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A simple synthesis of *trans*-RuCl(C≡CR)(dppe)$_2$ complexes and representative molecular structures

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ABSTRACT

The five-coordinate complex [RuCl(dppe)$_2$]OTf ([**2**]OTf) is obtained in high yield by the sequential reduction of $RuCl_3 \cdot nH_2O$ to $RuCl_2(PPh_3)_3$, subsequent phosphine substitution to give *trans*-$RuCl_2(dppe)_2$ (*trans*-**1**) and finally chloride abstraction (AgOTf, CH_2Cl_2). The use of [**2**]OTf as an entry point to mono-acetylide complexes *trans*-RuCl(C≡CC_6H_4R-4)(dppe)$_2$ (**3**) is described, and represents an alternative route to the long-standing methods based on *cis*-$RuCl_2(dppe)_2$ (*cis*-**1**), which is always prepared as a mixture with the more thermodynamically stable *trans* isomer when prepared by phosphine substitution reactions of $RuCl_2(dmso)_4$. The molecular structures of [**2**]OTf, *trans*-RuCl(C≡CC_6H_4OMe-4)(dppe)$_2$ (**3b**), *trans*-RuCl(C≡CC_6H_4Me-4)(dppe)$_2$ (**3c**) and *trans*-RuCl(C≡C$C_6H_4CO_2$Me-4)(dppe)$_2$ (**3e**) are described. A facile and reproducible synthesis of *cis*-**1** is also reported.

1. Introduction

The chemistry of transition metal complexes *trans*-RuCl(C≡CR)(dppe)$_2$ is very well established [1–10], with a considerable body of recent research demonstrating the utility of these moieties in the construction of multimetallic complexes [11–15], optical materials [16–18], including those that exhibit pH or redox-switchable NLO response [19–25], colorimetric [26] and fluorescent [27] sensing behaviour, the "wire-like" behaviour that arises from extensive d-π mixing along the Ru–C≡C fragment [28–37], and other characteristics that make these compounds potentially useful molecular electronic components [5,33,34,38–41]. The facile replacement of the chloride ligand in complexes *trans*-RuCl(C≡CR)(dppe)$_2$ either directly or from related vinylidenes with a second alkynyl ligand is well documented [1,2,4,17,34,42–44] leading to the preparation of monometallic, oligomeric, polymeric and dendritic compounds featuring *trans*-Ru(C≡CR)$_2$(dppe)$_2$ fragments [11,33,40,45–52]. The complexes *trans*-[Ru(NH_3)(C≡CR)(dppe)$_2$]PF_6 are also useful reagents in the preparation of *trans*-bis acetylides [53].

Complexes of the type *trans*-RuCl(C≡CR)(dppe)$_2$ are most often prepared from *cis*-$RuCl_2(dppe)_2$ (*cis*-**1**) using the method first reported by Dixneuf and colleagues (Scheme 1) [1]. Initial reaction between *cis*-**1** and $NaPF_6$ or similar salt in dichloromethane affords the five-coordinate species [RuCl(dppe)$_2$]$^+$ ([**2**]$^+$), which in turn reacts with terminal alkynes HC≡CR to give the mono-chloro, mono-vinylidene species *trans*-[RuCl{C=C(H)R}(dppe)$_2$]PF_6. Subsequent deprotonation of the vinylidene affords the corresponding neutral acetylide *trans*-RuCl(C≡CR)(dppe)$_2$ (**3**) which can be isolated, or, in the presence of excess terminal alkyne, triethylamine and $NaPF_6$, undergo further reaction to give the *trans*-bis(acetylide) complexes *trans*-Ru(C≡CR)$_2$(dppe)$_2$ (**4**).

Conversion of the thermodynamically stable isomer *trans*-**1** to acetylide complexes *trans*-RuCl(C≡CR)(dppe)$_2$ has been achieved following reaction of *trans*-**1** with trialkylstannyl alkynes, sometimes in the presence of a CuI catalyst [6,54]. Prolonged (5–7 day) reaction of the *trans*-**1** with terminal alkynes in the presence of $NaPF_6$ followed by deprotonation of the resulting vinylidene has also been shown to afford mono-acetylide complexes *trans*-RuCl(C≡CR)(dppe)$_2$ [55], the conversion of *trans*-**1** to the active 16-electron species [RuCl(dppe)$_2$]$^+$ under these conditions being rather slow [10,56].

The use of isolated [RuCl(dppe)$_2$]$^+$ ([**2**]$^+$) salts as an entry to acetylide complexes *trans*-RuCl(C≡CR)(dppe)$_2$ and related compounds has recently begun to attract attention [12,14,27,34,35,57,58]. In this contribution, we detail a convenient preparation of acetylide complexes **3** from *trans*-**1** that takes advantage of the ready abstraction of a chloride ligand from *trans*-**1** by AgOTf in dichloromethane to give the key reagent [**2**]OTf. A facile synthesis of *cis*-**1** from [**2**]OTf is also described for completeness. The molecular structures of [**2**]OTf and three aryl acetylide complexes featuring representative electron donating (OMe, Me) and withdrawing (CO_2Me) groups are also reported.

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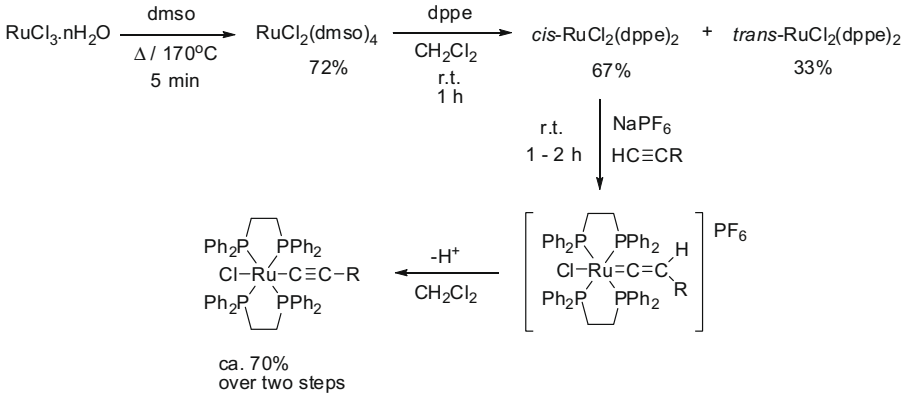


Scheme 1. The preparation of *trans*-RuCl(C≡CR)(dppe)$_2$ from *cis*-RuCl$_2$(dppe)$_2$ [1].

2. Results and discussion

2.1. Synthesis

As part of a larger study concerned with the electronic structure of transition metal acetylide complexes [28,59,60] we desired convenient access to complexes *trans*-RuCl(C≡CR)(dppe)$_2$. However, although *cis*-**1** is often cited as being prepared by the method originally described by Chaudret et al. [61] for the preparation of *cis*-RuCl$_2$(dppm)$_2$, in our hands reaction of RuCl$_2$(dmso)$_4$ [62] with two equivalents of the bis(phosphine) in toluene at 80 °C produced only pure *trans*-**1** [10]. At ambient temperature in dichloromethane under normal laboratory lighting conditions, mixtures of *cis*-**1** and *trans*-**1** are obtained in ca. 3:1 ratio (estimated here from integration of ^{31}P NMR resonances) over the course of approximately 1 h [6,10,39,55,63,64]. By lowering the temperature to 0 °C, the ratio of *cis*-**1**:*trans*-**1** can be increased as high as 10:1, although the reaction becomes very slow, taking well over 24 h for complete conversion. Careful fractional crystallisation, best carried out in the dark, results in separation of *cis*-**1** and *trans*-**1** from these mixtures.

The conversion of *cis*-**1** to the active five-coordinate species [RuCl(dppe)$_2$]$^+$ ([**2**]$^+$) takes place readily upon reaction with alkali metal salts including NaPF$_6$ [3] and KPF$_6$ [11], and salts of [**2**]$^+$ can be isolated from reaction of *cis*-**1** with NaPF$_6$ [42,65], NaOTf or NaBPh$_4$ [66]. The conversion of *trans*-**1** to salts of [**2**]$^+$ has been implicated under similar conditions, although the reaction is considerably slower [10,65]. In contrast, far more facile conversion of *trans*-**1** to [**2**]$^+$ is achieved by halide abstraction with Ag(I) salts [67,68]. Treatment of *trans*-**1** with two equivalents of AgOTf (dichloroethane, 50 °C) [67] or AgBF$_4$ (THF, room temperature or dichloromethane [68]) have been reported to yield [**2**]OTf or [**2**]BF$_4$, respectively. The complex [**2**]OTf has also been isolated from reaction of mixtures of *cis*- and *trans*-**1** with the rather carcinogenic reagent MeOTf [69].

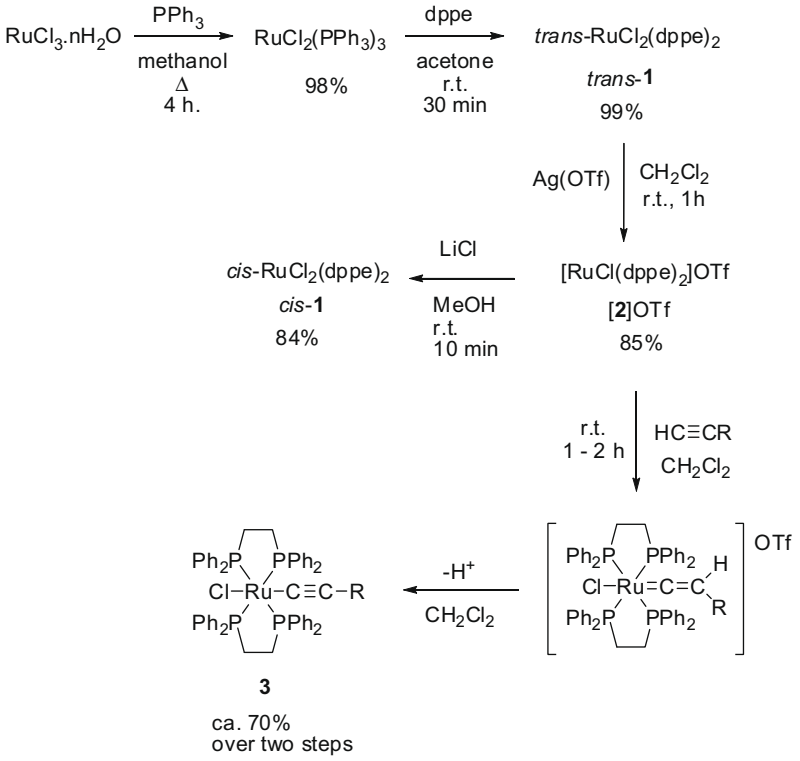
The formation of *cis*-**1** from the reaction of [**2**]BF$_4$ with LiCl has been noted previously, although experimental conditions and isomeric purity were not reported [65]. The reaction of [**2**]OTf with LiCl in methanol at ambient temperature results in the formation of a yellow precipitate within a few minutes, which was collected by filtration and identified by ^{31}P and ^{1}H NMR spectroscopy to be pure *cis*-**1** (ca. 84% isolated yield). Whilst solutions of *cis*-**1** are stable in the dark, *cis*-**1** converts to *trans*-**1** under both normal laboratory and natural lighting. The conversion of *cis*-**1** to equilibrium mixtures of *cis*-**1** and *trans*-**1** was followed by ^{31}P NMR spectroscopy in both CDCl$_3$ (1:1, 24 h) and dichloromethane (3:1, 48 h). This facile conversion of *cis*-**1** to *trans*-**1** in solution at room temperature under ambient lighting conditions must be taken into account when trying to separate mixtures of *cis*-**1** and *trans*-**1** by fractional crystallisation.

With these precedents in mind, a simple, high-yielding, stepwise sequence of reactions can be constructed that results in conversion of RuCl$_3 \cdot n$H$_2$O to the acetylide complexes **3** in good overall yield, via the readily prepared complexes *trans*-**1** and [**2**]OTf (Scheme 2). The syntheses of *trans*-**1** [70] from RuCl$_3 \cdot n$H$_2$O is most conveniently achieved by sequential reaction with PPh$_3$ in methanol to give RuCl$_2$(PPh$_3$)$_3$ [71], followed by ligand exchange with dppe [72]. Treatment of *trans*-**1** with 1 equiv. AgOTf in CH$_2$Cl$_2$ resulted in immediate colour change from yellow to red, with the precipitation of AgCl. Complete reaction was achieved within 1 h at room temperature. The product can be isolated as an air-stable solid by simple filtration and precipitation. With both the work-up and crystallisation of [**2**]OTf carried out in the open laboratory environment, no evidence of a yellow N$_2$ adduct was found [73].

The five-coordinate complex [**2**]OTf reacts rapidly with 1-alkynes in small volumes of CH$_2$Cl$_2$ at room temperature to give the corresponding vinylidene complexes. Simple washing of the crude vinylidene salts with further aliquots of hexane serves to remove any excess 1-alkyne, which is essential if formation of the bis(acetylide) complex is to be prevented during the next step. Formation and isolation of the desired acetylide complexes **3** is most conveniently performed by addition of a solution of KO^{t}Bu in methanol to a concentrated dichloromethane solution of the vinylidene. Under these conditions the acetylide precipitates essentially free of triflate salt by-products, and can be collected by filtration. The product obtained in this fashion is of high purity, with recrystallisation affording single crystals suitable for X-ray diffraction.

This reaction sequence was successfully applied in the preparation of a range of complexes *trans*-RuCl(C≡CR)(dppe)$_2$ [R = Ph (**3a**), C$_6$H$_4$OMe-4 (**3b**), C$_6$H$_4$Me-4 (**3c**), C$_6$H$_4$C$_5$H$_{11}$-4 (**3d**), C$_6$H$_4$CO$_2$Me-4 (**3e**), C$_6$H$_4$NO$_2$-4 (**3f**)] which were isolated in ca. 70–80% yield in most cases. However, attempts to prepare *trans*-RuCl(C≡CC$_6$H$_4$NH$_2$-4)(dppe)$_2$ were hampered by the basicity of the aniline moiety, which deprotonated the intermediate vinylidene, leading to formation of the bis(acetylide) *trans*-Ru(C≡CC$_6$H$_4$NH$_2$-4)$_2$(dppe)$_2$. Reactions with 4-ethynylbenzonitrile were complicated by competitive coordination and chloride substitution reactions involving the nitrile moiety.

The acetylide complexes were characterised by the usual spectroscopic (IR, ^{1}H, ^{13}C, ^{31}P NMR, ES-MS) methods. The acetylide ν(C≡C) band was observed between 2050 and 2070 cm^{-1}, the lowest wavenumber bands being associated with **3e** and **3f**. The electrospray mass spectra (ES-MS) featured species formed from loss of chloride, the molecular ion not being observed. In the ^{31}P NMR spectra the *trans* geometry of the complexes was confirmed by



Scheme 2. The preparation of *trans*-RuCl(C≡CR)(dppe)$_2$ from *trans*-RuCl$_2$(dppe)$_2$.

Table 1
^{1}H NMR data from complexes **3a**–**3f**.

	R = OMe	R = C_5H_{11}	R = Me	R = H	R = CO_2Me	R = NO_2
Ho/o′	7.57, 7.26 (2 × d, *J* = 7 Hz)	7.62, 7.20 (2 × d, unresolved)	7.58, 7.23 (2 × d, *J* = 7 Hz)	7.58, 7.25 (2 × d, *J* = 7 Hz)	7.42, 7.33 (2 × d, *J* = 7 Hz)	7.36, 7.34 (AB, *J* = 8 Hz)
Hm/m′	6.99, 6.97 (AB, *J* = 7 Hz)	6.94, 7.05 (unresolved)	6.99, 6.97 (AB) *J* = 7 Hz	6.99, 6.97 (dd) *J* = 7 Hz	7.01, 6.94 (dd) *J* = 7 Hz	7.03, 6.95 (dd) *J* = 8 Hz
Hp/p′	7.19 (t, *J* = 7 Hz)	7.20 (unresolved)	7.18 (t, *J* = 7 Hz)	7.18 (t, *J* = 7 Hz)	7.20, 7.18 (2 × t, *J* = 7 Hz)	7.21, 7.20 (2 × t, *J* = 8 Hz)
CH_2CH_2	2.65 (m)	2.66 (m)	2.65 (m)	2.68 (m)	2.69 (m)	2.69 (m)
H_2	6.64 (AB, *J* = 8 Hz)	6.65 (d, *J* = 8 Hz)	6.62 (d, *J* = 8 Hz)	6.70 (d, *J* = 8 Hz)	6.57 (d, *J* = 8 Hz)	6.44 (d, *J* = 8 Hz)
H_3	6.70 (AB, *J* = 8 Hz)	6.92 (d, *J* = 8 Hz)	6.93 (d, *J* = 8 Hz)	7.11 (d, *J* = 8 Hz)	7.77 (d, *J* = 8 Hz)	7.94 (d, *J* = 8 Hz)
R	3.80	0.92, 1.35, 1.61, 2.54	2.30	7.11 (dd, apparent triplet) *J* = 8 Hz	3.89	

Table 2
^{13}C NMR spectroscopic data from complexes **3a**–**3f**.

	R = OMe	R = C_5H_{11}	R = Me	R = H	R = CO_2Me	R = NO_2
C_α	119.2	121.2	121.5	124.1	136.7	148.4
C_β	112.7	113.7	113.6	113.9	114.9	116.8
C1	123.5	127.8	127.8	130.6	135.1	137.2
C2	131.0	129.9	130.0	130.2	129.9	130.0
C3	113.1	127.6	128.4	127.6	129.1	123.5
C4	155.8	137.5	132.4	123.0	123.6	142.4
Ci/i′	136.9	137.0	137.0	136.9	136.2	135.9
	135.8	135.7	135.8	135.8	135.6	135.5
Co/o′	134.5	134.6	134.6	134.6	134.5	134.5
		134.5		134.6	134.2	134.1
Cm/m′	127.3	127.3	127.4	127.4	127.4	127.5
	127.0	127.0	127.1	127.1	127.1	127.3
Cp/p′	129.0	128.9	129.0	129.1	129.0	129.2
	128.8	128.8	128.9	129.0		
CH_2CH_2	30.9	30.9	31.0	30.8	30.7	30.6
R	55.3	14.3, 22.8, 31.3, 31.9, 35.9	21.5	–	CO 167.7 Me 52.0	

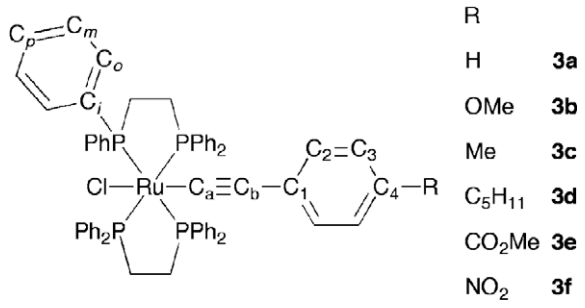


Fig. 1. The NMR labelling scheme used in this work.

the observation of a singlet near δ 50 ppm, whilst the ^{1}H (Table 1) and ^{13}C (Table 2) spectra featured characteristic resonances arising from both the dppe and aryl acetylide ligands. The acetylide C_a resonance, which was observed as a quintet ($^{2}J_{CP}$ ca. 15 Hz), proved to be sensitive to the electronic nature of the remote aryl substituent. The ^{1}H and ^{13}C NMR spectra could be fully assigned (see Fig. 1 for NMR labelling scheme) through correlation spectroscopy, although the couplings of the methylene protons from the dppe ligands were not fully resolved.

2.2. Molecular structures

In the course of this work, single crystals of [**2**]OTf, **3b**, **3c** (as both 0.5THF and $2CH_2Cl_2$ solvates) and **3e** suitable for X-ray diffraction were obtained, those of **3a** [6], **3f** [55], and the related complexes *trans*-RuCl(C≡CC_6H_3-Me-2-NO_2-4)(dppe)$_2$ [55], *trans*-RuCl(C≡CC_6H_4CHO-4)(dppe)$_2$ [24], *trans*-RuCl(C≡CC_6H_4F-4)(dppe)$_2$ [17], *trans*-RuCl(C≡CC_6H_4F-3)(dppe)$_2$ [35] and *trans*-RuCl(C≡CC_6H_4CH=$CHC_6H_4NO_2$-4)(dppe)$_2$ [24] having been reported earlier. Crystallographic data and important bond lengths and angles are summarized in Tables 3 and 4, with plots of [**2**]$^{+}$, **3b**, **3c** and **3e** illustrated in Figs. 2–5, respectively. There are no significant differences in the structures of two different solvates of **3c**.

The structures of salts containing five-coordinate ruthenium(II) cations of general form [RuCl(PP)$_2$]X (where PP = chelating diphosphine ligand) have been reported on several previous occasions [PP = dppe, X = $[PF_6]^-$ [65], $[BF_4]^-$ [68], $[C_2B_9H_{12}]^-$ [74]; PP = dppp, X = $[PF_6]^-$ [75]; PP = dcpe, X = $[PF_6]^-$ [76]; PP = $NH(CH_3)(PPh_2)_2$, X = $[SbF_6]^-$ [77]; PP = bnpe, X = $[PF_2O_2]^-$ [78]. The cation in [**2**]OTf is essentially identical to that in [**2**]PF_6 and [**2**]BF_4 with a similar degree of "Y"-shaped distortion of the equatorial plane from that in an idealised trigonal bipyramid. The two dppe ligands span axial and equatorial positions, with the equatorial plane defined by Cl,

Table 3
Selected bond lengths (Å) and angles (°) for [**2**]OTf and complexes *trans*-RuCl(C≡CC_6H_4R-4)(dppe)$_2$ (**3a**, **b**, **c**, **e** and **f**).

	[**2**]OTf	R = H **3a** · **CH_2Cl_2** [6]	R = OMe **3b** · **$2CH_2Cl_2$**	R = Me **3c** · **0.5THF**	R = Me **3c** · **$2CH_2Cl_2$**	R = CO_2Me **3e** · **THF**	R = NO_2 **3f** · **CH_2Cl_2** [55]
Ru–Cl	2.4061(5)	2.4786(13)	2.5118(9)	2.4907(12)	2.5096(8)	2.4806(13)	2.500(1)
Ru–P(1)	2.3786(5)	2.3680(14)	2.3526(9)	2.3792(12)	2.3539(8)	2.3753(14)	2.360(2)
Ru–P(2)	2.2449(5)	2.3524(14)	2.3824(9)	2.3642(11)	2.3827(8)	2.3552(14)	2.354(1)
Ru–P(3)	2.3639(5)	2.3917(14)	2.3610(9)	2.3433(11)	2.3627(8)	2.3768(13)	2.366(2)
Ru–P(4)	2.2434(5)	2.3734(14)	2.3812(9)	2.3549(11)	2.3781(8)	2.3679(14)	2.386(1)
Ru–P_{avg}	2.318_2	2.371_4	2.369_3	2.360_4	2.369_4	2.368_8	2.366_5
Ru–C(1)		2.007(5)	2.018(4)	2.009(5)	2.007(4)	1.998(5)	1.986(5)
C(1)–C(2)		1.198(7)	1.188(5)	1.196(6)	1.202(5)	1.195(8)	1.206(7)
C(2)–C(3)		1.445(8)	1.437(5)	1.447(6)	1.432(5)	1.431(7)	1.442(7)
Cl–Ru–C(1)		175.72(14)	179.25(9)	176.41(12)	179.22(8)	178.54(15)	176.20(13)
Ru–C(1)–C(2)		174.1(5)	177.0(3)	175.6(4)	176.8(3)	178.4(5)	175.3(4)
C(1)–C(2)–C(3)		178_3	175.1(4)	175.5(5)	176.8(4)	171.1(6)	174.4(5)
P(1)–Ru–P(2)	79.39(2)	82.43(14)	81.83(3)	82.29(4)	81.97(3)	82.71(5)	83.23(6)
P(2)–Ru–P(3)	97.77(2)	97.78(5)	98.09(3)	98.38(4)	98.28(3)	96.43(5)	95.52(6)
P(3)–Ru–P(4)	80.02(2)	80.93(5)	81.57(3)	80.73(4)	81.54(3)	81.25(5)	82.58(6)
P(1)–Ru–P(4)	97.35(2)	98.48(5)	98.48(3)	98.54(4)	98.18(3)	99.62(5)	98.66(6)

Table 4
Crystal data and refinement details.

Complex	[**2**]OTf	**3b**	**3c**	**3c**	**3e**
Formula	$C_{53}H_{48}OF_3SClP_4Ru \cdot 2CHCl_3$	$C_{61}H_{55}OClP_4Ru \cdot 2CH_2Cl_2$	$C_{61}H_{55}ClP_4Ru \cdot 0.5C_4H_8O$	$C_{61}H_{55}ClP_4Ru \cdot 2CH_2Cl_2$	$C_{62}H_{55}O_2ClP_4Ru \cdot C_4H_8O$
Molecular weight (g mol^{-1})	1321.11	1233.29	1084.50	1218.30	1128.51
Crystal system	Triclinic	Triclinic	Orthorhombic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$Pna2_1$	$P\bar{1}$	$P\bar{1}$
a (Å)	14.2259(2)	9.2242(3)	25.7427(6)	9.2375(5)	12.9760(4)
b (Å)	17.4740(3)	12.8045(4)	15.5668(4)	12.8488(7)	17.1779(5)
c (Å)	12.3513(3)	23.8399(7)	13.5683(3)	23.6105(12)	24.6946(7)
α (°)	72.08(1)	92.88(1)	90	92.97(1)	97.46(1)
β (°)	75.17(1)	94.63(1)	90	93.88(1)	90.47(1)
γ (°)	79.80(1)	99.13(1)	90	99.18(1)	104.20(1)
V (Å^3)	2807.86(9)	2765.35(15)	5437.2(2)	2754.5(3)	5286.6(3)
ρ_c (g cm^{-3})	1.563	1.481	1.325	1.469	1.418
Z	2	2	4	2	4
$2\theta_{max}$ (°)	60	58	56	58	56
μ (Mo Kα) (mm^{-1})	0.817	0.684	0.496	0.685	0.515
Crystal size (mm)	0.20 × 0.18 × 0.14	0.28 × 0.08 × 0.02	0.26 × 0.10 × 0.06	0.20 × 0.20 × 0.06	0.20 × 0.18 × 0.07
N_{Tot}	41337	34263	55975	26206	50880
N (R_{int})	16 339 (0.0263)	14 655 (0.0662)	12 966 (0.0765)	14 447 (0.0332)	25 401 (0.0412)
R_1	0.0324	0.0481	0.0484	0.0528	0.0891
wR_2	0.0868	0.1265	0.1289	0.1640	0.2964
GOOF	1.001	0.988	1.030	1.072	1.113

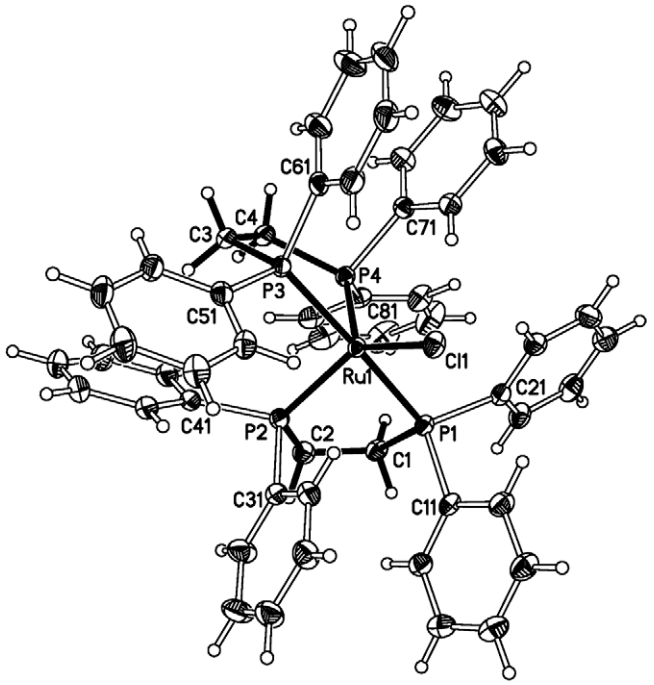


Fig. 2. Plot of the cation in [RuCl(dppe)$_2$]OTf ([**2**]OTf). In this and all subsequent plots, hydrogen atoms have been omitted for clarity, with thermal ellipsoids at 50%.

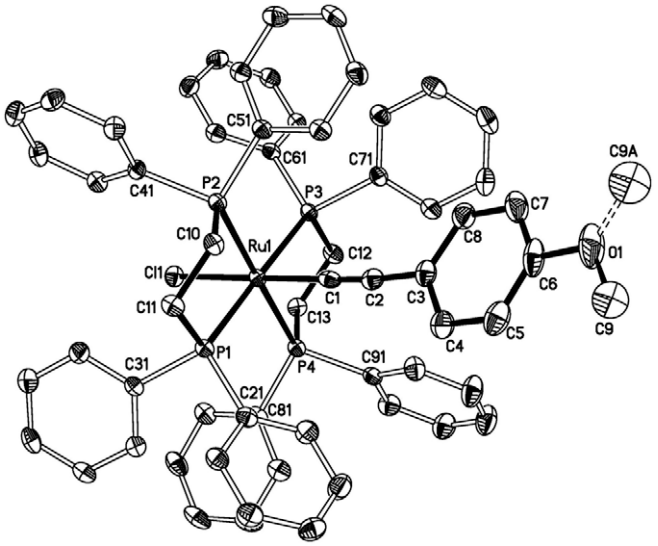


Fig. 3. Plot of a molecule of *trans*-RuCl(C≡CC$_6$H$_4$OMe-4)(dppe)$_2$ (**3b**).

P(2) and P(4). Around the equatorial plane, the donor atoms define angles Cl(1)–Ru(1)–P(2, 4) 134.49(2), 130.35(2)° and the rather small angle P(2)–Ru(1)–P(4) 95.16° to relieve degeneracy in the "e" type orbitals associated with a d^6 trigonal bipyramid. The electronic factors that underpin this distortion have been described in detail elsewhere [79]. The cation of [**2**]OTf is more sterically crowded than other acetylide complexes described in the paper and as a result the planes of axial Ph-rings of the dppe ligands are almost parallel to each other. The triflate anions are connected to cations via CH···O close contacts and link them in double layers, perpendicular to *b*-axis.

The structures of the acetylide complexes illustrate the usual octahedral geometry around Ru, and linear Cl–Ru–C(1)–C(2)–C(3) chain. The C(1)–C(2) acetylide bond lengths fall in the range 1.188(5)–1.202(5) Å, whilst the Ru–P bond lengths are insensitive to the electron donating (OMe) or withdrawing (CO_2Me) properties of the acetylide substituent. The Ru–C(1) [2.018(4) Å] and Ru–Cl [2.5118(9) Å] bond lengths in **3b** are at the longer end of the range of values typically offered by complexes of general type **3** (Table 3), possibly due to greater Cl 3p/Ru 3d/C≡C π filled orbital-filled orbital repulsive interactions along the linear back-bone [80,81].

As usual, in the absence of strong hydrogen bonds the packing of complexes in crystals is determined by a fine balance between a number of attractive intermolecular weak interactions of various nature (C–H···O, Cl, π; Cl···Cl, etc.). The presence and the nature of solvent molecules also significantly affects the crystal packing. For example, the metal complexes in isostructural crystals **3b** and **3c** · **CH_2Cl_2** form double layers perpendicular to *b*-axis and disordered solvent molecules are located in channels between the layers, while ordered dichloromethane molecules are "trapped" in the voids of these layers. There are a number of weak C–H···π interactions in the structures. Hydrogen atoms of both methylene groups of dichloromethane molecules and aromatic rings take part in these interactions, while the methylene groups of the dppe ligands do not show any shortened contacts.

In the absence of solvent dichloromethane molecules in structure of **3c** · **THF** the character of packing changes and complexes form chains along *c*-axis of the crystal. In this case the methylene groups of dppe ligands became stereochemically active and link the adjacent complexes by C–H···Cl contacts. These groups are also active in the structure of **3e** where they are involved in C–H···π interactions, while Cl atoms are linked with an aromatic hydrogen atom. Finally, the absence of stacking interactions between aromatic rings in these structures should be noted.

2.3. Electrochemistry

The highest occupied molecular orbitals of ruthenium aryl acetylide complexes have significant aryl acetylide ligand character [22,28,29,59,60,80–82]. The cyclic voltammograms of **3a–f** each exhibit two anodic processes, the first being fully reversible, the potential of which reflect the variation in the electronic properties of the aryl substituent (Table 5). The nitro-substituted derivative **3f** also contains a partially chemically reversible reduction with a cathodic peak potential E_{pc} −1.13 V (vs. FcH/FcH$^+$), most likely localised on the nitroaromatic portion of the molecule. The sensitivity of the redox response to the nature of the remote substituent and the chemical reversibility of the first redox couple is consistent with the aryl acetylide character of the HOMO in *trans*-RuCl(C≡CR)(dppe)$_2$ complexes.

3. Conclusion

A simple reaction protocol has been described that allows the preparation of acetylide complexes *trans*-RuCl(C≡CR)(dppe)$_2$ (**3**) from the five-coordinate complex [RuCl(dppe)$_2$]OTf ([**2**]OTf), which is obtained in three high yielding steps from $RuCl_3 \cdot nH_2O$. The use of [**2**]OTf as an entry point to mono-acetylide complexes **3** is an alternate, and in our experience more convenient, method to the long-standing routes based on *cis*-RuCl$_2$(dppe)$_2$.

4. Experimental

All reactions were carried out under an atmosphere of nitrogen using standard Schlenk techniques as a matter of routine, although no special precautions were taken to exclude air or moisture during work-up. Dichloromethane was purified and dried using an Innovative Technology SPS-400, and degassed before use. Diethyl ether,

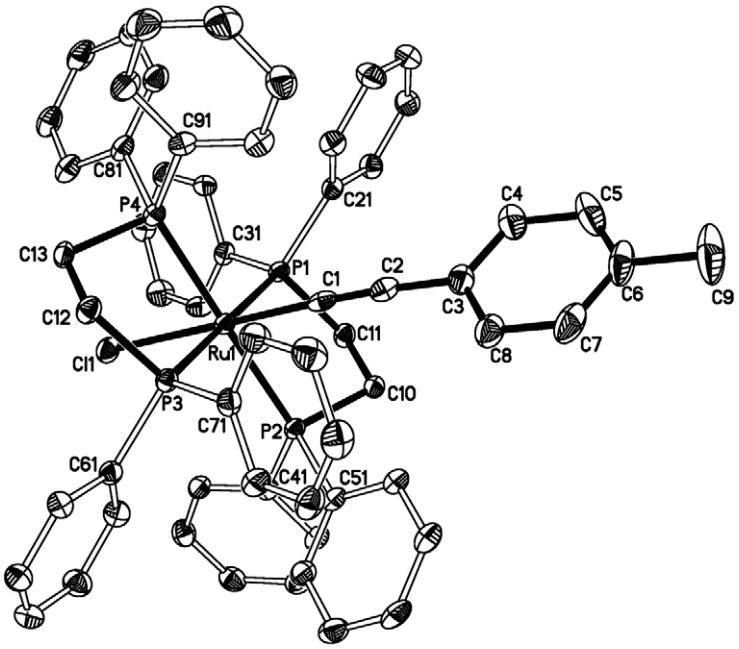


Fig. 4. Plot of a molecule of *trans*-RuCl(C≡CC_6H_4Me-4)$(dppe)_2$ (**3c**).

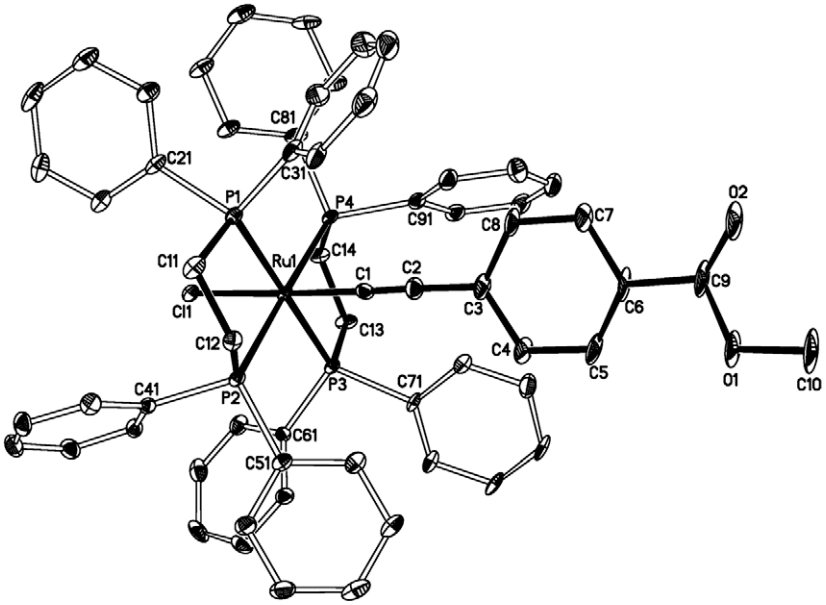


Fig. 5. Plot of a molecule of *trans*-RuCl(C≡$CC_6H_4CO_2$Me-4)$(dppe)_2$ (**3e**).

Table 5
Electrochemical data[a] from *trans*-RuCl(C≡CC_6H_4R-4)$(dppe)_2$ (**3a**–**f**).

R	E_1 (V)	E_2 (V)
OMe (**3b**)	−0.10	+0.69[b]
C_5H_{11} (**3d**)	−0.04	+0.83[b]
Me (**3c**)	−0.03	+0.85[b]
H (**3a**)	+0.01	+0.89[b]
CO_2Me (**3e**)	+0.10	+0.98[b]
NO_2 (**3f**)	+0.20	+1.07[b]

[a] $E_{1/2}$ vs. ferrocene/ferrocenium (FcH/FcH^+) (CH_2Cl_2, 0.1 M NBu_4BF_4, Pt dot working electrode). Data are reported against an internal decamethylferrocene/decamethylferrocenium (FcH^*/FcH^{*+}) standard. Under these conditions FcH^*/FcH^{*+} = −0.53 V vs. FcH/FcH^+.

[b] Irreversible, anodic peak potential E_{pa} reported.

hexane and methanol were the best available commercial grade, and used without further purification. Reagents were purchased and used as received, with minor modifications to the literature procedures being used to prepare $RuCl_2(PPh_3)_3$ [71], *trans*-$RuCl_2(dppe)_2$ [72], and [RuCl$(dppe)_2$]OTf [67] as detailed below.

NMR spectra were recorded on a Bruker Avance (^{1}H 400.13 MHz, ^{13}C 100.61 MHz, ^{31}P 161.98 MHz) spectrometer from $CDCl_3$ solutions and referenced against solvent resonances (^{1}H, ^{13}C) or external H_3PO_4 (^{31}P). IR spectra (CH_2Cl_2) were recorded using a Nicolet Avatar spectrometer from cells fitted with CaF_2 windows. Electrospray ionisation mass spectra were recorded using Thermo Quest Finnigan Trace MS-Trace GC or WATERS Micromass LCT spectrometers. Samples in dichloromethane (1 mg/mL) were 100 times diluted in either methanol or

acetonitrile, and analysed with source and desolvation temperatures of 120 °C, with cone voltage of 30 V.

Cyclic voltammograms were recorded at $v = 100–800$ mV s^{-1} from solutions of approximately 10^{-4} M in analyte in dichloromethane containing 10^{-1} M NBu_4BF_4, using a gastight single-compartment three-electrode cell equipped with platinum disk working, coiled platinum wire auxiliary, and platinum wire pseudo-reference electrodes. The working electrode surface was polished before scans with an alumina paste. The cell was connected to a computer-controlled Autolab PGSTAT-30 potentiostat. All redox potentials are reported against the ferrocene/ferrocenium coupling, and referenced against the decamethylferrocene/decamethylferrocenium ($FcH^*/FcH^{*+} = -0.53$ V) redox couple used as an internal reference system.

Single crystal X-ray data for all structures were collected on a Bruker SMART CCD 6000 diffractometer equipped with a Cryostream (Oxford Cryosystems) cooling device at 120 K using λMo Kα radiation. All the structures were solved by direct methods and refined by full-matrix least squares on F^2 for all data using SHELXTL software. All non-hydrogen atoms were refined with anisotropic displacement parameters, H-atoms were placed into calculated positions and refined in a "riding" mode. Further details of data collections and refinement are given in Supplementary material.

4.1. Preparation of $RuCl_2(PPh_3)_3$

A suspension of $RuCl_3 \cdot nH_2O$ (1.00 g, 3.83 mmol for $n = 3$) and PPh_3 (6.00 g, 22.9 mmol) in methanol (50 ml) was heated for 4 h at reflux. The brown solid that precipitated was collected by filtration, washed with diethyl ether and dried in air to give $RuCl_2(PPh_3)_3$ as a dark brown powder (3.59 g, 98%). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 81 MHz): δ 30.2 (s, PPh_3).

4.2. Preparation of trans-$RuCl_2(dppe)_2$ (trans-**1**)

A suspension of $RuCl_2(PPh_3)_3$ (3.59 g, 3.75 mmol) and dppe (3.14 g, 7.89 mmol) in acetone (40 ml) was stirred for 1 h at room temperature. The resulting yellow precipitate was collected by filtration, washed with acetone and dried in air to give *trans*-**1** as an orange-yellow powder (3.40 g, 99%). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 46.1 (s); ^1H NMR ($CDCl_3$): 7.26 (d, $J_{HH} = 7.6$ Hz, 16H, *ortho*-CH), 7.19 (t, $J_{HH} = 6.8$, 8H, *para*-CH), 6.99 (dd, $J_{HH} \sim 7.2$, 16H, *meta*-CH), 2.70 (m, 8H, CH_2); ^{13}C NMR ($CDCl_3$): ^{13}C NMR ($CDCl_3$): 135.0 (m, *ipso* C), 134.4 (m, *ortho* C), 128.8 (m, *para*-C), 127.0 (m, *meta* C), 28.8 (m, CH_2).

4.3. Preparation of $[RuCl(dppe)_2][OTf]$ ([**2**]OTf)

A suspension of *trans*-**1** (3.40 g, 3.51 mmol) and AgOTf (0.90 g, 3.51 mmol) in dichloromethane (40 ml) was stirred 1 h. The resulting dark red solution was filtered (Celite) to remove the precipitated AgCl, and the filtrate diluted with hexane. Careful removal of the CH_2Cl_2 on a rotary evaporator resulted in the precipitation of [**2**]OTf as well-formed red crystals, which were collected, washed with hexane and dried to give [**2**]OTf as a dark red solid, which is stable in air and chlorinated solvents (3.22 g, 85%). Crystals suitable for X-ray diffraction were obtained following recrystallisation from $CHCl_3$/hexane. ^{31}P NMR ($CDCl_3$): δ 84.0 (dd, $J_{PP} \sim 12.8$, 2P), 56.7 (dd, $J_{PP} \sim 12.8$, 2P); ^1H NMR ($CDCl_3$): δ 7.73 (m, 4H, *meta*-CH), 7.52 (t, J_{HH} 7.2, 2H, *para*-CH), 7.32 (t, J_{HH} 7.4, 2H, *para*-CH), 7.19 (m, 16H, phenyl-CH), 6.99 (m, 12H, phenyl-CH), 6.71 (m, 4H, *meta*-CH), 2.65 (m, 2H, CH_2); 2.44 (m, 4H, CH_2); 1.57 (m, 2H, CH_2); ^{13}C NMR ($CDCl_3$): 133.7 (m), 133.1 (m, *ipso* C), 132.7 (m), 132.3 (m, *para* C), 132.1 (m), 132.0 (m, *ipso* C), 131.7 (m), 131.1 (m, *para* C × 2), 130.4 (m, *ipso* C), 129.4 (m, *ipso*-C + other C), 129.3 (m, *para* C), 128.7 (m), 128.0 (m), 127.5 (m), 120.9 (q, $J_{CF} = 321$, CF_3), 30.1 (m, CH_2), 18.4 (m, CH_2); ^{19}F NMR ($CDCl_3$): δ −78.5 (s). A mixture of *cis*-**1** and *trans*-**1** can also be used to give high yields of [**2**]OTf by this procedure.

4.4. Preparation of cis-$RuCl_2(dppe)_2$ (cis-**1**)

A solution of [**2**]OTf (198 mg, 0.182 mmol) in methanol (25 ml) was added to a stirred solution of LiCl (80 mg, 1.93 mmol) in methanol (4 ml). The yellow solid formed after 15 min was filtered, washed with 2 × 2 ml of methanol and dried *in vacuo*. This solid (148 mg, 0.152 mmol, 84%) was identified as pure *cis*-**1** by ^{31}P, ^1H and ^{13}C NMR spectroscopy. ^{31}P NMR ($CDCl_3$): δ 53.6 (dd, $J_{PP} \sim 19.4$, 2P), 38.8 (dd, $J_{PP} \sim 19.6$, 2P); ^1H NMR ($CDCl_3$): δ 8.22 (m, 4H), 7.54 (m, 4H), 7.26 (m, 4H), 7.24 (t, $J_{HH} = 6.4$, 2H, *para*-CH), 7.01 (m, 4H), 6.93 (t, $J_{HH} = 6.4$, 2H, *para*-CH), 6.84 (m, 4H), 6.78 (m, 8H), 6.73 (m, 8H), 2.98 (m, 2H, CH_2), 2.486 (m, 4H, CH_2), 2.55 (m, 2H, CH_2); ^{13}C NMR ($CDCl_3$): 139.7 (m, *ipso* C), 137.9 (m, *ipso* C), 135.2 (m, *ipso* C), 134.7 (m), 134.3 (m, *ipso* C), 133.9 (m), 131.5 (m), 131.2 (m), 128.9 (m, *para* C), 128.7 (m, *para* C), 128.5 (m, *para* C), 128.0 (m), 127.7 (m, *para* C), 127.5 (m), 127.2 (m), 126.6 (m), 31.9 (m, CH_2), 24.6 (m, CH_2).

4.5. Preparation of trans-$RuCl(C{\equiv}CPh)(dppe)_2$ (**3a**)

A solution of [**2**]OTf (100 mg, 0.092 mmol) in CH_2Cl_2 (3 ml) was treated with phenylacetylene (10 μl, 0.09 mmol) and stirred at room temperature for 1 h. The solvent was removed *in vacuo* and the residue containing the crude vinylidene salt washed with hexane (2 × 10 ml) to remove any excess alkyne. The crude vinylidene salt was redissolved in dichloromethane (2 ml) and treated with a solution of $KOBu^t$ (35 mg) in methanol (5 ml), prompting the precipitation of a pale yellow solid, which was immediately collected by filtration and dried to give **3a** (72 mg, 75%). IR: $\nu(C{\equiv}C)$ 2072 cm^{-1}. ^{31}P NMR: δ 50.8 (s, PPh_2). ES-MS: *m/z* 1039 $[M-Cl+K+H]^+$.

4.6. Preparation of trans-$RuCl(C{\equiv}CC_6H_4OMe\text{-}4)(dppe)_2$ (**3b**)

Prepared in a similar fashion to that described for **3a** from [**2**]OTf (100 mg, 0.092 mmol), 1-ethynyl-4-anisole (11 μl, 0.09 mmol), the vinylidene being formed after 2 h a room temperature. After deprotonation, yellow **3c** was collected by filtration (42 mg, 43%). Crystals suitable for X-ray diffraction were obtained from CH_2Cl_2/hexane. IR: $\nu(C{\equiv}C)$ 2070 cm^{-1}. ^{31}P NMR: δ 50.9 (s, dppe). ES-MS: *m/z* 1069 $[M-Cl+K+H]^+$.

4.7. Preparation of trans-$RuCl(C{\equiv}CC_6H_4Me\text{-}4)(dppe)_2$ (**3c**)

Prepared in a similar fashion to that described for **3a** from [**2**]OTf (100 mg, 0.092 mmol), 1-ethynyl-4-toluene (11 μl, 0.09 mmol), the vinylidene being formed after 2 h a room temperature. After deprotonation, yellow **3c** was isolated (75 mg, 78%). Crystals suitable for X-ray diffraction were obtained from CH_2Cl_2/hexane and also THF/hexane. IR: $\nu(C{\equiv}C)$ 2073 cm^{-1}. ^{31}P NMR: δ 50.9 (s, PPh_2). ES-MS: *m/z* 1053, $[M-Cl+K+H]^+$.

4.8. Preparation of trans-$RuCl(C{\equiv}CC_6H_4C_5H_{11}\text{-}4)(dppe)_2$ (**3d**)

Prepared in a similar fashion to that described for **3a** from [**2**]OTf (100 mg, 0.092 mmol) and 4-pentyl phenylacetylene (18 μl, 0.09 mmol), the vinylidene being formed after 2 h at room temperature. After deprotonation **3d** was obtained as a yellow powder (86 mg, 84%). IR: $\nu(C{\equiv}C)$ 2071 cm^{-1}. ^{31}P NMR: δ 50.9 (s, PPh_2). ES-MS: *m/z* 1069, $[M-Cl]^+$.

4.9. Preparation of trans-RuCl(C≡CC$_6$H$_4$CO$_2$Me-4)(dppe)$_2$ (**3e**)

Prepared in a similar fashion to that described for **3a** from [**2**]OTf (100 mg, 0.092 mmol) and methyl 4-ethynylbenzoate (15 mg, 0.09 mmol), the vinylidene being formed after 2 h a room temperature. After deprotonation, **3e** was isolated as a yellow powder (66 mg, 66%). Crystals suitable for X-ray diffraction were obtained from THF/hexane. IR: ν(C≡C) 2065 cm^{-1}. ^{31}P NMR: δ 50.1 (s, PPh$_2$). ES-MS: *m/z* 1097, [M−Cl+K+H]$^+$.

4.10. Preparation of trans-RuCl(C≡CC$_6$H$_4$NO$_2$-4)(dppe)$_2$ (**3f**)

Prepared in a similar fashion to that described for **3a** from [**2**]OTf (100 mg, 0.092 mmol) and 4-nitro phenylacetylene (14 mg, 0.09 mmol) the vinylidene being formed after 6 h at room temperature. After deprotonation **3f** was obtained as a red powder (73 mg, 73%). IR: ν(C≡C) 2051 cm^{-1}. ^{31}P NMR: δ 49.7 (s, PPh$_2$). ES-MS: *m/z* 1084, [M−Cl+K+H]$^+$.

5. Supplementary material

CCDC 719111, 719112, 719113, 719114 and 719115 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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References

[1] D. Touchard, C. Morice, V. Cadierno, P. Haquette, L. Toupet, P.H. Dixneuf, J. Chem. Soc., Chem. Commun. (1994) 859.
[2] D. Touchard, P. Haquette, S. Guesmi, L. Le Pichon, A. Daridor, L. Toupet, P.H. Dixneuf, Organometallics 16 (1997) 3640.
[3] P. Haquette, D. Touchard, L. Toupet, P. Dixneuf, J. Organomet. Chem. 565 (1998) 63.
[4] C. Lebreton, D. Touchard, L. Le Pichon, A. Daridor, L. Toupet, P.H. Dixneuf, Inorg. Chim. Acta 272 (1998) 188.
[5] S. Rigaut, J. Perruchon, L. Le Pichon, D. Touchard, P.H. Dixneuf, J. Organomet. Chem. 670 (2003) 37.
[6] C.W. Faulkner, S.L. Ingham, M.S. Khan, J. Lewis, N.J. Long, P.R. Raithby, J. Organomet. Chem. 482 (1994) 139.
[7] S. Rigaut, F. Monnier, F. Mousset, D. Touchard, P.H. Dixneuf, Organometallics 21 (2002) 2654.
[8] B. Gomez-Lor, A. Santos, M. Ruiz, A.M. Echavarren, Eur. J. Inorg. Chem. (2001) 2305.
[9] D. Touchard, P. Haquette, A. Daridor, L. Toupet, P.H. Dixneuf, J. Am. Chem. Soc. 116 (1994) 11157.
[10] R.F. Winter, K.-W. Klinkhammer, S. Záliš, Organometallics 20 (2001) 1317.
[11] M. Uno, P.H. Dixneuf, Angew. Chem., Int. Ed. 37 (1998) 1714.
[12] S. Rigaut, J. Perruchon, S. Guesmi, C. Fave, D. Touchard, P.H. Dixneuf, Eur. J. Inorg. Chem. (2005) 447.
[13] O. Lavastre, J. Plass, P. Bachmann, S. Guesmi, C. Moinet, P.H. Dixneuf, Organometallics 16 (1997) 184.
[14] J.-L. Fillaut, N. Nagpal Dua, F. Geneste, L. Toupet, S. Sinbandhit, J. Organomet. Chem. 691 (2006) 5610.
[15] S.K. Hurst, N.T. Lucas, M.G. Humphrey, T. Isoshima, K. Wostyn, I. Asselberghs, K. Clays, A. Persoons, M. Samoc, B. Luther-Davies, Inorg. Chim. Acta 350 (2003) 62.
[16] S.K. Hurst, M.P. Cifuentes, A.M. McDonagh, M.G. Humphrey, M. Samoc, B. Luther-Davies, I. Asselberghs, A. Persoons, J. Organomet. Chem. 642 (2002) 259.
[17] J.P.L. Morrall, M.P. Cifuentes, M.G. Humphrey, R. Kellens, E. Robjins, I. Asselberghs, K. Clays, A. Persoons, M. Samoc, A.C. Willis, Inorg. Chim. Acta 359 (2006) 998.
[18] S.K. Hurst, M.G. Humphrey, T. Isoshima, K. Wostyn, I. Asselberghs, K. Clays, A. Persoons, M. Samoc, B. Luther-Davies, Organometallics 21 (2002) 2024.
[19] S.K. Hurst, M.G. Humphrey, J.P. Morrall, M.P. Cifuentes, M. Samoc, B. Luthur-Davies, G.A. Heath, A.C. Willis, J. Organomet. Chem. 670 (2003) 56.
[20] M. Samoc, N. Guthier, M.P. Cifuentes, F. Paul, C. Lapinte, M.G. Humphrey, Angew. Chem., Int. Ed. 45 (2006) 7376.
[21] G.T. Dalton, M.P. Cifuentes, S. Petrie, R. Stranger, M.G. Humphrey, M. Samoc, J. Am. Chem. Soc. 129 (2007) 11882.
[22] C.E. Powell, M.P. Cifuentes, J.P. Morrall, R. Stranger, M.G. Humphrey, M. Samoc, B. Luther-Davies, G.A. Heath, J. Am. Chem. Soc. 125 (2003) 602.
[23] M.P. Cifuentes, C.E. Powell, J.P. Morrall, A.M. McDonagh, N.T. Lucas, M.G. Humphrey, M. Samoc, S. Houbrechts, I. Asselberghs, K. Clays, A. Persoons, T. Isooshima, J. Am. Chem. Soc. 128 (2006) 10819.
[24] S.K. Hurst, M.P. Cifuentes, J.P.L. Morrall, N.T. Lucas, I.R. Whittall, M.G. Humphrey, I. Asselberghs, A. Persoons, M. Samoc, B. Luther-Davies, A.C. Willis, Organometallics 20 (2001) 4664.
[25] M.P. Cifuentes, C.E. Powell, M.G. Humphrey, G.A. Heath, M. Samoc, B. Luther-Davies, J. Phys. Chem. A 105 (2001) 9625.
[26] J.-L. Fillaut, J. Andries, J. Perruchon, J.P. Desvergne, L. Toupet, L. Fadel, B. Zouchoune, J.Y. Saillaird, Inorg. Chem. 46 (2007) 5922.
[27] J.-L. Fillaut, J. Andriès, R.D. Marwaha, P.-H. Lanoë, O. Lohio, L. Toupet, J.A.G. Williams, J. Organomet. Chem. 693 (2008) 228.
[28] M.A. Fox, R.L. Roberts, W.M. Khairul, F. Hartl, P.J. Low, J. Organomet. Chem. 692 (2007) 3277.
[29] O.F. Koentjoro, R. Rousseau, P.J. Low, Organometallics 20 (2001) 4502.
[30] M.I. Bruce, P.J. Low, K. Costuas, J.F. Halet, S.P. Best, G.A. Heath, J. Am. Chem. Soc. 122 (2000) 1949.
[31] B. Kim, J.M. Beebe, C. Olivier, S. Rigaut, D. Touchard, J.G. Kushmerick, X.Y. Zhu, C.D. Frisbie, J. Phys. Chem. C 111 (2007) 7521.
[32] N. Gauthier, G. Argouarch, F. Paul, M.G. Humphrey, L. Toupet, S. Ababou-Girard, H. Sabbah, P. Hapiot, B. Fabre, Adv. Mater. 20 (2008) 1952.
[33] A. Klein, O. Lavastre, J. Fielder, Organometallics 25 (2006) 635.
[34] C. Oliver, B.S. Kim, D. Touchard, S. Rigaut, Organometallics 27 (2008) 509.
[35] N. Gauthier, C. Oliver, S. Rigaut, D. Touchard, T. Roisnel, M.G. Humphrey, F. Paul, Organometallics 27 (2008) 1063.
[36] S. Rigaut, C. Olivier, K. Costuas, S. Choua, O. Fadhel, J. Massue, P. Turek, J.Y. Saillaird, P.H. Dixneuf, D. Touchard, J. Am. Chem. Soc. 128 (2006) 5859.
[37] S. Rigaut, L. Le Pichon, D. Touchard, P.H. Dixneuf, J.-C. Daran, Chem. Commun. (2001) 1206.
[38] Z. Wei, S. Guo, S.A. Kandrel, J. Phys. Chem. B 110 (2006) 21846.
[39] H. Qi, A. Gupta, B.C. Noll, G.L. Snider, Y. Lu, C. Lent, T.P. Fehlner, J. Am. Chem. Soc. 127 (2005) 15218.
[40] K. Onitsuka, N. Ohara, F. Takei, S. Takahashi, Dalton Trans. (2006) 3693.
[41] Q.Y. Hu, W.X. Lu, H.D. Tang, H.H.Y. Sung, T.B. Wen, I.D. Williams, G.K.L. Wong, Z. Lin, G. Jia, Organometallics 24 (2005) 3966.
[42] S. Guesmi, D. Touchard, P.H. Dixneuf, Chem. Commun. (1996) 2773.
[43] D. Touchard, P. Haquette, A. Daridor, A. Romero, P.H. Dixneuf, Organometallics 17 (1998) 3844.
[44] O. Lavastre, M. Even, P.H. Dixneuf, A. Pacreau, J.-P. Vairon, Organometallics 15 (1996) 1530.
[45] C.E. Powell, S.K. Hurst, J.P. Morrall, M.P. Cifuentes, R.L. Roberts, M. Samoc, M.G. Humphrey, Organometallics 26 (2007) 4456.
[46] S.K. Hurst, M.P. Cifuentes, M.G. Humphrey, Organometallics 21 (2002) 2353.
[47] N. Matsumi, Y. Chujo, O. Lavastre, P.H. Dixneuf, Organometallics 20 (2001) 2425.
[48] G.R. Whittell, I. Manners, Adv. Mater. 19 (2007) 3439.
[49] M. Samoc, J.P. Morrall, G.T. Dalton, M.P. Cifuentes, M.G. Humphrey, Angew. Chem., Int. Ed. 46 (2007) 731.
[50] C.E. Powell, J.P. Morrall, S.A. Ward, M.P. Cifuentes, E.G.A. Notaras, M. Samoc, M.G. Humphrey, J. Am. Chem. Soc. 126 (2004) 12234.
[51] A.M. McDonagh, M.G. Humphrey, M. Samoc, B. Luther-Davies, Organometallics 18 (1999) 5195.
[52] A.M. McDonagh, C.E. Powell, J.P. Morrall, M.P. Cifuentes, M.G. Humphrey, Organometallics 22 (2003) 1402.
[53] D. Touchard, S. Guesmi, L. Le Pichon, A. Daridor, P.H. Dixneuf, Inorg. Chim. Acta 280 (1998) 118.
[54] Z. Atherton, C.W. Faulkner, S.L. Ingham, A.K. Kakkar, M.S. Khan, J. Lewis, N.J. Long, P.R. Raithby, J. Organomet. Chem. 462 (1993) 265.
[55] M. Younus, N.J. Long, P.R. Raithby, J. Lewis, N.A. Page, A.J.P. White, D.J. Williams, M.C.B. Colbert, A.J. Hodge, M.S. Khan, D.G. Parker, J. Organomet. Chem. 578 (1999) 198.
[56] M. Bressan, P. Rigo, Inorg. Chem. 14 (1975) 2286.
[57] D. Weiss, P.H. Dixneuf, Organometallics 22 (2003) 2209.
[58] Y. Liu, C. Lagrost, K. Costuas, N. Tchouar, H. Le Bozec, S. Rigaut, Chem. Commun. (2008) 6117.
[59] M.A. Fox, B. Le Guennic, R.L. Roberts, T.E. Baines, D.S. Yufit, D. Albesa-Jove, J.F. Halet, F. Hartl, J.A.K. Howard, P.J. Low, J. Am. Chem. Soc. 130 (2008) 3566.
[60] D.J. Armitt, M.I. Bruce, M. Gaudio, N.N. Zaitseva, B.W. Skelton, A.H. White, B. Le Guennic, J.-F. Halet, M.A. Fox, R.L. Roberts, F. Hartl, P.J. Low, Dalton Trans. (2008) 6763.
[61] B. Chaudret, G. Commenges, R. Poilblanc, Dalton Trans. (1984) 1635.
[62] I.P. Evans, A. Spencer, G. Wilkinson, J. Chem. Soc., Dalton (1973) 204.
[63] M.T. Bautista, E.P. Cappellani, S.D. Drouin, R.H. Morris, C.T. Schweitzer, A. Sella, J. Zubkowski, J. Am. Chem. Soc. 113 (1991) 4876.
[64] L. Russo, J. Figueira, J. Rodrigues, K. Rissanen, Acta Crystallogr., Sect. E Struct. Rep. Online 62 (2006) m1154.
[65] B. Chin, A.J. Lough, R.H. Morris, C.T. Schweitzer, C. D'Agostino, Inorg. Chem. 33 (1994) 6278.
[66] Y. Nishibayashi, S. Takemoto, S. Iwai, M. Hidai, Inorg. Chem. 39 (2000) 5946.
[67] S.J. Higgins, A. La Pensée, J.M. Charnock, J. Chem. Soc., Dalton Trans. (2001) 902.

[68] J.R. Polam, L.C. Porter, J. Coord. Chem. 29 (1993) 109.
[69] N. Mantovani, M. Brugnati, L. Gonsalvi, E. Grigiotti, F. Laschi, L. Marvelli, M. Peruzzini, G. Reginato, R. Rossi, P. Zanello, Organometallics 24 (2005) 405.
[70] J. Chatt, R.G. Hayter, J. Chem. Soc. (1961) 896.
[71] (a) T.A. Stephenson, G. Wilkinson, J. Inorg. Nucl. Chem. 28 (1966) 1945;
(b) P.S. Hallman, T.A. Stephenson, G. Wilkinson, Inorg. Synth. 12 (1970) 237.
[72] (a) R. Mason, D.W. Meek, G.R. Scollary, Inorg. Chim. Acta 16 (1976) L11;
(b) M. Rohr, M. Günther, F. Jutz, J.-D. Grunwaldt, H. Emerich, W. von Beek, A. Baiker, Appl. Catal. A: Gen. 296 (2005) 238.
[73] I. Takei, Y. Nishibayashi, Y. Ishii, Y. Mizobe, S. Uemura, M. Hidai, J. Organomet. Chem. 679 (2003) 32.
[74] D.N. Cheredilin, F.M. Dolgushin, E.V. Balagurova, I.A. Godovikov, I.T. Chizhevsky, Russ. Chem. Bull. 53 (2004) 2086.
[75] A.A. Batista, L.A.C. Cordeiro, G. Olivia, Inorg. Chim. Acta 203 (1993) 185.
[76] A. Mezzetti, A. Del Zotto, P. Rigo, N. Pahor, J. Chem. Soc., Dalton Trans. (1989) 1045.
[77] J. Diez, M.P. Gamasa, J. Gimeno, Y. Rodgriguez, S. Garcia-Granda, Eur. J. Inorg. Chem. (2004) 2078.
[78] R.M. Stoop, C. Bauer, P. Setz, T.Y.H. Wong, A. Mezzetti, Organometallics 18 (1999) 5691.
[79] (a) I.E. Rachidi, O. Eisenstein, New J. Chem. 14 (1990) 671;
(b) D.L. Thorn, R. Hoffmann, New J. Chem. 3 (1979) 39.
[80] J.E. McGrady, T. Lovell, R. Stranger, M.G. Humphrey, Organometallics 16 (1997) 4004.
[81] C.D. Delfts, R. Stranger, M.G. Humphrey, A.M. McDonagh, J. Organomet. Chem. 607 (2000) 208.
[82] F. Paul, B.G. Ellis, M.I. Bruce, L. Toupet, T. Roisnel, K. Costuas, J.-F. Halet, C. Lapinte, Organometallics 25 (2006) 649.