



Reactions of phenylacetylene and *p*-tolylacetylene with a five-coordinate Ru^{II} complex



Erin S.F. Ma, Brian O. Patrick, Brian R. James*

Department of Chemistry, The University of British Columbia, Vancouver, BC V6T 1Z1, Canada

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ABSTRACT

The acetylenes R'C≡CH react with the known 5-coordinate, green, square-pyramidal *trans*-RuCl₂-(P–N)(PR₃) complexes (R', R = Ph, *p*-tolyl; P–N = *o*-diphenylphosphino-*N,N'*-dimethylaniline) in CH₂Cl₂ solution to form the orange vinylidene derivatives, *cis*-RuCl₂(P–N)(PR₃)(C=C(H)R') (**2**); this is a well-known type reaction, but is the first to involve a bidentate P–N ligand, and convert a 5-coordinate precursor to a 6-coordinate product. Crystal structure and ³¹P{¹H} NMR data for the R = R' = Ph complex (**2a**), extend significantly an established linear correlation between the Ru–P bond length (within the P–N ligand) and the ³¹P{¹H} chemical shift of this P-atom. Complex **2a** reacts with H₂S to form the thioaldehyde species *cis*-RuCl₂(P–N)(PPh₃)(SCHCH₂Ph), and reacts with H₂O to form poorly characterized carbonyl species; the reactivity resembles that of an earlier studied Ru-PNP species, where PNP = Me(CH₂)₂N[(CH₂)₂PPh₂]₂.

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1. Introduction

Our group has shown that the 5-coordinate, square pyramidal complexes *trans*-RuCl₂(P–N)(PR₃) (R = Ph, *p*-tolyl; P–N = *o*-diphenylphosphino-*N,N'*-dimethylaniline) readily bind, under mild conditions, a wide range of small molecules (L) to form the 6-coordinate species RuCl₂(P–N)(PR₃)L (L = H₂, N₂, CO, N₂O, NH₃, H₂O, alcohols, H₂S, thiols) in which the chloride ligands are either *cis* or *trans*, as shown in Scheme 1 [1,2].

The use of crystallographic and ³¹P{¹H} NMR data for these 1:1 adducts (with either *cis* or *trans* chlorides) revealed an excellently linear correlation between Ru–P bond length (within the P–N ligand) and chemical shift of this P-atom; more specifically, there is an inverse dependence of the shift with increase in bond length [2]. In this current paper, the studies are extended to reactions of the acetylenes R'C≡CH (R' = Ph, *p*-tolyl) with the *trans*-RuCl₂-(P–N)(PR₃) complexes to form the vinylidene species *cis*-RuCl₂-(P–N)(PR₃)(C=C(H)R'). Such 1-alkyne to vinylidene tautomerization chemistry at Ru^{II} centers was first reported in 1978 [3], and continues to attract organometallic interest because of its relevance in catalyzed reactions of hydrocarbons [4]. Thus, such chemistry is well-established, but we are unaware of a previous example where a 5-coordinate species reacts to form a 6-coordinate product, and where a bidentate P–N ligand system is involved; the closest analogy to our system, and which prompted our selection of acetylenes, was one from Bianchini's group (see

Results and discussion) [5]. The new X-ray crystallographic and solution ³¹P{¹H} data are of significance in extending the correlation noted above.

2. Experimental

2.1. General

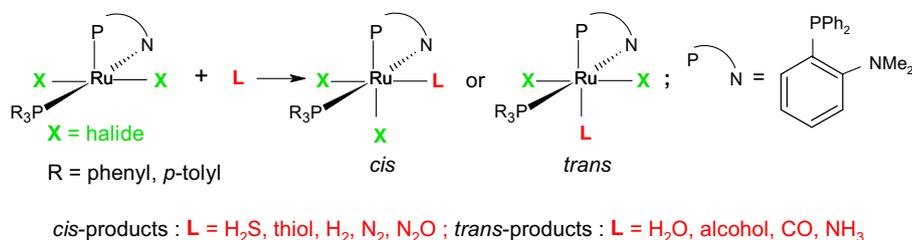
All manipulations were carried out under an oxygen-free, Ar atmosphere at room temperature (r.t., ~22 °C) using Schlenk techniques. The phenyl- and *p*-tolyl-acetylenes were Fisher Scientific products, and were used as received. The *trans*-RuCl₂(P–N)(PR₃) complexes (R = Ph, **1a**; *p*-tolyl, **1b**) were prepared by the reported methods [1c,d], the precursor RuCl₃·xH₂O being donated by Colonial Metals, Inc. Analytical grade solvents and CDCl₃ were purified and stored by standard methods [2], and the Ar (HP grade, Matheson Gas Co) was dried by passage through CaSO₄. Details on the measurements of NMR and IR spectra were provided recently [2], with *J* values reported in Hz, and *s* = singlet, *d* = doublet, *m* = multiplet, *br* = broad. Microanalyses were performed in this department on a Carlo Erba 1106 instrument.

2.2. *Cis*-RuCl₂(P–N)(PPh₃)(C=C(H)Ph) (**2a**)

Addition of a solution of PhC≡CH (0.60 mL, 5.46 mmol) in CH₂Cl₂ (3 mL) to the green solution of **1a** (385.0 mg, 0.52 mmol) in CH₂Cl₂ (20 mL) generated an orange solution, which was refluxed at 40 °C for 2 h. The solution was then cooled to r.t. and stirred for ~15 h; the volume was then reduced to ~5 mL and hexanes

* Corresponding author. Tel.: +1 604 822 6645; fax: +1 604 822 2847.

E-mail address: brj@chem.ubc.ca (B.R. James).



Scheme 1. Reactivity of *trans*-RuCl₂(P-N)(PR₃) toward small molecules (L).

(20 mL) was then added to give a dark orange precipitate, that was collected, washed with hexanes (4 x 5 mL), and dried under a flow of Ar. Yield: 380 mg, 86%. *Anal. Calc.* for C₄₆H₄₁NCl₂P₂Ru: C, 65.64; H, 4.91; N, 1.66. Found: C, 65.45; H, 4.92; N, 1.55%. ³¹P{¹H} NMR (CDCl₃): δ 37.85 (d), 36.40 (d); ²J_{PP} = 26.5. ¹H NMR (CDCl₃): δ 8.2–6.2 (34H, m, Ph), 3.60 (3H, s, NMe), 3.11 (3H, s, NMe), 2.43 (1H, d of d, =CH, ⁴J_{HP} ~ 6). ¹³C{¹H} NMR (CDCl₃): δ 358.2 (pseudo t, C_α, ²J_{CP} = 18.6), 111.0 (s, C_β), 57.26 (s, C_{Me}), 52.52 (s, C_{Me}) – see [Scheme 2](#) for labeling of C-atoms.

The red-orange crystals of **2a**, which deposited over 2 days on evaporation of CDCl₃ from the solution in the NMR tube, were analyzed crystallographically (Section 2.7).

2.3. *Cis*-RuCl₂(P-N)(P(*p*-tolyl)₃)(=C=CHPh) (**2b**)

Complex **2b** was prepared as a dark orange solid in the same manner as described for **2a** but using **1b** as precursor (390 mg, 0.50 mmol). Yield: 350 mg, 80%. *Anal. Calc.* for C₄₉H₄₇NCl₂P₂Ru: C, 66.59; H, 5.36; N, 1.58%. Found: C, 66.43; H, 5.29; N, 1.55%. ³¹P{¹H} NMR (CDCl₃): δ 35.86 (d), 32.96 (d); ²J_{PP} = 26.6. ¹H NMR (CDCl₃): δ 7.8–6.2 (31H, m, Ph), 3.54 (3H, s, NMe), 3.08 (3H, s, NMe), 2.40 (1H, d of d, =CH, ⁴J_{HP} ~ 6), 2.16 (9H, s, *p*-CH₃).

2.4. *Cis*-RuCl₂(P-N)(PPh₃)(=C=CH-C₆H₄-CH₃) (**2c**)

The dark yellow **2c** was made as described for **2a** but using five equiv. of 4-ethynyltoluene (*p*-tolylacetylene). Yield: 270 mg, 61%. *Anal. Calc.* for C₄₇H₄₃NCl₂P₂Ru: C, 65.96; H, 5.06; N, 1.64. Found: C, 65.75; H, 5.02; N, 1.52%. ³¹P{¹H} NMR (CDCl₃): δ 38.33 (d), 36.72 (d); ²J_{PP} = 26.1. ¹H NMR (CDCl₃): δ 8.1–6.1 (33H, m, Ph), 3.59 (3H, s, NMe), 3.08 (3H, s, NMe), 2.43 (1H, dd, =CH, ⁴J_{HP} ~ 6), 2.16 (3H, s, C₆H₄-CH₃).

2.5. *Cis*-RuCl₂(P-N)(PPh₃)(SCH₂CH₂Ph) (**3**)

H₂S was bubbled through a solution of **2a** (100 mg, 0.12 mmol) in CD₂Cl₂ (15 mL) under reflux for 5 h, the original orange solution becoming brown. The solution was then concentrated to ~5 mL and hexanes (15 mL) was added to precipitate a brown solid that was collected, washed with hexanes (2 x 10 mL), and dried under Ar. Yield: 65 mg, but analytically pure **3** was not obtained even after reprecipitations from CH₂Cl₂/hexanes. ³¹P{¹H} NMR (CDCl₃): δ 59.61 (d, P-N), 42.36 (d, PPh₃); ²J_{PP} = 28.2. ¹H NMR (CDCl₃): δ 8.7–6.1 (34H, m, Ph), 3.04 (3H, s, NMe), 2.52 (3H, s, NMe), 3.18 (1H, t, S=CH, ³J_{HH} = 15), 1.30 (2H, d, CH₂, ³J_{HH} = 15).

2.6. Reaction of **2a** with H₂O

H₂O (1 mL) was added to a solution of **2a** (100 mg, 0.12 mmol) in CH₂Cl₂ (15 mL), and the mixture was refluxed for 5 h during which time the solution became brown. Addition of hexanes (20 mL) precipitated a brown solid that consisted of two major components in about a 1:1 ratio, as suggested by ³¹P{¹H} NMR data in CDCl₃: δ 44.57 (br), 38.28 (br), perhaps due to RuCl(P-N)(PPh₃)-(CH₂Ph)(CO) (**4**), and δ 50.55 (br), 18.74 (br), which is possibly RuCl₂(P-N)(PPh₃)(CO) (**5**) (see Section 3, [Scheme 4](#)). ¹H NMR: δ 8.5–6.0 (m), 3.5–1.2 (overlapping br signals). IR (KBr): ν_{CO} 2046, 1990 cm⁻¹. Species **4** and **5** were not separated.

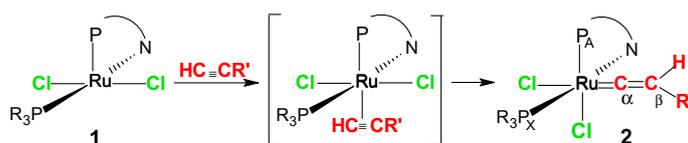
2.7. X-ray crystallographic analysis

X-ray analysis of **2a** was carried out at 295 K on a Rigaku AFC6S diffractometer with graphite-monochromated CuKα radiation (1.54178 Å). Some crystallographic data for **2a** are: 4271 total reflections, 4008 unique (*R*_{int} = 0.066), 6132 observed [*I* > 2σ(*I*)], *R*₁ = 0.043; *wR*₂ = 0.094; GOF = 1.07; residual density = -0.87 e/Å³. The structure was solved by direct methods [6], with all refinements being performed using the SHELXL-2012 program [7] via the Olex2 interface [8]. All non H-atoms were refined anisotropically, and all other H-atoms were placed in calculated positions. The ORTEP plot and selected bond lengths and angles are shown in [Fig. 1](#) and [Table 1](#), while the full experimental parameters and details of the structure are given in CIF format in the [Supplementary information](#).

3. Results and discussion

The green solution of the *trans*-RuCl₂(P-N)(PR₃) complexes (R = Ph, **1a**; *p*-tolyl, **1b**) and a 10-fold excess of the HCCR' acetylenes (R' = Ph, *p*-tolyl) react at reflux temperature in CH₂Cl₂ to give an orange solution from which dark orange, vinylidene complexes of the type *cis*-RuCl₂(P-N)(PR₃)(C=C(H)R') (**2a–c**) are readily isolated, see [Scheme 2](#). Presumably the acetylene would initially bind in the vacant site, trans to the P-atom of the P-N ligand (P_A), to give an intermediate with *trans*-chlorides, with a subsequent isomerization needed to form **2** that contains *cis*-chlorides (see also [Scheme 3](#), later).

Crystallographic data for *cis*-RuCl₂(P-N)(PPh₃)(C=C(H)Ph) (**2a**) ([Fig. 1](#)), together with essentially identical, key NMR data for **2a–c**, reveal a pseudo octahedral structure containing *cis* Cl-atoms, with P_A and the vinylidene group *trans* to the chlorides; the PR₃



Scheme 2. Reaction of **1** [R = Ph (**1a**); *p*-tolyl (**1b**)] with acetylenes to form **2** [R = R' = Ph (**2a**); R = *p*-tolyl, R' = Ph (**2b**); R = Ph, R' = *p*-tolyl (**2c**)].

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