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Note

Selectivity in alkynylation: the reaction between $Ru_2(LL)_4Cl$ and $Me_3SnC{\equiv}CR$ (LL = 2-anilinopyridine, 2-chloro- and 2-bromo-oxypyridine)

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Abstract

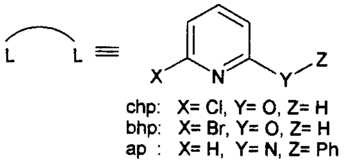
The reaction via a Pd(II)/CuI catalyst of phenylethynyl(trimethyl)stannane ($Me_3SnC{\equiv}CPh$) with $Ru_2(chp)_4Cl$, $Ru_2(bhp)_4Cl$ and $Ru_2(ap)_4Cl$ gave the organometallic terminal alkynes $Ru_2(chp)_4C{\equiv}CPh$ (**1**), $Ru_2(bhp)_4C{\equiv}CPh$ (**2**) and $Ru_2(ap)_4C{\equiv}CPh$ (**3**), respectively in 80–85% yields, without an attack on other functionalities. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Alkynyl complexes; Coupling reaction; Diruthenium; Oxopyridine

1. Introduction

New, gentler methods to prepare the $Ru_2{-}C{\equiv}CR$ moieties have been studied. Previously, these had been prepared by the direct reaction between the Ru_2L_4 halide, for example $Ru_2(ap)_4Cl$ (Hap = 2-anilinopyridine), and the lithiated acetylide [1]. Recently, however, Bear and coworkers have shown that this method may lead to multiple alkynylation steps and thus to unintended products [2].

An alternative method, well known to organic chemists [3], and more recently extended to inorganic compounds [4], is the Pd(II)-catalyzed reaction between the bromide or iodide of the target moiety and the trimethylstannyl derivative of the acetylide. Since this method was shown to be efficacious in the preparation of Fe acetylides [4], we have examined this reaction as a route to alkynyl derivatives of diruthenium complexes of the paddlewheel type. In addition, some of the ancillary ligands of the parent dimetal compound occasionally contain aromatic halides [5], as, for example, the 2-chloro-6-oxypyridine (chp) or 2-bromo-6-oxypyridine (bhp) (see below). Since a reaction between the aromatic halide function and the trimethylstannyl would be unwelcome, it was of interest to learn whether or not the alkynylation would occur preferentially at the Ru–halogen bond.



2. Experimental

2.1. General information

Reaction vessels were assembled and loaded with reactants under ambient air but all subsequent steps were carried out under an atmosphere of dry N_2 using standard vacuum-line technique. Solvents used were of commercial grade and were freshly distilled from an appropriate drying agent under an atmosphere of dry

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N_2 prior to use. $Pd(PPh_3)_2Cl_2$ was purchased from the Aldrich Chemical Co. and CuI from Fluka Chemical Co. and used as received. $Ru_2(chp)_4Cl$ (Hchp = 2-chloro-6-hydroxypyridine) [6], $Ru_2(ap)_4Cl$ (Hap = 2-anilinopyridine) [7], and $Me_3SnC{\equiv}CPh$ [8] were prepared according to literature methods. $Ru_2(bhp)_4Cl$ (Hbhp = 2-bromo-6-hydroxypyridine) was prepared by employing a method similar to that used for $Ru_2(chp)_4Cl$ [6].

Reaction products were identified via mass spectrometry. Due to the many stable isotopes of Ru, a situation compounded by the fact that two Ru atoms are present in each molecule, determination of accurate mass spectra was not deemed practical and not undertaken. However, isotopic distribution ratios matched the expected distributions. Due to the fact that molecules containing the Ru_2^{5+} core are paramagnetic, usually with three unpaired electrons, no NMR spectra were recorded. The IR spectra were performed on a Perkin–Elmer 16PC FT-IR spectrophotometer using KBr pellets. M.p.s were determined in sealed evacuated capillaries. Elemental analyses were done by Canadian Microanalytical Services, Ltd.

*2.2. Reaction between $Ru_2(ap)_4Cl$ and $Me_3SnC{\equiv}CPh$: formation of $Ru_2(ap)_4C{\equiv}CPh$ (**1**)*

2.2.1. Method A (1:1 stoichiometry)

$Ru_2(ap)_4Cl$ (0.051 g, 0.056 mmol), $Me_3SnC{\equiv}CPh$ (0.015 g, 0.057 mmol) and 1 mg each of $Pd(PPh_3)_2Cl_2$ and CuI were placed in a three-neck flask equipped with a magnetic stirring bar and a reflux condenser. The flask was evacuated and 10 ml of tetrahydrofuran (THF) was added by syringe, forming a dark green solution. This solution was heated at reflux overnight. No change in color was observed. The THF was removed at reduced pressure and the remaining solid was washed several times with hot toluene to remove any remaining free ligand as well as the Me_3SnCl formed in the reaction. The solid residue was redissolved in CH_2Cl_2 and precipitated by rapidly adding hexanes to give 0.048 g of $Ru_2(ap)_4C{\equiv}CPh$ (85% yield). IR (KBr, *v* (cm^{-1})): 3042, w; 3021, w; 2142, w; 1592, s; 1579, s; 1531, m; 1474, s; 1462, s; 1422, s; 1410, w; 1350, s; 1278, s; 1249, m; 1216, s; 1198, w; 1154, m; 1066, m; 1039, w; 1025, w; 1016, s; 916, s; 860, s; 755, s; 734, s; 696, s; 502, s. MS (+FAB/DP, 300°C, *m/z* (%)): 980 (15, $[M]^+$); 878 (100, $[M–C{\equiv}CPh]^+$); 709 (30, $[M–C{\equiv}CPh–ap]^+$). M.p. (*t*/°C): 155–158. Anal. Calc. for $C_{52}H_{41}N_8Ru_2$: C, 63.72; H, 4.21. Found: C, 63.24; H, 4.53.

2.2.2. Method B (1:2 stoichiometry)

This reaction was conducted as described for **1** above except that $Ru_2(ap)_4Cl$ (0.055 g, 0.06 mmol) and $Me_3SnC{\equiv}CPh$ (0.032 g, 0.12 mmol) were used to give 0.046 g of $Ru_2(ap)_4C{\equiv}CPh$ (83% yield). The IR spectrum of the product was indistinguishable from that obtained from reaction A. The mass spectrum for this compound did not show any peak higher than *m/z* = 980 $[M]^+$.

*2.3. Reaction between $Ru_2(chp)_4Cl$ and $Me_3SnC{\equiv}CPh$: formation of $Ru_2(chp)_4C{\equiv}CPh$ (**2**)*

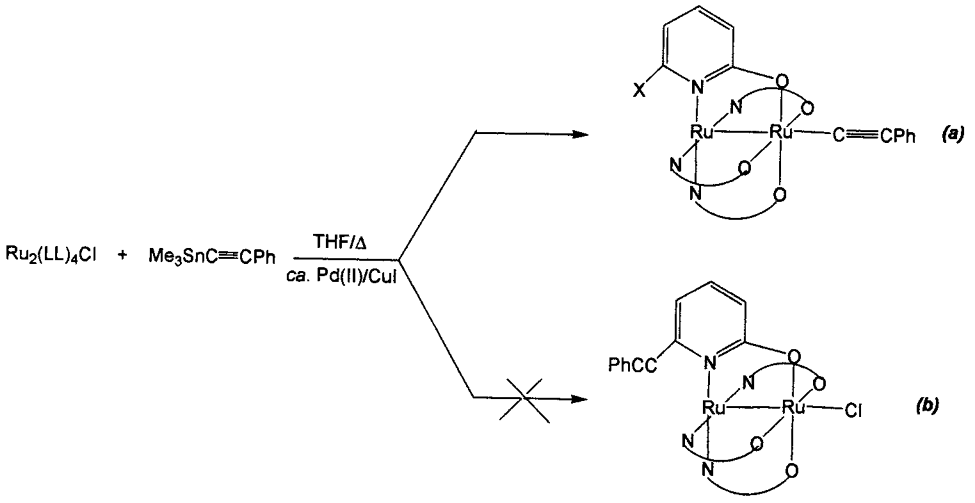
This reaction was carried out in the same man ner as that which yielded **1** above, except that $Ru_2(chp)_4Cl$ (0.053 g, 0.071 mmol) and $Me_3SnC{\equiv}CPh$ (0.019 g, 0.072 mmol) were used for the reaction. The solution changed gradually from purple to brown during reflux. Isolation of the product yielded 0.047 g $Ru_2(chp)_4C{\equiv}CPh$ (82% yield). IR (KBr, *v* (cm^{-1})): 2962, m; 2922, m; 2855, w; 2135, w; 1595, m; 1532, m; 1053, m; 1441, s; 1349, m; 1261, s; 1173, m; 1096, s; 1018, s; 931, w; 862, w; 807, s; 721, m; 698, w; 522, w; 474, w. MS (+FAB/DP, 300°C, *m/z* (%)): 817 (10, $[M]^+$); 716 (100, $[M–C{\equiv}CPh]^+$); 588 (35, $[M–chp–C{\equiv}CPh]^+$). M.p. (*t*/°C): 135–139. Anal. Calc. for, $C_{28}H_{17}O_4N_4Cl_4Ru_2$: C, 41.14; H, 2.09. Found: C, 41.95; H, 2.00.

*2.4. Reaction between $Ru_2(bhp)_4Cl$ and $Me_3SnC{\equiv}CPh$: formation of $Ru_2(bhp)_4C{\equiv}CPh$ (**3**)*

This reaction was also carried out in the same manner as that which yielded **1** above except that $Ru_2(bhp)_4Cl$ (0.055 g, 0.059 mmol) and $Me_3SnC{\equiv}CPh$ (0.016 g, 0.06 mmol) were used. The initially purple solution slowly became brown during reflux. Isolation of the product yielded 0.050 g of $Ru_2(bhp)_4C{\equiv}CPh$ (85% yield). IR (KBr, *v* (cm^{-1})): 2962, w; 2922, w; 2855, w; 2132, w; 1694, m; 1497, m; 1442, s; 1257, s; 1173, m; 1096, s; 1018, s; 1018, s; 926, w; 871, w; 807, s; 714, w; 514, w. MS (+FAB/DP, 300°C, *m/z* (%)): 995 (5, $[M]^+$; 894 (40, $[M–C{\equiv}CPh]^+$, 822 (100, $[M–bhp–C{\equiv}CPh]^+$). M.p. (*t*/°C): 134–138. Anal. Calc. for, $C_{28}H_{17}O_4N_4Br_4Ru_2$: C, 33.79; H, 2.09. Found: C, 33.21; H, 2.43.

3. Results and discussion

The reaction between equimolar amounts of $Ru_2(ap)_4Cl$ and $Me_3SnC{\equiv}CPh$ in THF at reflux, and in the presence of a catalytic amount of $Pd(PPh_3)_2Cl_2$ and CuI, led to the formation, in good yield, of a green product identified as $Ru_2(ap)_4C{\equiv}CPh$ (**1**) by mass spectrometry and comparison of its IR spectrum with that of an authentic sample [1]. The same product was obtained when an excess of $Me_3SnC{\equiv}CPh$ was used, as observed by mass spectrometry. We have also observed that in the absence of both catalysts, $Pd(PPh_3)_2Cl_2$ and CuI, $Me_3SnC{\equiv}CPh$ proved to be reactive towards



Scheme 1.

alkynylation of Ru(II)–Ru(III)–Cl compounds. However, reactions in presence of the catalysts were faster [9].

The formation of the desired Ru_2–C≡CPh bond was also observed when $Ru_2(chp)_4Cl$ or $Ru_2(bhp)_4Cl$ was used as reactant. By replacing the chlorine substituent in the equatorial ligand by bromine, one can further distinguish whether the halide that is replaced is the Cl on Ru or the aryl bromine. The mass spectrum showed a peak at 955 *m*/*z*, which can be attributed to $Ru_2(bhp)_4C{\equiv}CPh$ (**3**), and no peak corresponding to $Ru_2(bhp)_3(PhCCC_5H_3NO)Cl$ was observed, so it can be said with considerable certainty that the substitution occurs only at the Ru–Cl bond.

4. Conclusions

The conclusions from this work are summarized in Scheme 1, and are as follows: the reaction between $Me_3SnC{\equiv}CPh$ and the diruthenium chloride results in the formation of the desired Ru_2–C≡CR bond (Scheme 1(a)). We believe that this will also be true for other, similar dimetal complexes with axially bound halides. Furthermore, the axial halide is sufficiently reactive that the reaction occurs preferentially at this position, even when organic halogens are present (Scheme 1(b)). Finally, even in the presence of an excess of $Me_3SnC{\equiv}CPh$ reagent the reaction leads to the formation of only the compound containing one axially coordination acetylenic group, that is, no oxidation of the Ru_2 unit occurs.

Acknowledgements

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