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Oxidative addition of (bromoethynyl)benzene to κ²-acetylacetonatobis(trimethylphosphine)rhodium(I)

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ABSTRACT

The reaction of (bromoethynyl)benzene with κ²-acetylacetonatobis(trimethylphosphine)rhodium(I), $[Rh(acac)(PMe_3)_2]$ **1**, was followed by *in situ* ^{1}H and ^{31}P NMR spectroscopy. The kinetic product is that of *cis*-oxidative addition of the C–Br bond to Rh, and this species rearranges to the thermodynamically more stable *trans*-oxidative addition product *trans*-$[Rh(acac)(Br)(CCPh)(PMe_3)_2]$ **3**. The structures of both **1** and **3** have been determined by single-crystal X-ray diffraction.

1. Introduction

Our group has been interested in the synthesis of rhodium–acetylide complexes for many years. We have reported several examples of hydrido-acetylide and bis(acetylide) rhodium(III) complexes, including mono-, dinuclear and oligomeric rigid-rods [1] and rhodium(I)–acetylide [2] complexes, and have recently used the Rh(I) acetylides as precursors to prepare novel, highly fluorescent 2,5-bis(arylethynyl)rhodacyclopentadienes [3]. Typical syntheses of the rhodium acetylide complexes included oxidative addition of terminal alkynes to Rh(I) [1a], elimination of methane from Rh–Me complexes [1b,d,e,2], and deprotonation of hydrido-acetylide complexes by KOH [2]. Unsymmetrically substituted bis(acetylide)rhodium(III) were difficult to obtain in pure form via these synthetic pathways [1b] and the mechanism of the acetylide scrambling process has been studied in some detail [4]. While we were successful in isolating unsymmetrical donor–acceptor substituted platinum bis(acetylide) complexes for studies of their nonlinear optical properties [5], other methods to access related rhodium complexes are still required. Herein, we present the first step of a possible route to unsymmetrically substituted bis(acetylide)rhodium(III) complexes by oxidative addition of (bromoethynyl)benzene to κ²-acetylacetonatobis(trimethylphosphine) rhodium(I).

2. Experimental

2.1. General

All syntheses and purifications were performed in a nitrogen-filled Innovative Technology Inc. glovebox or using standard Schlenk techniques. $[RhCl_3 \cdot 3H_2O]$ was purchased from Precious Metals Online, Australia, and used without further purification. $[RhMe(PMe_3)_4]$ was synthesized according to a published method [6]. The compound (bromoethynyl)benzene was synthesized using a variation of a published method [7]. HPLC grade solvents (Fisher Scientific and J.T. Baker) were nitrogen saturated, dried and deoxygenated using an Innovative Technology Inc. Pure-Solv 400 Solvent Purification System, and further deoxygenated using the freeze–pump–thaw method. THF-d_8 and C_6D_6 were purchased

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from Goss Scientific, dried with potassium/benzophenone (THF-d_8) or with sodium or potassium (C_6D_6), and vacuum transferred into sealed vessels.

NMR spectra were recorded using Varian Mercury 400 (^{1}H: 400 MHz), Bruker Avance 400 (^{1}H: 400 MHz), Varian Inova 500 (^{1}H: 500 MHz), Varian VNMRS-600 (^{1}H: 600 MHz) or Varian DD-700 (^{1}H: 700 MHz) spectrometers. ^{1}H and ^{13}C NMR chemical shifts are reported relative to TMS and were referenced via residual proton or carbon resonances, respectively, of the deuterated solvent employed, whereas ^{31}P{^{1}H} NMR spectra were referenced to external 85% H_3PO_4. Elemental analysis was carried out using an Exeter Analytical Inc. CE-440 elemental analyzer in the Department of Chemistry at Durham University. Mass spectrometric determinations were obtained using either a MALDI ToF Applied Biosystems Voyager-DE STR mass spectrometer, or by ES using a Thermo-Finnigan LTQ FT spectrometer operating in positive ion mode.

2.2. Preparation of *κ*^{2}-acetylacetonatobis(trimethylphosphine) rhodium(I) **1**

Acetylacetone (0.0095 g, 0.095 mmol) in THF (1 mL) was added to a stirred solution of [$RhMe(PMe_3)_4$] (0.0401 g, 0.095 mmol) in THF (1 mL), and the resulting solution was stirred at room temperature for 5 min, after which the solvent was removed *in vacuo*. THF (2 mL) was added, the solution was stirred for 2 min and the solvent was removed *in vacuo*. This cycle was repeated three more times, after which the solvent was removed to give **1** as a yellow solid. The product was recrystallized in a Young's tube via slow diffusion of a layer of hexane into a concentrated THF solution of **1**. Yield: 0.029 g, 86%. ^{1}H NMR (400 MHz, C_6D_6) δ: 5.36 (s, 1H), 1.83 (s, 6H), 1.13 (s, 18H). ^{13}C{^{1}H} NMR (100.60 MHz, THF-d_8) δ: 184.5, 99.6, 27.8, 19.1 (br). ^{31}P{^{1}H} NMR (202.33 MHz, in 10% C_6D_6/THF at 203 K) δ: 5.8 (d, J_{Rh-P} = 185 Hz). Anal. Calcd. for $C_{11}H_{25}P_2O_2Rh$: C, 37.30; H, 7.11. Found: C, 37.10; H, 7.38%. MS (ES$^+$) m/z = 354 [M$^+$].

2.3. Preparation of *κ*^{2}-acetylacetonatobromo(phenylacetylide) bis(trimethylphosphine)rhodium(III) **3**

Compound **1** (20 mg, 0.056 mmol) and (bromoethynyl)benzene (10.2 mg, 0.056 mmol) were dissolved in 0.7 mL of THF-d_8 in an NMR tube at room temperature. The reaction was followed *in situ* by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy for 30 days, by which time 90% conversion was observed. Crystals were obtained by slow diffusion of a layer of hexane into the THF-d_8 solution in the NMR tube. ^{1}H NMR (400 MHz, C_6D_6) δ: 7.12 (m, 4H), 7.01 (t, J = 12 Hz, 1H), 5.23 (s, 1H), 1.79 (s, 6H), 1.74 (vt, $J_{apparent}$ = 13 Hz, 18H) ppm. ^{13}C{^{1}H} NMR (100.60 MHz, THF-d_8) δ: 185.8, 132.9, 129.7, 128.6, 125.8, 101.7, 99.3, 98.0, 28.0 (t, J = 5 Hz), 16.5 (m) ppm. ^{31}P{^{1}H} NMR (283.26 MHz, THF-d_8) δ: 15.6 (d, J_{Rh-P} = 115 Hz) ppm.

2.4. X-ray structure determinations

Intensity data ($2\theta \leq 60°$) were collected at T = 120 K on Bruker 3-circle diffractometers with CCD area detectors SMART 1000 (**1**) and SMART 6000 (**3**), using graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The data were corrected for absorption by numerical integration (**1**) or empirical method based on Laue equivalents (**3**) [8]. The structures were solved by direct methods and refined by full-matrix least squares, using SHELXTL [9] and OLEX2 [10] software. Crystal data and other experimental parameters are listed in Table 1.

Table 1
Crystal data for **1** and **3**.

Compound	**1**	**3**
Formula	$C_{11}H_{25}O_2P_2Rh$	$C_{19}H_{30}BrO_2P_2Rh$
Formula weight	354.16	535.19
Size (mm)	0.45 × 0.44 × 0.32	0.57 × 0.41 × 0.35
Crystal system	Tetragonal	Monoclinic
Space group	$P\overline{4}\,2_1c$ (#114)	$P2_1/c$ (#14)
a (Å)	18.090(2)	18.0504(8)
b (Å)	18.090(2)	8.4293(5)
c (Å)	10.1741(14)	14.6450(9)
β (°)	90	91.075(7)
V (Å^3)	3329.6(8)	2227.9(2)
Z	8	4
D_{calc} (g cm^{-3})	1.413	1.596
μ, mm^{-1}	1.21	2.71
Reflns total/unique/obsd	33,857/4820/4693	39,527/6499/6117
R_{int}	0.023	0.020
R_1 [$I > 2\sigma(I)$], wR_2 (all data)	0.015, 0.036	0.016, 0.038
CCDC dep. no.	902096	902097

3. Results and discussion

The reaction of **1** with (bromoethynyl)benzene (**2**) in THF-d_8 was followed *in situ* by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy over the course of 30 days. The structure of the final product **3** was confirmed by single-crystal X-ray diffraction (Fig. 1) *vide infra*, and NMR spectroscopy. Thus, **3** is an octahedral rhodium(III) complex with *trans* disposed bromo and phenylacetylide ligands, resulting from the oxidative addition of (bromoethynyl)benzene to the Rh(I) center (Scheme 1). Following the reaction by ^{31}P{^{1}H} NMR spectroscopy allowed the identification of an intermediate in the formation of **3**. Within 10–15 min of addition of (bromoethynyl) benzene to a THF-d_8 solution of **1**, the doublet in the ^{31}P NMR spectrum of **1** (5.8 ppm, J_{Rh-P} = 185 Hz) disappeared, and a series of new signals appeared, principally two doublets of doublets at 17.6 (J_{Rh-P} = 119 Hz, J_{P-P} = 27 Hz) and 14.0 ppm (J_{Rh-P} = 115 Hz, J_{P-P} = 27 Hz), in a 1:1 intensity ratio. The coupling pattern and the coupling constants are indicative of two non-equivalent, *cis*-disposed trimethylphosphine ligands. The ^{1}H NMR spectrum also shows a major species displaying doublet signals for two trimethylphosphines at 1.77 (J_{H-P} = 12 Hz) and 1.49 ppm (J_{H-P} = 12 Hz), respectively, integrating for nine protons each. Furthermore, two singlets at 1.91 and 1.84 ppm, each integrating for three protons, are attributed to non-equivalent methyl groups on the acac ligand. As the reaction proceeds, these signals gradually decrease and disappear, while those of **3** increase, the reaction reaching 90% conversion in 30 days. The intermediate can be identified as an isomer of **3** having the bromo and acetylide ligands *cis* to each other, *i.e.*, **4** or **4′**, of which **4** is more probable based on the ^{31}P NMR spectroscopic data. Thus, the similarity of the two ^{31}P NMR shifts and, especially, the values of the Rh–P coupling constants, suggest that both PMe_3 ligands are *trans* to weak trans-influence ligands, *i.e.*, Br and acac, rather than to the stronger trans-influence acetylide ligand. After 30 days, in addition to **3** (90%), ca. 5% of **4** remained, along with very small amounts of two unidentified Rh(III) species, indicated by doublets at 11.1 ppm (J_{Rh-P} = 113 Hz, 3%) and −2.4 ppm (J_{Rh-P} = 90 Hz, 2%) in the ^{31}P NMR spectrum.

It is clear, therefore, that in the case above, namely involving oxidative addition of a bromoalkyne to a d^8-Rh(I) center, the kinetic oxidative addition product is a *cis*-complex which rearranges slowly to the thermodynamically more stable *trans*-product. This suggests, but does not prove, that the oxidative addition reaction is concerted. Interestingly, oxidative addition of haloalkynes to d^{10}-[$Ni(PMe_3)_4$] has been shown to give either 5-coordinate [$Ni(CCR)(PMe_3)_4$]X salts, or [$Ni(CCR)(X)(PMe_3)_3$]