



Protonation of metal–metal bonds in nitrosyl-bridged diruthenium complexes



Tobias Mayer, Hans-Christian Böttcher*

Department Chemie, Ludwig-Maximilians-Universität München, Butenandtstrasse 5-13, 81377 München, Germany

ARTICLE INFO

Article history:

Received 17 October 2013

Accepted 11 December 2013

Available online 18 December 2013

Dedicated to Professor Helmut Werner on the Occasion of his 80th Birthday.

Keywords:

Ruthenium

Carbonyl

Nitrosyl ligands

Phosphanido-bridged

Crystal structure

ABSTRACT

The addition reaction of a proton towards the nitrosyl-bridged diruthenium complexes $[\text{Ru}_2(\text{CO})_4(\mu\text{-NO})(\mu\text{-P}^t\text{Bu}_2)(\mu\text{-P}^{\wedge}\text{P})]$ ($\text{P}^{\wedge}\text{P} = \text{Me}_2\text{PCH}_2\text{PMe}_2$, dmpm, **1b**; $\text{P}^{\wedge}\text{P} = \text{Ph}_2\text{PC}(\text{=CH}_2)\text{PPh}_2$, dppen, **1c**; $\text{P}^{\wedge}\text{P} = \text{Ph}_2\text{PN}(\text{H})\text{PPh}_2$, dppa, **1d**) has been investigated. The species **1b–d** exhibit an enhanced metal basicity and react spontaneously with a proton (from HBF_4) in diethyl ether to afford the corresponding oxidative addition products $[\text{Ru}_2(\text{CO})_4(\mu\text{-NO})(\mu\text{-H})(\mu\text{-P}^t\text{Bu}_2)(\mu\text{-P}^{\wedge}\text{P})]\text{BF}_4$ (**2b–d**) in good yields. The molecular structures of **2b–d** were confirmed by X-ray diffraction studies revealing a shortening of the metal–metal bond upon protonation in each case.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Recently we described the synthesis and molecular structures of some new nitrosyl-bridged dimetal complexes $[\text{Ru}_2(\text{CO})_4(\mu\text{-NO})(\mu\text{-P}^t\text{Bu}_2)(\mu\text{-P}^{\wedge}\text{P})]$ (**1**, $\text{P}^{\wedge}\text{P} =$ diphosphanes and *N*-substituted bis(diphenylphosphanyl)amines, respectively) [1]. The bridging nitrosyl ligands were introduced in the coordinatively unsaturated species $[\text{Ru}_2(\text{CO})_4(\mu\text{-H})(\mu\text{-P}^t\text{Bu}_2)(\mu\text{-P}^{\wedge}\text{P})]$ by hydride abstraction using the nitrosylating agent diazald (*N*-methyl-*N*-nitroso-*p*-toluenesulfonamide). At first we found that this reaction principle was successful in the case of the coordinatively unsaturated compound $[\text{Ru}_2(\text{CO})_4(\mu\text{-H})(\mu\text{-P}^t\text{Bu}_2)(\mu\text{-dppm})]$ (dppm = $\text{Ph}_2\text{PCH}_2\text{PPh}_2$) affording the complex $[\text{Ru}_2(\text{CO})_4(\mu\text{-NO})(\mu\text{-P}^t\text{Bu}_2)(\mu\text{-dppm})]$ (**1a**). The latter species reacted spontaneously with HBF_4 in diethyl ether resulting in the complex salt $[\text{Ru}_2(\text{CO})_4(\mu\text{-H})(\mu\text{-NO})(\mu\text{-P}^t\text{Bu}_2)(\mu\text{-dppm})]\text{BF}_4$ (**2a**) [2]. Since we observed a general shortening of the metal–metal bonding distance during protonation reactions in dinuclear metal complexes [3], we were also interested in such investigations including the new nitrosyl-bridged compounds $[\text{Ru}_2(\text{CO})_4(\mu\text{-NO})(\mu\text{-P}^t\text{Bu}_2)(\mu\text{-P}^{\wedge}\text{P})]$ ($\text{P}^{\wedge}\text{P} = \text{Me}_2\text{PCH}_2\text{PMe}_2$, dmpm, **1b**; $\text{P}^{\wedge}\text{P} = \text{Ph}_2\text{PC}(\text{=CH}_2)\text{PPh}_2$, dppen, **1c**; $\text{P}^{\wedge}\text{P} = \text{Ph}_2\text{PN}(\text{H})\text{PPh}_2$, dppa, **1d**). Oxidative additions of protons towards metal–metal bonds play an important role in studies on bioinorganic model complexes

including [NiFe] and [Fe₂] hydrogenases, whereas the nature of metal–metal bonds in such systems seems to be questionable [4]. Very recently some investigations were reported which support the importance of the formation of a metal–metal bond in the light-induced state of [NiFe] hydrogenases [5]. In this paper we report some new results on investigations in the field of protonation reactions of the metal–metal bond in nitrosyl-bridged diruthenium complexes which confirm in these cases furthermore the usually observed bond shortening effect upon the oxidative addition of a proton.

2. Experimental

2.1. General considerations

All manipulations were performed under an atmosphere of dry nitrogen using conventional Schlenk techniques. Solvents were dried over sodium-benzophenone ketyl or molecular sieves and were distilled under argon prior to use. Chemicals were purchased commercially from ABCR. The ligands dmpm, dppen, and dppa were obtained from ABCR. The compounds **1b–d** were prepared as reported recently [1]. IR spectra were recorded as solid with a JASCO FT/IR-460 plus spectrometer equipped with an ATR unit. NMR spectra were obtained using Jeol Eclipse 270 and 400 instruments operating at 270 and 400 (¹H) and at 109 and 161 MHz (³¹P), respectively. Chemical shifts are given in ppm from SiMe₄ (¹H) or

* Corresponding author. Tel.: +49 89218077422; fax: +49 89218077407.
E-mail address: hans.boettcher@cup.uni-muenchen.de (H.-C. Böttcher).

85% H₃PO₄ (³¹P). Microanalyses (C, H, N) were performed by the Microanalytical Laboratory of the Department of Chemistry, LMU Munich, using a Heraeus Elementar Vario EI instrument.

2.2. Synthesis of [Ru₂(CO)₄(μ-NO)(μ-H)(μ-P^tBu₂)(μ-P[^]P)]BF₄ (P[^]P = dmpm, **2b**; dppen, **2c**; dppa, **2d**)

In a typical experiment, a solution of the corresponding complex **1b–d** (0.22 mmol) in diethyl ether (15 mL) was treated with HBF₄ (51% in diethyl ether, 0.22 mmol, 59.2 μL) at room temperature. After rigorous stirring for 1 h the yellow-green precipitate was filtered off, washed with diethyl ether, and dried in vacuo. Yellow-green crystals suitable for X-ray diffraction were grown in each case by slow diffusion of diethyl ether into a dichloromethane solution of the complex salt at room temperature overnight.

2b: Yield: 120 mg (87%). *Anal. Calc.* for C₁₇H₃₃BF₄NO₅P₃Ru₂ (713.32): C, 28.62; H, 4.66; N, 1.96. Found: C, 28.36; H, 4.69; N, 2.15%. IR (solid): ν (CO): 2060 m, 2029s, 2012s, 1978vs; ν (NO): 1539vs. ¹H NMR (400 MHz, CD₂Cl₂): δ 1.89–1.85 (m, 6H, PCH₃), 1.63 (d, 9H, ³J_{PH} = 15.3 Hz, t-C₄H₉), 1.65–1.60 (m, 2H, CH₂), 1.52–1.45 (m, 6H, PCH₃), 1.10 (d, 9H, ³J_{PH} = 15.0 Hz, t-C₄H₉), –9.63 (m, 1H, μ-H). ³¹P{¹H} NMR (162 MHz, CD₂Cl₂): δ 170.9 (t, ²J_{PP} = 129.0 Hz, μ-P^tBu₂), 23.7 (d, ²J_{PP} = 129.0 Hz, μ-dmpm).

2c: Yield: 176 mg (83%). *Anal. Calc.* for C₃₈H₄₁BF₄NO₅P₃Ru₂ (973.61): C, 46.88; H, 4.24; N, 1.44. Found: C, 47.16; H, 4.19; N, 1.35%. IR (solid): ν (CO): 2038s, 2006s; ν (NO): 1547s. ¹H NMR (400 MHz, CD₂Cl₂): δ 7.60–7.09 (m, 20H, C₆H₅), 6.54 (t, 2H, ³J_{PH} = 21.4 Hz, =CH₂), 1.77 (d, 9H, ³J_{PH} = 15.9 Hz, t-C₄H₉), 1.18 (d, 9H, ³J_{PH} = 15.3 Hz, t-C₄H₉), –8.37 (dt, 1H, ²J_{PH} = 13.8 Hz, ²J_{PH} = 23.2 Hz, μ-H). ³¹P{¹H} NMR (109 MHz, CD₂Cl₂): δ 169.8 (t, ²J_{PP} = 133.8 Hz, μ-P^tBu₂), 37.0 (d, ²J_{PP} = 133.8 Hz, μ-dppen).

2d: Yield: 167 mg (78%). *Anal. Calc.* for C₃₆H₄₀BF₄N₂O₅P₃Ru₂ (962.59): C, 44.92; H, 4.19; N, 2.91. Found: C, 45.16; H, 4.39; N, 3.05%. IR (solid): ν (CO): 2068s, 2036vs, 2026vs, 1989s; ν (NO): 1595vs. ¹H NMR (270 MHz, CD₂Cl₂): δ 7.62–7.36 (m, 20H, C₆H₅), 4.00 (br, 1H, NH), 1.69 (d, 9H, ³J_{PH} = 15.5 Hz, t-C₄H₉), 1.15 (d, 9H, ³J_{PH} = 15.6 Hz, t-C₄H₉), –8.67 (m, 1H, μ-H). ³¹P{¹H} NMR (109 MHz, CD₂Cl₂): δ 188.5 (t, ²J_{PP} = 140.9 Hz, μ-P^tBu₂), 83.3 (d, ²J_{PP} = 140.9 Hz, μ-dppa).

2.3. X-ray structural determination

Suitable single crystals for X-ray diffraction were selected by means of a polarization microscope, mounted on the tip of a glass fiber, and investigated on an Oxford XCalibur (**2b**) and a Bruker Nonius-Kappa CCD diffractometer (**2c** and **2d**), respectively, using Mo Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods (SHELXS) [6] and refined by full-matrix least-squares calculations on F² (SHELXL-97) [7]. The positions of the hydrido ligands have been located from the difference map. Details of the crystal data, data collection, structure solution, and refinement parameters of compounds **2b**, **2c**, and **2d** are summarized in Table 1.

3. Results and discussion

3.1. Synthesis and characterization of compounds

Very recently we reported the synthesis and molecular structures of some new nitrosyl-bridged complexes [Ru₂(CO)₄(μ-NO)(μ-P^tBu₂)(μ-P[^]P)] (P[^]P = Me₂PCH₂PMe₂, dmpm, **1b**; P[^]P = Ph₂PC(=CH₂)PPh₂, dppen, **1c**; P[^]P = Ph₂PN(H)PPh₂, dppa, **1d**) [1]. As described previously for some closely related unsaturated complexes bearing the hydrido ligand instead of the nitrosyl-bridging group [3], we examined in a similar manner the

protonation reaction towards the Ru–Ru bond of **1b–d** with tetrafluoridoboric acid (see Scheme 1).

The complexes **1b–d** reacted spontaneously with HBF₄ in diethyl ether at room temperature with precipitating the products as yellow-green crystals. Thus the complex salts [Ru₂(CO)₄(μ-NO)(μ-H)(μ-P^tBu₂)(μ-P[^]P)]BF₄ (**2b–d**) were obtained in good yields which were characterized by analytical and spectroscopic methods.

The ¹H NMR spectra of compounds **2b–d** exhibited resonances corresponding to the phosphanido group and the bridging diphosphane ligands (see Experimental). Beside these signals in each case a signal according to the bridging hydrido ligand was observed. However the chemical shifts were found at values between –8.37 and –9.63 ppm, whereas usually these signals were observed at –13 to –15 ppm in our complexes, e.g., [3]. A similar deshielding effect of the hydrido resonances was described by other authors in dimanganese complexes containing bridging hydrido ligands across nitrosyl groups [8]. However, for comparative purposes, such examples are relatively rare. The ³¹P{¹H} NMR spectra showed the characteristic triplet/doublet pattern indicative of the symmetrical arrangement of the phosphorus-containing ligands.

The protonation of the metal–metal bond can be considered as an oxidative addition reaction, therefore the oxidation state of the ruthenium atoms changes formally from +I to +II. Therefore a decrease in the electron density at the metal atoms causes a shift of the terminal carbonyl bands in the IR spectra to higher wave numbers. In the average the values for **1b** (1940), **1c** (1939), and **1d** (1988) were shifted to 2020 (**2b**), 2022 (**2c**), and 2030 (**2d**) cm^{–1} confirming this increase in the oxidation state. Consequently the same trend is observed in the shift of the ν (NO) bands. Thus the values for **1b** (1488), **1c** (1490), and **1d** (1551), respectively, were shifted to 1539 (**2b**), 1547 (**2c**), and 1595 (**2d**) cm^{–1}. The latter trend was also observed on going from [Ru₂(CO)₄(μ-NO)(μ-P^tBu₂)(μ-dppm)] (dppm = Ph₂PCH₂PPh₂, **1a**), ν (NO) = 1467 cm^{–1}, to [Ru₂(CO)₄(μ-H)(μ-NO)(μ-P^tBu₂)(μ-dppm)]BF₄, ν (NO) = 1547 cm^{–1}, [2] and reported in a corrected manner in [1]. Moreover, for a comparative purpose, the values of the found ν (NO) bands in our neutral diruthenium complexes **1b** and **1c** are in good agreement with the reported one of [Mn₂(μ-H)(μ-NO)(CO)₆(μ-dppm)] (1471 cm^{–1}) [8].

3.2. Molecular structures of **2b**, **2c**, and **2d** in the crystal

Suitable single crystals for X-ray diffraction studies of the new compounds were grown as described in the experimental section. Yellow-green crystals of compound **2b** belonging to the monoclinic space group P2₁/c were obtained. The asymmetric unit contains one complex cation and the tetrafluoridoborate as the counter ion. Fig. 1 shows a selected ORTEP view of the cationic complex of **2b**, selected bond lengths and angles are given in the caption.

The molecular structure of the cation in **2b** is closely related to that in the complex salt [Ru₂(CO)₄(μ-H)(μ-NO)(μ-P^tBu₂)(μ-dppm)]BF₄ [2]. The dimetal core is bridged by the phosphanido group, the nitrosyl ligand, and the hydrido ligand, respectively. The complex cation in **2b** affords an electron count of 34 VE and, in the sense of the 18e rule, it should exhibit a metal–metal bonds. Thus the Ru–Ru distance found in **2b** is in good agreement with this. A comparison of the Ru–Ru distances between **1b** and **2b** revealed a shortening of the M–M bond upon protonation on going from **1b**, d(Ru–Ru) = 2.7516(6) [1] to **2b**, d(Ru–Ru) = 2.7401(5) Å.

The cationic complex **2c** crystallized as its tetrafluoridoborate salt in the monoclinic space group P2₁/c with four molecules in the unit cell. The asymmetric unit contains the complex cation and the tetrafluoridoborate as the counter ion. A selected view of

Download English Version:

<https://daneshyari.com/en/article/1338084>

Download Persian Version:

<https://daneshyari.com/article/1338084>

[Daneshyari.com](https://daneshyari.com)