Packard BP1 Detector in Canberra, using a 12.5 m long column.

Infrared spectra in the range 4000–400 cm^{-1} were measured as KBr discs or Nujol mulls on a Perkin–Elmer Spectrum One spectrometer (Canberra) or a Perkin–Elmer Paragon 1000 spectrometer (Cambridge). Spectra in the range 500–150 cm^{-1} were recorded on a Perkin–Elmer FT-1800 instrument in Canberra.

Microanalyses were carried out at the Analytical Services Unit, ANU, Canberra or at the University of Cambridge Chemical Laboratory. Cyclic voltammetry (CV) and alternating current voltammetry (ACV) measurements were performed on a PAR-170 Electrochemical System with use of a Ag | AgCl | acetonitrile reference electrode as described elsewhere [29]. Under these conditions ferrocene and decamethylferrocene were oxidised at $+0.55$ and -0.05 V, respectively. Melting points (m.p.) were determined on a Gallenkamp apparatus and are uncorrected.

3.2. Preparation of 1-bromo-3-(pentamethylphenyl)-propane, $C_6Me_5(CH_2)_3Br$

This procedure is based on that described in Ref. [30]. A solution of bromopentamethylbenzene (10 g, 44 mmol) in dry THF (110 ml) was added dropwise to a stirred suspension of magnesium (1.72 g, 70 mmol) in dry THF (10 ml). The reaction was initiated with a small amount of reacting Mg–$BrCH_2CH_2Br$ and the mixture was heated at reflux for 1 h. The solution was allowed to cool, transferred to a separate dropping funnel with dry THF (20 ml), and added dropwise to a mixture of 1,3-dibromopropane (6.7 ml, 66 mmol), dry HMPA (4 ml), and freshly prepared CuBr (320 mg, 5 mol% to the Grignard reagent) in dry THF (20 ml) at reflux. Dry THF (20 ml) was then added and the reaction mixture was heated at reflux for 20 h. The reaction mixture was allowed to cool to room temperature (r.t.), poured on to a slurry of ice/conc. HCl (500 ml), and the aqueous phase extracted with Et_2O (6×100 ml). The organic phase was washed with 1 M KOH (6×100 ml) and dried (Na_2SO_4). The solvent was removed by evaporation and the product was precipitated by addition of EtOH at -20°C to afford the title compound as a white solid, m.p. 34–38°C (7.54 g, 63%). ^1H-NMR (400 MHz, $CDCl_3$): δ 2.00 (m, 2H, $CH_2CH_2CH_2$), 2.21 (s, 6H, C^2–Me), 2.22 (s, 3H, C^4–Me), 2.25 (s, 6H, C^3–Me), 2.83 (m, 2H, $CH_2C_6Me_5$), 3.51 (t, 2H, $J = 6.5$ Hz, CH_2Br). $^{13}C\{^1H\}$-NMR (75.4 MHz, $CDCl_3$): δ 16.41 (C^2–*Me*), 16.80 (C^4–*Me*), 16.85 (C^3–*Me*), 29.30 ($CH_2CH_2CH_2$), 32.74 ($CH_2C_6Me_5$), 34.10 (CH_2Br), 131.71 (C^4), 132.62 (C^2 or C^3), 132.87 (C^3 or C^2), 134.61 (C^1). IR (KBr, cm^{-1}): 553 m [ν(C–Br)]. EIMS; m/z: 270 [M^+]. High resolution MS; m/z, Found: 268.083032, 270.080666; Calc. for $C_{14}H_{21}^{79}Br$ and $C_{14}H_{21}^{81}Br$: 268.082662, 270.080616, respectively. Anal. Found: C, 62.13; H, 7.91. Calc. for $C_{14}H_{21}Br$: C, 62.46; H, 7.86%.

3.3. Preparation of 1-bromo-3-(mesityl)propane, 2,4,6-$Me_3C_6H_2(CH_2)_3Br$

This compound was prepared from mesityl magnesium bromide and 1,3-dibromopropane in a similar way. ^1H-NMR (300 MHz, $CDCl_3$): δ 1.99 (m, 2H, $CH_2CH_2CH_2$), 2.24 (s, 3H, C^4–Me), 2.29 (s, 6H, C^2–Me), 2.73 (m, 2H, $CH_2C_6H_2Me_3$), 3.50 (t, 2H, $J =$ 6.5 Hz, CH_2Br), 6.83 (s, 2H, H^3). High resolution MS; m/z, Found: 242.04972, 242.04785; Calc. for $C_{12}H_{17}^{79}Br$ and $C_{12}H_{17}^{81}Br$: 240.05136, 242.04945, respectively.

3.4. Preparation of (3-phenylpropyl)dimethylphosphine, $Me_2P(CH_2)_3C_6H_5$

1-Bromo-3-phenylpropane (15.3 ml, 0.10 mol) was added dropwise to a stirred suspension of magnesium (2.57 g, 0.11 mol) in dry THF (30 ml). Dry THF (20 ml) was added and the reaction mixture was heated at reflux for 30 min. The solution was allowed to cool, transferred to a separate flask with Et_2O (30 ml), stirred, and treated dropwise with chlorodimethylphosphine (7.5 ml, 0.095 mol) in Et_2O (40 ml) at 0°C. The mixture was heated at reflux for 30 min, cooled to 0°C, and treated dropwise with degassed 10% aqueous NH_4Cl (30 ml). The mixture was allowed to come to r.t., the organic phase removed, and the aqueous phase extracted with Et_2O (3×50 ml). The combined organic phases were dried (Na_2SO_4), solvents were removed in vacuo, and the residue was distilled under reduced pressure to afford the title compound as a colourless liquid, b.p. 86–88°C/1.5 mm (8.60 g, 48%). ^1H-NMR (300 MHz, CD_2Cl_2): δ 1.07 (dd, 6H, $J = 2$, 0.5 Hz, Me_2P), 1.46 (m, 2H, $CH_2CH_2CH_2$), 1.83 (m, 2H,

CH_2P), 2.78 (t, 2H, $J = 8$ Hz, $CH_2C_6H_5$), 7.25–7.30 (m, 3H, H^3, H^4), 7.35–7.40 (m, 2H, H^2). $^{13}C\{^1H\}$-NMR (75.4 MHz, CD_2Cl_2): δ 14.25 (d, $^1J_{PC} = 13$ Hz, Me_2P), 28.14 (d, $^2J_{PC} = 13$ Hz, $CH_2CH_2CH_2$), 32.08 (d, $^1J_{PC} = 10$ Hz, CH_2P), 37.84 (d, $^3J_{PC} = 11$ Hz, $CH_2C_6H_5$), 126.12 (C^4), 128.66 (C^2 or C^3), 128.87 (C^3 or C^2), 142.73 (C^1). $^{31}P\{^1H\}$-NMR (121.5 MHz, CD_2Cl_2): δ −51.6. EIMS; m/z: 179 [M^+]. High resolution MS; m/z, Found: 180.106818; Calc. for $C_{11}H_{17}P$: 180.106789. Anal. Found: C, 73.11; H, 9.27. Calc. for $C_{11}H_{17}P$: C, 73.31; H, 9.51%.

3.5. Preparation of (3-phenylpropyl)diphenylphosphine, $Ph_2P(CH_2)_3C_6H_5$

This compound was prepared in 76% yield as a white solid, m.p. 56–58°C, from 1-bromo-3-phenylpropane and chlorodiphenylphosphine in a similar way. ^{1}H-NMR (300 MHz, CD_2Cl_2): δ 1.76 (m, 2H, $CH_2CH_2CH_2$), 2.08 (m, 2H, CH_2P), 2.75 (t, 2H, $J = 8$ Hz, $CH_2C_6H_5$), 7.15–7.45 (m, 15H, PPh_2). $^{13}C\{^1H\}$-NMR (75.4 MHz, CD_2Cl_2); δ 27.59 (d, $^2J_{PC} = 12$ Hz, $CH_2CH_2CH_2$), 28.10 (d, $^1J_{PC} = 17$ Hz, CH_2P), 37.43 (d, $^3J_{PC} = 13$ Hz, $CH_2C_6H_5$), 126.13 (C^4), 128.34 (d, $J_{PC} = 5$ Hz), 128.79 (d, $J_{PC} = 3$ Hz), 132.98 (d, $J_{PC} = 19$ Hz), 139.36 (d, $J_{PC} = 14$ Hz, PPh_2), 142.29 (C^1). $^{31}P\{^1H\}$-NMR (121.5 MHz, CD_2Cl_2): δ −16.2. GC–MS; m/z: 303 [M^+]. Anal. Found: C, 82.68; H, 6.66; P, 10.34. Calc. for $C_{21}H_{21}P$: C, 82.87; H, 6.95; P, 10.18%.

3.6. Preparation of (3-mesitylpropyl)diphenylphosphine, $Ph_2P(CH_2)_3$-2,4,6-$C_6H_2Me_3$

A solution of 1-bromo-3-(mesityl)propane (5.97 g, 24.7 mmol) in THF (20 ml) was added dropwise to a stirred suspension of magnesium (0.66 g, 27.1 mmol) in dry THF (10 ml). The reaction was initiated with a small amount of reacting Mg–$BrCH_2CH_2Br$. The reaction mixture was heated at reflux for 30 min, allowed to cool, and transferred to a separate flask with Et_2O (20 ml). Chlorodiphenylphosphine (4.2 ml, 23.4 mmol) in Et_2O (10 ml) was added dropwise to the stirred Grignard reagent at 0°C. After addition of Et_2O (50 ml), the reaction mixture was allowed to warm to r.t., heated at reflux for 1 h, cooled to 0°C, stirred, and treated dropwise with degassed 10% aqueous NH_4Cl (30 ml). The organic phase was removed and the aqueous layer extracted with Et_2O (4 × 50 ml). The combined organic layers were dried (Na_2SO_4) and the solvents were removed in vacuo. The residue was purified by column chromatography (activity I acidic alumina, CH_2Cl_2). The solvent was removed in vacuo to afford the title compound as a white solid, m.p. 74–76°C (7.41 g, 80%). ^{1}H-NMR (300 MHz, CD_2Cl_2): δ 1.54 (m, 2H, $CH_2CH_2CH_2$), 2.19 (s, 6H, C^2–Me), 2.20 (s, 3H, C^4–Me), 2.27–2.33 (m, 2H, CH_2P), 2.70 (t, 2H, $J = 8$ Hz, $CH_2C_6H_2Me_3$), 6.77 (s, 2H, H^3), 7.30–7.35 (m, 6H), 7.40–7.45 (m, 4H, PPh_2). $^{13}C\{^1H\}$-NMR (100.6 MHz, CD_2Cl_2): δ 19.71 (C^2–Me), 20.73 (C^4–Me), 25.78 (d, $^2J_{PC} = 16$ Hz, $CH_2CH_2CH_2$), 28.42 (d, $^1J_{PC} = 12$ Hz, CH_2P), 30.99 (d, $^3J_{PC} = 13$ Hz, $CH_2C_6H_2Me_3$), 128.59, 128.65, 128.72 (C^{2-4}), 128.94, 132.88 (d, $J_{PC} = 19$ Hz), 135.95 (PPh_2), 136.00 (C^1), 139.36 (d, $J_{PC} = 14$ Hz, PPh_2). $^{31}P\{^1H\}$-NMR (121.5 MHz, CD_2Cl_2): δ −16.5. EIMS; m/z: 346 [M^+]. High resolution MS; m/z, Found: 346.18562; Calc. for $C_{24}H_{27}P$: 346.18504.

3.7. Preparation of (3-pentamethylphenylpropyl)diphenylphosphine, $Ph_2P(CH_2)_3C_6Me_5$

This compound was prepared from 1-bromo-3-(pentamethyl)propane (4.03 ml, 15 mmol), magnesium (0.37 g, 15 mmol) and chlorodiphenylphosphine (2.6 ml, 15 mmol) in a similar way. In the final step the residue obtained by evaporation of the combined organic layers was washed with cold ethanol to give the title compound as a white solid, m.p. 90–92°C (4.33 g, 77%). ^{1}H-NMR (300 MHz, CD_2Cl_2): δ 1.54 (m, 2H, $CH_2CH_2CH_2$), 2.15 (s, 6H, C^2–Me), 2.17 (s, 6H, C^3–Me), 2.19 (s, 3H, C^4–Me), 2.22–2.25 (m, 2H, CH_2P), 2.80 (t, 2H, $J = 8$ Hz, $CH_2C_6Me_5$), 7.30–7.35 (m, 6H), 7.40–7.45 (m, 4H, PPh_2). $^{13}C\{^1H\}$-NMR (75.4 MHz, CD_2Cl_2): δ 16.48 (C^2–*Me*), 16.86 (C^3–*Me*, C^4–*Me*), 26.49 (d, $^2J_{PC} = 16$ Hz, $CH_2CH_2CH_2$), 28.47 (d, $^1J_{PC} = 12$ Hz, CH_2P), 32.34 (d, $^3J_{PC} = 13$ Hz, $CH_2C_6Me_5$), 128.64 (C^4), 128.75 (d, $J_{PC} = 3$ Hz), 131.61 (C^2, C^3), 132.53 (d, $J_{PC} = 3$ Hz), 132.97 (d, $J_{PC} = 18$ Hz), 135.98 (C^1), 139.50 (d, $J_{CP} = 14$ Hz, PPh_2). $^{31}P\{^1H\}$-NMR (121.5 MHz, CD_2Cl_2): δ −16.5. EIMS; m/z: 374 [M^+]. High resolution MS; m/z, Found: 374.217049; Calc. for $C_{26}H_{31}P$: 374.216340.

3.8. Preparation of (phenyldimethylsilyl)methyldiphenylphosphine, $Ph_2PCH_2SiMe_2C_6H_5$

(Chloromethyl)dimethylphenylsilane (3.9 ml, 22 mmol) was added dropwise to a stirred suspension of magnesium (0.56 g, 23 mmol) in dry THF (10 ml). After addition of THF (10 ml), the mixture was heated at reflux for 30 min, allowed to cool, transferred to a separate flask with Et_2O (20 ml), stirred, and treated dropwise at 0°C with a solution of chlorodiphenylphosphine (3.7 ml, 21 mmol) in Et_2O (15 ml). After addition of more Et_2O (10 ml), the solution was heated at reflux for 30 min and worked up as described above to give a sticky solid that contained $Ph_2PCH_2SiMe_2C_6H_5$ and

Ph_2MeP in ca. 7:1 ratio, as shown by ^{31}P-NMR spectroscopy. The minor product was removed by sublimation (50°C, 7.10^{-6} mm) on to a liquid nitrogen-cooled probe and the residue was recrystallised from hot ethanol (5 ml) to give the title compound as a white solid, m.p. 62–64°C (3.18 g, 44%). ^1H-NMR (300 MHz, CD_2Cl_2): δ 0.17 (s, 6H, Me_2Si), 1.62 (d, 2H, $J = 1$ Hz, CH_2P), 7.30–7.35, 7.40–7.50 (m, 15H, H^{2-4}, PPh_2). $^{13}C\{^1H\}$-NMR (75.4 MHz, CD_2Cl_2): δ −1.76 (d, $^4J_{PC} = 4$ Hz, Me_2Si), 14.02 (d, $^1J_{PC} = 30$ Hz, CH_2P), 128.01 (C^4), 128.52 (C^2 or C^3), 128.65 (d, $J_{PC} = 6$ Hz, PPh_2), 129.28 (C^3 or C^2), 132.77 (d, $J_{PC} = 20$ Hz, PPh_2), 133.85 (C^1), 141.53 (d, $J_{PC} = 15$ Hz, PPh_2). $^{31}P\{^1H\}$-NMR (121.5 MHz, CD_2Cl_2): δ −22.3. EIMS; m/z: 333 [M^+]. High resolution MS; m/z, Found: 333.123063; Calc. for $C_{21}H_{23}PSi$: 333.122843.

3.9. Preparation of P-donor complexes[$RuCl_2(\eta^6$-1,2-$MeC_6H_4CO_2Me)\{Me_2P(CH_2)_3C_6H_5\}$]

A solution containing [$RuCl_2(\eta^6$-1,2-$MeC_6H_4CO_2Me)]_2$ (**4**) (46 mg, 0.071 mmol) and 3-(phenylpropyl)dimethylphosphine (30 mg, 0.17 mmol) in CH_2Cl_2 (10 ml) was stirred for 1 h and filtered through Celite, which was then washed with CH_2Cl_2 (2 × 20 ml). Addition of hexane (40 ml) to the filtrate and removal of the solvents in vacuo gave the title compound as an orange-pink solid (61 mg, 85%). ^1H-NMR (300 MHz, $CDCl_3$): δ 1.53 (overlapping d, 6H, sep = 10 Hz, Me_2P), 1.85 (m, 2H, $CH_2CH_2CH_2$), 2.04 (m, 2H, CH_2P), 2.49 (s, 3H, MeC_6H_4), 2.70 (m, 2H, $CH_2C_6H_5$), 3.83 (s, 3H, CO_2Me), 4.78 (t, 1H, $J = 5.5$ Hz), 5.38 (d, 1H, $J = 5.5$ Hz), 5.54 (m, 1H), 6.21 (dd, 1H, $J = 5.5$, 3.5 Hz, $C_6H_4CO_2Me$), 7.15–7.20 (m, 3H), 7.25–7.30 (m, 2H, C_6H_5). $^{13}C\{^1H\}$-NMR (75.4 MHz, $CDCl_3$): δ 12.33 (d, $^1J_{PC} = 35$ Hz, $MeMeP$), 13.25 (d, $^1J_{PC} = 34$ Hz, $MeMeP$), 19.84 (MeC_6H_4), 25.61 (d, $^2J_{PC} = 4$ Hz, $CH_2CH_2CH_2$), 30.38 (d, $^1J_{PC} = 30$ Hz, CH_2P), 36.83 (d, $^3J_{PC} = 13$ Hz, $CH_2C_6H_5$), 52.77 (CO_2Me), 76.06, 87.74 (d, $J_{PC} = 8$ Hz), 90.57, 91.37, 102.83, 114.84 (d, $J_{PC} = 5$ Hz, $MeC_6H_4CO_2Me$), 126.25, 128.54, 141.09 (C_6H_5), 165.78 (CO_2Me).$^{31}P\{^1H\}$-NMR (121.5 MHz, $CDCl_3$): δ 15.7. IR (KBr and polythene, cm^{-1}): 1722 m, 1259 m [$\nu(CO_2)$], 279 s [ν(Ru–Cl)]. FABMS; m/z: 467 [M − Cl]$^+$. Anal. Found: C, 47.43; H, 5.62; P, 6.29. Calc. for $C_{20}H_{27}Cl_2O_2PRu$: C, 47.82; H, 5.42; P, 6.17%.

The following complexes were prepared likewise.

3.10. [$RuCl_2(\eta^6$-1,2-$MeC_6H_4CO_2Me)\{Ph_2P(CH_2)_3C_6H_5\}$], brown solid (96% yield)

^1H-NMR (300 MHz, $CDCl_3$): δ 1.46 (m, 2H, $CH_2CH_2CH_2$), 2.41 (m, 2H, CH_2P), 2.45 (s, 3H, MeC_6H_4), 2.70 (m, 2H, $CH_2C_6H_5$), 3.77 (s, 3H, CO_2Me), 4.41 (t, 1H, $J = 5$ Hz), 4.77 (d, 1H, $J = 6$ Hz), 5.38 (q, 1H, $J = 6$ Hz), 6.17 (d, 1H, $J = 5$ Hz, $C_6H_4CO_2Me$), 6.90–7.80 (m, 15H, PPh_2). $^{13}C\{^1H\}$-NMR (75.4 MHz, $CDCl_3$): δ 19.25 (MeC_6H_4), 23.72 (d, $^2J_{PC} = 30$ Hz, $CH_2CH_2CH_2$), 24.95 (d, $^1J_{PC} = 7$ Hz, CH_2P), 36.46 (d, $^3J_{PC} = 13$ Hz, $CH_2C_6H_5$), 52.54 (CO_2Me), 79.17, 85.44, 89.16, 94.44, 113.56 (d, $^1J_{PC} = 4$ Hz, $MeC_6H_4CO_2Me$), 125.45 (C^4), 127.87, 128.06, 128.13 (C^2, C^3, PPh_2), 130.46 (d, $J_{PC} = 15$ Hz), 132.44 (d, $J_{PC} = 9$ Hz), 132.84 (d, $J_{PC} = 9$ Hz, PPh_2), 141.01 (C^1), 164.69 (CO_2Me). $^{31}P\{^1H\}$-NMR (121.5 MHz, $CDCl_3$): δ 27.8. IR (KBr and polythene, cm^{-1}): 1727 m, 1261 m [$\nu(CO_2)$], 290 s [ν(Ru–Cl)]. FABMS; m/z: 591 [M − Cl]$^+$. Anal. Found: C, 57.59; H, 5.35; P, 4.79. Calc. for $C_{30}H_{31}Cl_2O_2PRu$: C, 57.51; H, 4.99; P, 4.94%.

3.11. [$RuCl_2(\eta^6$-1,2-$MeC_6H_4CO_2Me)\{Ph_2PCH_2SiMe_2C_6H_5\}$], orange solid (96% yield)

^1H-NMR (300 MHz, $CDCl_3$): δ −0.19 (s, 6H, Me_2Si), 2.33 (d, 2H, $J_{PC} = 8$ Hz, CH_2P), 2.41 (s, 3H, MeC_6H_4), 3.75 (s, 3H, CO_2Me), 4.23 (t, 1H, $J = 5$ Hz), 4.69 (d, 1H, $J = 5$ Hz), 5.31 (q, 1H, $J = 5$ Hz), 6.13 (d, 1H, $J = 5$ Hz, $C_6H_4CO_2Me$), 7.10–7.85 (m, 15H, PPh_2). $^{13}C\{^1H\}$-NMR (75.4 MHz, $CDCl_3$): δ −1.35 (d, $^4J_{PC} = 6$ Hz, Me_2Si), 11.30 (d, $^1J_{PC} = 25$ Hz, CH_2P), 19.59 (MeC_6H_4), 52.73 (CO_2Me), 79.31, 85.08 (d, $J_{PC} = 4$ Hz), 89.75, 94.67, 113.74 (d, $J_{PC} = 4$ Hz, $MeC_6H_4CO_2Me$), 127.43 (C^4), 128.12 (d, $J_{PC} = 10$ Hz, PPh_2), 128.63 (C^2 or C^3), 130.61 (d, $J_{PC} = 11$ Hz), 132.35 (d, $J_{PC} = 9$ Hz), 132.77 (d, $J_{PC} = 9$ Hz, PPh_2), 133.13 (C^3 or C^2), 138.64 (d, $J_{PC} = 3$ Hz, C^1), 165.06 (CO_2Me). $^{31}P\{^1H\}$-NMR (121.5 MHz, $CDCl_3$): δ 26.3. IR (KBr and polythene, cm^{-1}): 1722 m, 1258 m [$\nu(CO_2)$], 288 s [ν(Ru–Cl)]. FABMS; m/z: 506 [M − arene]$^+$. Anal. Found: C, 54.54; H, 5.04; P, 4.52. Calc. for $C_{30}H_{33}Cl_2O_2PRuSi$: C, 54.88; H, 5.07; P, 4.72%.

3.12. [$RuCl_2(\eta^6$-1,2-$MeC_6H_4CO_2Me)\{Ph_2P(CH_2)_3C_6Me_5\}$], orange solid (98% yield)

^1H-NMR (300 MHz, $CDCl_3$): δ 1.95 (s, 6H, C^2–Me), 2.09 (s, 6H, C^3–Me), 2.13 (s, 3H, C^4–Me), 2.21 (m, 2H, $CH_2CH_2CH_2$), 2.44 (s, 3H, MeC_6H_4), 2.52 (m, 2H, CH_2P), 2.76 (m, 2H, $CH_2C_6Me_5$), 3.75 (s, 3H, CO_2Me), 4.44 (t, 1H, $J = 5.5$ Hz), 4.83 (d, 1H, $J = 5$ Hz), 5.42 (q, 1H, $J = 5$ Hz), 6.14 (d, 1H, $J = 6$ Hz, $C_6H_4CO_2Me$), 7.40–7.45 (m, 6H), 7.75–7.85 (m, 4H, PPh_2). $^{13}C\{^1H\}$-NMR (75.4 MHz, $CDCl_3$): δ 16.23 (C^2–Me), 16.71 (C^3–Me), 16.81 (C^4–Me), 19.63 (MeC_6H_4), 23.19 (d, $^2J_{PC} = 9$ Hz, $CH_2CH_2CH_2$), 24.13 (d, $^1J_{PC} = 30$ Hz, CH_2P), 31.95 (d, $^3J_{PC} = 13$ Hz, $CH_2C_6Me_5$), 52.89 (CO_2Me), 79.41, 85.64 (d, $J_{PC} = 9$ Hz), 86.01 (d, $J_{PC} = 4$ Hz), 89.64, 94.45, 113.85 (d, $J_{PC} = 4$ Hz,

$C_6H_4CO_2Me$), 128.34 (d, $J_{PC} = 10$ Hz), 130.69 (d, $J_{PC} = 14$ Hz, PPh_2), 131.64 (C^4), 132.40 (C^2 or C^3), 132.62 (C^3 or C^2), 132.87 (d, $J_{PC} = 8$ Hz), 133.28 (d, $J_{PC} = 9$ Hz, PPh_2), 135.50 (C^1), 165.09 (CO_2Me). $^{31}P\{^1H\}$-NMR (80.96 MHz, $CDCl_3$): δ 27.9. IR (KBr and polythene, cm^{-1}): 1721 m, 1262 m [$\nu(CO_2)$] 289 s [ν(Ru–Cl)]. FABMS; m/z: 661 $[M-Cl]^+$. Anal. Found: C, 59.24; H, 6.00; P, 4.12. Calc. for $C_{35}H_{41}Cl_2O_2PRu.0.2CH_2Cl_2$: C, 59.24; H, 5.85; P, 4.34%. The presence of CH_2Cl_2 was evident from the ^{1}H-NMR spectrum.

3.13. [$RuCl_2(\eta^6$-1,2-$MeC_6H_4CO_2Me)$-{$Ph_2P(CH_2)_3$-2,4,6-$Me_3C_6H_2$}], red solid (95% yield)

^{1}H-NMR (300 MHz, $CDCl_3$): δ 2.00 (s, 6H, C^2–Me), 2.15 (s, 3H, C^4–Me), 2.22 (m, 2H, $CH_2CH_2CH_2$), 2.41–2.46 (m, 2H, CH_2P), 2.45 (s, 3H, MeC_6H_4), 2.74 (m, 2H, $CH_2C_6H_2Me_3$), 3.75 (s, 3H, CO_2Me), 4.44 (t, 1H, $J = 5$ Hz), 4.82 (d, 1H, $J = 6$ Hz), 5.42 (q, 1H, $J = 5$ Hz), 6.14 (d, 1H, $J = 6$ Hz, $C_6H_4CO_2Me$), 6.69 (s, 2H, H^3), 7.40–7.45 (m, 6H), 7.75–7.85 (m, 4H, PPh_2). $^{13}C\{^1H\}$-NMR (75.4 MHz, CD_2Cl_2): δ 19.52 (C^2–Me, MeC_6H_4), 20.66 (C^4–Me), 22.67 (d, $^2J_{PC} = 9$ Hz, $CH_2CH_2CH_2$), 24.33 (d, $^1J_{PC} = 30$ Hz, CH_2P), 30.62 (d, $^3J_{PC} = 13$ Hz, $CH_2C_6H_2Me_3$), 52.82 (CO_2Me), 79.40, 85.75 (d, $J_{PC} = 9$ Hz), 86.02 (d, $J_{PC} = 4$ Hz), 89.61, 94.44, 113.78 ($C_6H_4CO_2Me$), 128.35 (d, $J_{PC} = 10$ Hz, PPh_2), 128.66 (C^4), 130.59 (C^2 or C^3), 130.77 (C^3 or C^2), 132.85 (d, $^1J_{PC} = 8$ Hz), 133.19 (d, $J_{PC} = 8$ Hz), 135.16 (d, $J_{PC} = 43$ Hz, PPh_2), 135.91 (C^1), 165.04 (CO_2Me). $^{31}P\{^1H\}$-NMR (161.97 MHz, $CDCl_3$): δ 27.9. IR (KBr and polythene, cm^{-1}): 1727 m, 1259 m [$\nu(CO_2)$] 291 s [ν(Ru–Cl)]. FABMS; m/z: 633 $[M-Cl]^+$. Anal. Found: C, 59.47; H, 5.97; P, 4.44. Calc. for $C_{33}H_{37}Cl_2O_2PRu$: C, 59.28; H, 5.58; P, 4.63%.

3.14. Preparation of tethered complexes [$RuCl_2\{\eta^1:\eta^6$-$Me_2P(CH_2)_3C_6H_5\}$] (6)

(i) A solution of [$RuCl_2(\eta^6$-1,2-$MeC_6H_4CO_2Me$)-{$Me_2P(CH_2)_3C_6H_5$}] (99 mg, 0.20 mmol) in CH_2Cl_2 (2.5 ml) in a 10 ml pressure Schlenk tube fitted with a Rotaflo tap was subjected to three freeze–pump–thaw cycles and then heated at 120°C for 48 h. The solution was cooled to 0°C and the solvent was removed in vacuo. The residue was extracted with CH_2Cl_2, transferred to a column of neutral alumina (activity III), and the product was eluted with CH_2Cl_2 followed by THF. The eluate was evaporated to dryness in vacuo and the title compound was isolated as an orange solid (42 mg, 61%) by addition of hexane to a solution in CH_2Cl_2. Crystals suitable for X-ray structural analysis were obtained from CH_2Cl_2–Et_2O by vapour diffusion. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.54 (d, 6H, $^2J_{PH} = 12$ Hz, Me_2P), 1.79 (m, 2H, $CH_2CH_2CH_2$), 2.26 (m, 2H, $CH_2C_6H_5$), 2.54 (m, 2H, CH_2P), 4.96 (d, 2H, $J = 5$ Hz, H^2), 5.62 (t, 2H, $J = 6$ Hz, H^3), 6.33 (t, 1H, $J = 6$ Hz, H^4). $^{13}C\{^1H\}$-NMR (75.4 MHz, $CDCl_3$): δ 13.22 (d, $^1J_{PC} = 36$ Hz, Me_2P), 21.20 ($CH_2CH_2CH_2$), 24.72 (d, $^1J_{PC} = 30$ Hz, CH_2P), 30.08 ($CH_2C_6H_5$), 80.27 (C^2), 89.92 (C^1), 92.35 (d, $J_{PC} = 4$ Hz, C^3), 98.39 (d, $J_{PC} = 12$ Hz, C^4). $^{31}P\{^1H\}$-NMR (121.5 MHz, $CDCl_3$): δ 13.7. IR (cm^{-1}, polythene): 297 s, 278 s [ν(Ru–Cl)]. FABMS; m/z: 352 $[M^+]$. Anal. Found: C, 37.25; H, 4.92; P, 8.50. Calc. for $C_{11}H_{17}Cl_2PRu$: C, 37.51; H, 4.86; P, 8.79%.

A similar experiment employing CH_2Cl_2 (2.5 ml) containing a drop of THF heated at 120°C for 36 h gave the complex in 71% yield.

(ii) A solution of complex **4** (200 mg, 0.31 mmol) in CH_2Cl_2 (10 ml) was treated with $Me_2P(CH_2)_3C_6H_5$ (119 mg, 0.66 mmol) and stirred for 1 h at r.t.. The mixture was then heated at 120°C for 48 h in a 35 ml pressure Schlenk tube and worked up as described above. The yield of the title compound was 157 mg (72%). The reaction time could be reduced to 36 h by the addition of a few drops of THF to the CH_2Cl_2 solution.

The following complexes were prepared in a similar way.

3.15. [$RuCl_2\{\eta^1:\eta^6$-$Ph_2P(CH_2)_3C_6H_5\}$] (5)

Compound **5** was obtained by heating [$RuCl_2(\eta^6$-1,2-$MeC_6H_4CO_2Me$){$Ph_2P(CH_2)_3C_6H_5$}] (840 mg, 1.34 mmol) in CH_2Cl_2 (20 ml) at 120°C for 72 h. The yield was 420 mg (66%). Yields of 70–80% could be achieved using CH_2Cl_2 containing a few drops of THF and heating for 48 h. The ^{1}H- and $^{13}C\{^1H\}$-NMR spectra are generally in good agreement with those reported [9,18]. $^{31}P\{^1H\}$-NMR (121.5 MHz, $CDCl_3$); δ 22.2 (cf. 20.1 [18], −117.08 [9], the latter value presumably being relative to $P(OMe)_3$). IR (polythene cm^{-1},): 303 m, 277 m [ν(Ru–Cl)]. EIMS; m/z: 476 $[M^+]$.

3.16. [$RuCl_2\{\eta^1:\eta^6$-$Ph_2PCH_2SiMe_2C_6H_5\}$] (7)

Compound **7** was obtained by heating [$RuCl_2(\eta^6$-1,2-$MeC_6H_4CO_2Me$){$Ph_2PCH_2SiMe_2C_6H_5$}] (675 mg, 1.03 mmol) in CH_2Cl_2 (17 ml) containing 14 drops of THF at 120°C for 72 h. The yield of orange solid was 371 mg (71%). Orange crystals suitable for X-ray crystallography were obtained by layering a CH_2Cl_2 solution with hexane. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 0.33 (s, 6H, Me_2Si), 2.80 (d, 2H, $J = 15$ Hz, CH_2P), 5.18 (d, 2H, $J = 6$ Hz, H^2), 5.88 (t, 2H, $J = 6$ Hz, H^3), 6.26 (t, 1H, $J = 6$ Hz, H^4), 7.25–7.40 (m, 6H), 7.70–7.75 (m, 4H, PPh_2). $^{13}C\{^1H\}$-NMR (75.4 MHz, $CDCl_3$): δ −2.77 (d, $^4J_{PC} = 5$ Hz, Me_2Si), 29.71 (d, $^1J_{PC} = 17$ Hz, CH_2P), 86.30 (C^2), 92.13 (d, $J_{PC} = 2$ Hz, C^5), 92.68 (d, $J_{PC} = 6$

Hz, C^3), 95.80 (d, $J_{PC} = 12$ Hz, C^4), 128.02 (d, $J_{PC} = 10$ Hz), 130.40 (d, $J_{PC} = 3$ Hz), 132.97 (d, $J_{PC} = 10$ Hz), 133.91 (d, $J_{PC} = 45$ Hz, PPh_2). $^{31}P\{^1H\}$-NMR (121.5 MHz, $CDCl_3$): δ 24.0. IR (polythene cm^{-1},): 303 s, 270 s [ν(Ru–Cl)]. FABMS; m/z: 508 [M^+]. Anal. Found: C, 50.09; H, 4.55; P, 6.20. Calc. for $C_{21}H_{23}Cl_2PRuSi$: C, 49.80; H, 4.58; P, 6.12%.

The complex was also obtained directly from complex **4** and $Ph_2PCH_2SiMe_2C_6H_5$ in a similar yield.

3.17. [$RuCl_2\{\eta^1:\eta^6$-$Ph_2P(CH_2)_3C_6Me_5\}$] (9)

Compound **9** was obtained by heating [$RuCl_2(\eta^6$-1,2-$MeC_6H_4CO_2Me\{PPh_2(CH_2)_3C_6Me_5\}$] (104 mg, 0.15 mmol) in Bu^n_2 (10 ml) at 140°C for 16 h. The yield of orange solid was 29 mg (35%). Use of CH_2Cl_2 containing a few drops of THF instead of Bu^n_2 gave a yield of only 7%. X-ray quality crystals were obtained from CH_2Cl_2–Et_2O. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.73 (s, 6H, C^2–Me), 2.06 (d, 6H, $J = 0.5$ Hz, C^3–Me), 2.16 (m, 2H, $CH_2CH_2CH_2$), 2.22 (d, 3H, $J = 2.5$ Hz, C^4–Me), 2.40 (m, 2H, CH_2P), 2.56 (t, 2H, $J = 6$ Hz, $CH_2C_6Me_5$), 7.25–7.30 (m, 6H), 7.60–7.65 (m, 4H, PPh_2). $^{13}C\{^1H\}$-NMR (100.6 MHz, $CDCl_3$): δ 14.94 (C^4–*Me*), 15.58 (C^3–*Me*), 16.08 (C^2–*Me*), 21.73 (d, $^1J_{PC} = 31$ Hz, CH_2P), 22.67 ($CH_2CH_2CH_2$), 25.01 ($CH_2C_6Me_5$), 85.50 (C^2), 91.59 (C^3), 101.23 (d, $J_{PC} = 4.5$ Hz, C^4), 106.29 (d, $J_{PC} = 11$ Hz, C^1), 127.63 (d, $J_{PC} = 10$ Hz), 129.67, 132.81 (d, $J_{PC} = 46$ Hz), 133.39 (d, $J_{PC} = 8.5$ Hz, PPh_2). $^{31}P\{^1H\}$-NMR (121.5 MHz, $CDCl_3$): δ 26.2. IR (polythene cm^{-1},): 307 s, 286 s [ν(Ru–Cl)]. FABMS; m/z: 546 [M^+]. Anal. Found: C, 57.41; H, 5.96; P, 5.66. Calc. for $C_{26}H_{31}Cl_2PRu$: C, 57.14; H, 5.72; P, 5.67%.

3.18. [$RuCl_2\{\eta^1:\eta^6$-$Ph_2P(CH_2)_3$-2,4,6-$C_6H_2Me_3\}$] (8)

Compound **8** was obtained by heating [$RuCl_2(\eta^6$-1,2-$MeC_6H_4CO_2Me\{PPh_2(CH_2)_3$-2,4,6-$C_6H_2Me_3\}$] (170 mg, 0.23 mmol) in CH_2Cl_2 (3 ml) at 120°C for 24 h. In the work-up, the chromatographic eluate was evaporated to dryness and re-chromatographed. The eluate was evaporated to dryness, redissolved in CH_2Cl_2 and treated with hexane. Evaporation to dryness gave a gummy residue, which on trituration with hexane, afforded the title compound as an orange solid (24 mg, 18%). X-ray quality crystals were obtained by layering a CH_2Cl_2 solution with hexane. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.36 (s, 6H, C^2–Me), 1.79 (s, 6H, C^4–Me), 2.16 (m, 2H, $CH_2CH_2CH_2$), 2.39 (m, 4H, CH_2P, $CH_2C_6H_2Me_3$), 5.25 (s, 2H, H^3), 7.20–7.25 (m, 6H), 7.50–7.55 (m, 4H, PPh_2). ^{13}C $\{^1H\}$-NMR (100.6 MHz, $CDCl_3$): δ 11.39 (C^4–*Me*), 18.73 (C^2–*Me*), 20.54 (d, $^1J_{PC} = 26$ Hz, CH_2P), 25.26 ($CH_2CH_2CH_2$), 34.64 ($CH_2C_6H_2Me_3$), 84.81 (C^2), 92.34 (C^3), 96.30 (C^4), 127.65 (d, $J_{PC} = 10$ Hz), 129.90, 132.73 (d, $J_{PC} = 48$ Hz), 133.78 (d, $J_{PC} = 9$ Hz, PPh_2). $^{31}P\{^1H\}$-NMR (161.97 MHz, $CDCl_3$): δ 28.8. IR (polythene cm^{-1},): 304 s, 288 s [ν(Ru–Cl)]. EIMS; m/z: 518 [M^+]. Anal. Found: C, 57.21; H, 5.83. Calc. for $C_{24}H_{27}Cl_2PRu.0.4CH_3(CH_2)_4CH_3$: C, 57.35; H, 5.94%. The presence of hexane was evident from the ^{1}H-NMR spectrum.

3.19. X-ray crystallography

Details of crystal data, data collection and data refinement are listed in Table 6. The diffraction data were collected with graphite-monochromated Cu–Kα radiation in the case of **6** and with graphite-monochromated Mo–Kα radiation for **7**–**9** on the following diffractometers: Rigaku AFC-6R (**6**), Rigaku AFC-6S (**7**), and Nonius Kappa CCD (**8**, **9**). The structures were solved by direct methods (SIR-92 [31] for **6**, **7** and **8**, and DIRDIF-92 [32] for **9**), and expanded by use of Fourier techniques (DIRDIF-94 [33] for **6** and **7**, SHELXL-97 [34] for **8**, and (DIRDIF-92 [32] for **9**). Refinement was by full-matrix least-squares on F for **6**, **7** and **9**, and on F^2 for **8**. Neutral atom scattering factors for **6** and **7** were taken from standard compilations [35,36] and for **9** from Ref. [37]. Calculations for **6** and **7** were performed with TEXSAN [38] for **8** with SHELXL-97 [34], and for **9** with MAXUS [39].

4. Supplementary material

Crystallographic data for the structures reported here have been deposited with the Cambridge Crystallographic Data Centre, the CCDC deposition numbers being 155393, 155392, 152318 and 155322 for compounds **6**, **7**, **8** and **9**, respectively. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk

Acknowledgements

The authors wish to thank the Crystallographic Service at Monash University for collecting the data for complex **9**, Mr Horst Neumann (ANU) for the preparation of chlorodimethylphosphine, Dr Richard Webster (ANU) for assistance with some of the electrochemical measurements, Professor Brian Johnson (University of Cambridge) for helpful discussions, and the EPSRC for financial support of the purchase of the Nonius Kappa CCD at the University of Cambridge.

Table 6
Crystal and structure refinement data for complexes **6–9**

Complex	**6**	**7**	**8**	**9**
Empirical formula	$C_{11}H_{17}Cl_2PRu$	$C_{21}H_{23}Cl_2PRuSi$	$C_{24}H_{27}Cl_2PRu{\cdot}CH_2Cl_2$	$C_{26}H_{31}Cl_2PRu$
Formula weight	352.21	506.45	603.32	546.48
Temperature (K)	296(1)	296(1)	180(2)	200(2)
Wavelength (Å)	1.54178	0.71069	0.71070	0.71073
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)	$P\bar{1}$	$C2/c$
Unit cell dimensions				
a (Å)	13.649(1)	11.124(3)	8.1450(5)	29.4890(4)
b (Å)	13.453(1)	13.114(2)	9.0570(5)	8.4700(1)
c (Å)	14.479(1)	14.965(2)	18.7720(6)	22.7143(4)
α (°)			101.286(3)	
β (°)	102.892(7)	95.85(2)	91.615(3)	125.4491(6)
γ (°)			113.800(2)	
V (Å^3)	2591.8(4)	2171.8(7)	1233.64(11)	4621.72(12)
Z	8	4	2	8
D_{calc}(g cm^{-3})	1.805	1.549	1.624	1.571
F(000)	1408	1024	612	2903
μ(M–Kα) (cm^{-1})	148.50 (Cu)	10.86 (Mo)	11.46 (Mo)	9.9 (Mo)
Crystal size (mm)	$0.14\times0.14\times0.07$	$0.37\times0.20\times0.08$	$0.16\times0.14\times0.05$	$0.10\times0.03\times0.03$
Crystal colour, habit	Orange, block	Orange, plate	Orange, block	Orange, needle
θ Range for data collection (°)	2–60	2–60	3.71–25.05	2.91–26.37
Number of reflections	4226	6541	6616	16326
Unique	4049 [$R_{int}=0.049$]	5247 [$R_{int}=0.015$]	4248 [$R_{int}=0.054$]	4879 [$R_{int}=0.065$]
Observed	2589 [$I>2\sigma(I)$]	3892 [$I>2\sigma(I)$]	3529 [$I>2\sigma(I)$]	3487 [$I>3\sigma(I)$]
Absorption correction	Analytical	Analytical	None	Empirical [40,41]
Transmission factors	0.15–0.41	0.81–0.92		
Number of parameters	272	236	283	272
Final R indices	$R_1=0.042$, $wR_2=0.056$	$R_1=0.025$, $wR_2=0.023$	$R_1=0.041$, $wR_2=0.093$	$R_1=0.032$, $wR_2=0.072$
Goodness-of-fit on F	1.81	1.48	1.03[a]	2.38
Largest difference peak and hole (e Å^{-3})	1.35 and −1.14	0.45 and −0.45	0.594 and −0.855	0.54 and −0.64

[a] Goodness-of-fit on F^2.

References

[1] J. Okuda, Comments Inorg. Chem. 16 (1994) 185.
[2] H. Butenschön, Chem. Rev. 100 (2000) 1527.
[3] U. Siemeling, Chem. Rev. 100 (2000) 1495.
[4] E.T. Singewald, C.A. Mirkin, A.D. Levy, C.L. Stern, Angew. Chem. Int. Ed. Engl. 33 (1994) 2473.
[5] E.T. Singewald, X. Shi, C.A. Mirkin, S.J. Schofer, C.L. Stern, Organometallics 15 (1996) 3062.
[6] E.T. Singewald, C.S. Slone, C.L. Stern, C.A. Mirkin, G.P.A. Yap, L.M. Liable-Sands, A.L. Rheingold, J. Am. Chem. Soc. 119 (1997) 3048.
[7] M.A. Bennett, G.A. Heath, D.C.R. Hockless, I. Kovacik, A.C. Willis, J. Am. Chem. Soc. 120 (1998) 932.
[8] M.A. Bennett, G.A. Heath, D.C.R. Hockless, I. Kovacik, A.C. Willis, Organometallics 17 (1998) 5867.
[9] P.D. Smith, A.H. Wright, J. Organomet. Chem. 559 (1998) 141.
[10] F. Simal, D. Jan, A. Demonceau, A.F. Noels, Tetrahedron Lett. 40 (1999) 1653.
[11] D. Jan, L. Delaude, F. Simal, A. Demonceau, A.F. Noels, J. Organomet. Chem. 606 (2000) 55.
[12] A. Fürstner, M. Liebl, C.W. Lehmann, M. Picquet, R. Kunz, C. Bruneau, D. Touchard, P.H. Dixneuf, Chem. Eur. J. 6 (2000) 1847.
[13] B. Therrien, T.R. Ward, M. Pilkington, C. Hoffmann, F. Gilardoni, J. Weber, Organometallics 17 (1998) 330.
[14] B. Therrien, R. Ward, Angew. Chem. Int. Ed. Engl. 38 (1999) 405.
[15] B. Therrien, A. König, T.R. Ward, Organometallics 18 (1999) 1565.
[16] A. Abele, R. Wursche, M. Klinga, B. Rieger, J. Mol. Catal. A 160 (2000) 23.
[17] Y. Miyaki, T. Onishi, H. Kurosawa, Inorg. Chim. Acta 300–302 (2000) 369.
[18] K.Y. Ghebreyessus, J.H. Nelson, Organometallics 19 (2000) 3387.
[19] M.A. Bennett, J.R. Harper, B.F.G. Johnson, Oral Presentation I077, 34th International Conference on Coordination Chemistry, University of Edinburgh, Scotland, UK, 9–14 July, 2000.
[20] P. Pertici, P. Salvadori, A. Biasci, G. Vitulli, M.A. Bennett, L.A.P. Kane-Maguire, J. Chem. Soc. Dalton Trans. (1988) 315.
[21] C.A.L. Mahaffy, P.L. Pauson, Inorg. Synth. 19 (1979) 154.
[22] R. Davis, L.A.P. Kane-Maguire, in: G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, vol. 3, Pergamon, Oxford, 1982, p. 1001.
[23] M.A. Bennett, G.B. Robertson, A.K. Smith, J. Organomet. Chem. 43 (1972) C41.
[24] D. Devanne, P.H. Dixneuf, J. Organomet. Chem. 390 (1990) 371.
[25] L.I. Smith, J. Nichols, J. Org. Chem. 6 (1941) 489.
[26] H. Reinhardt, D. Bianchi, D. Mölle, Chem. Ber. 90 (1957) 1656.
[27] H. Niebergall, B. Langenfeld, Chem. Ber. 92 (1962) 64.
[28] G.W. Parshall, Inorg. Synth. 15 (1974) 191.
[29] C.M. Duff, G.A. Heath, Inorg. Chem. 30 (1991) 2528.
[30] J. Nishimura, N. Yamada, Y. Horiuchi, E. Ueda, A. Ohbayashi, A. Oku, Bull. Chem. Soc. Jpn. 59 (1986) 2035.

[31] A. Altomare, M. Cascarano, C. Giacovazzo, A. Guagliardi, M.C. Burla, G. Polodori, M. Camalli, J. Appl. Crystallogr. 27 (1994) 435.
[32] P.T. Beurskens, G. Admiraal, G. Beurskens, W.P. Bosman, R.O. Gould, J.M.M. Smits, C. Smykalla, The DIRDIF-92 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands, 1992.
[33] P.T. Beurskens, G. Admiraal, G. Beurskens, W.P. Bosman, R. de Gelder, R. Israel, J.M.M. Smits, The DIRDIF-94 program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands, 1994.
[34] G.M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1997.
[35] International Tables for X-ray Crystallography, Kynoch Press, Birmingham, England, vol. IV, 1974.
[36] A.J.C. Wilson (Ed.), International Tables for Crystallography, vol. C, Kluwer Academic, Dordrecht, 1992.
[37] D. Waasmeier, A. Kirfel, Acta Crystallogr. Sect A 51 (1995) 416.
[38] TEXSAN, Single Crystal Structure Analysis Software, Version 1.8, Molecular Structure Corp., 3200 Research Forest Drive, The Woodlands, TX 77381, USA, 1997.
[39] S. Mackay, C.J. Gilmore, C. Edwards, N. Stewart, K. Shankland, MAXUS Computer Program for the Solution and Refinement of Crystal Structures, Nonius, The Netherlands; Macscience, Japan and the University of Glasgow, 1999.
[40] R.H. Blessing, Acta Crystallogr. Sect. A 51 (1995) 33.
[41] R.H. Blessing, J. Appl. Crystallogr. 30 (1997) 421.