Journal of Organometallic Chemistry 694 (2009) 2350–2358

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

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

Mark A. Fox, Jonathan E. Harris, Silvio Heider, Victor Pérez-Gregorio, Małgorzata E. Zakrzewska, Julian D. Farmer, Dmitry S. Yufit, Judith A.K. Howard, Paul J. Low *

Department of Chemistry, Durham University, South Rd, Durham DH1 3LE, UK

ARTICLE INFO

Article history:
Received 5 February 2009
Received in revised form 17 March 2009
Accepted 19 March 2009
Available online 27 March 2009

Keywords:
Ruthenium
Acetylide
Vinylidene

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].

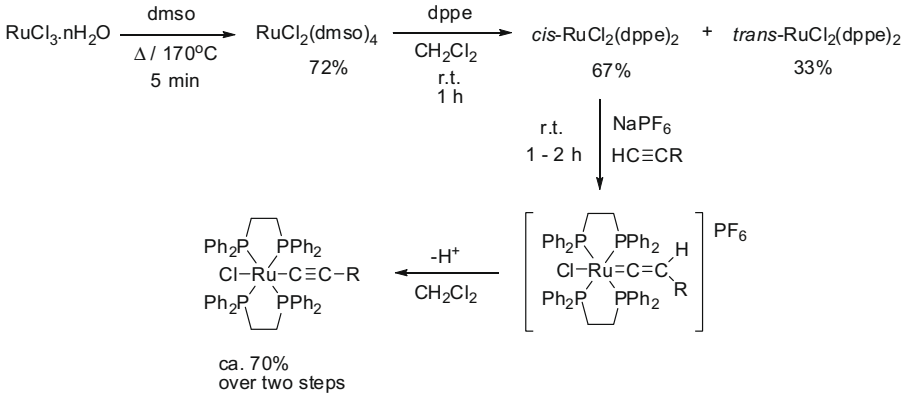
Complexes of the type *trans*-RuCl(C≡CR)(dppe)$_2$ are most often prepared from *cis*-$RuCl_2(dppe)_2$ (*cis*-**1**) using the method first reported by Dixneuf and colleagues (Scheme 1) [1]. Initial reaction between *cis*-**1** and $NaPF_6$ or similar salt in dichloromethane affords the five-coordinate 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.

* Corresponding author. Tel.: +44 (0)191 334 2114.
E-mail address: p.j.low@durham.ac.uk (P.J. Low).

0022-328X/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2009.03.033



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