

# Reductive Dimerization of Nitric Oxide to *trans*-Hyponitrite in the Coordination Sphere of a Dinuclear Ruthenium Complex

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During the reaction of the coordinatively unsaturated compound  $[\text{Ru}_2(\text{CO})_4(\mu\text{-H})(\mu\text{-P}^t\text{Bu}_2)(\mu\text{-dppm})]$  (**1**; dppm =  $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ ) with nitric oxide, the latter dimerizes and yields the unusual *trans*-hyponitrite complex  $[\text{Ru}_2(\text{CO})_4(\mu\text{-H})(\mu\text{-P}^t\text{Bu}_2)(\mu\text{-dppm})(\mu\text{-}\eta^2\text{-ONNO})]$  (**2**). The molecular structure of **2** has been determined by X-ray diffraction and is discussed together with the results of DFT calculations. The compound stands out by having only one of the two hyponitrite NO units bonded to Ru. The second one is not connected to Ru but in the solid state exhibits a weak intramolecular bond to the carbon atom of a neighboring carbonyl group.

## Introduction

The interest in the chemistry of nitric oxide has intensified in recent years due to its importance in biological systems.<sup>1</sup> Since some of its chemistry in this light is mediated by transition metals, we are investigating interactions of NO with the coordinatively unsaturated complexes  $[\text{M}_2(\text{CO})_3\text{L}(\mu\text{-H})(\mu\text{-P}^t\text{Bu}_2)(\mu\text{-dppm})]$  (M = Fe, Ru; L = CO, phosphines; dppm =  $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ ).<sup>2</sup> Recently we reported the synthesis and the X-ray crystal structure of  $[\text{Ru}_2(\text{CO})_4(\mu\text{-NO})(\mu\text{-P}^t\text{Bu}_2)(\mu\text{-dppm})]$  (**3**), a complex obtained by deprotonation of  $[\text{Ru}_2(\text{CO})_4(\mu\text{-H})(\mu\text{-NO})(\mu\text{-P}^t\text{Bu}_2)(\mu\text{-dppm})][\text{BF}_4]$  with strong bases.<sup>3</sup> An efficient synthesis of **3** directly by the reaction of  $[\text{Ru}_2(\text{CO})_4(\mu\text{-H})(\mu\text{-P}^t\text{Bu}_2)(\mu\text{-dppm})]$  (**1**) with NO under various conditions could not be accomplished. In the course of a more detailed study on the reactivity of **1** toward nitric oxide, we are now able to report the synthesis and characterization of a diruthenium complex containing a *trans*-hyponitrite ligand in an unprecedented coordination mode. The ligand is formed by reductive coupling of two NO molecules in the protective coordination sphere of a diruthenium cluster core.

## Experimental Section

All synthetic operations were performed under a dry argon atmosphere using conventional Schlenk techniques. Solvents

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were dried over sodium–benzophenone ketyl or molecular sieves and were distilled under argon prior to use.  $[\text{Ru}_2(\text{CO})_4(\mu\text{-H})(\mu\text{-P}^t\text{Bu}_2)(\mu\text{-dppm})]$ <sup>4</sup> was prepared according to the reported procedure, and nitric oxide was purchased from Aldrich. Photochemical reactions were carried out with a Heraeus TQ 150 high-pressure mercury lamp in a 250 mL photoreactor. IR spectra were recorded as KBr pellets or  $\text{CH}_2\text{Cl}_2$  solutions on a Mattson 5000 FTIR spectrometer. NMR spectra were obtained on Varian Unity 400 MHz or Varian Gemini 200 MHz equipment. Chemical shifts are given in ppm from  $\text{SiMe}_4$  (<sup>1</sup>H) or 85%  $\text{H}_3\text{PO}_4$  (<sup>31</sup>P{<sup>1</sup>H}). Microanalyses (C, H, N) were performed by the University of Halle microanalytical laboratory.

**$[\text{Ru}_2(\text{CO})_4(\mu\text{-H})(\mu\text{-P}^t\text{Bu}_2)(\mu\text{-dppm})(\mu\text{-}\eta^2\text{-ONNO})]$  (**2**).** A solution of  $[\text{Ru}_2(\text{CO})_4(\mu\text{-H})(\mu\text{-P}^t\text{Bu}_2)(\mu\text{-dppm})]$  (845 mg, 1 mmol) in toluene (25 mL) was cooled to  $-60^\circ\text{C}$ , and a slow stream of nitric oxide was bubbled through the solution for about 10 min. During this time the color of the solution changed from deep violet to orange. The mixture was warmed to room temperature by stirring for 30 min. The initial yellow-orange solution converted to a pale yellow suspension. The yellow solid was collected on a glass frit, washed with hexane ( $3 \times 10$  mL), and dried under vacuum. **2** was recrystallized from  $\text{CH}_2\text{Cl}_2$ /hexane (1:6). Yield: 787 mg (87%). Mp:  $150\text{--}152^\circ\text{C}$  dec. Anal. Calcd for  $\text{C}_{37}\text{H}_{41}\text{N}_2\text{O}_6\text{P}_3\text{Ru}_2$ : C, 49.12; H, 4.57; N, 3.10. Found: C, 50.23; H, 4.51; N, 2.86. IR (KBr):  $\nu(\text{CO})$  2028 s, 1973 vs, 1965 vs, 1742 s. IR ( $\text{CH}_2\text{Cl}_2$ ):  $\nu(\text{CO})$  2038 s, 1978 vs  $\text{cm}^{-1}$ . <sup>1</sup>H NMR ( $\text{CDCl}_3$ ):  $\delta$  7.55–6.97 (m, 20H,  $\text{PC}_6\text{H}_5$ ), 2.56 (m, 1H,  $\text{PCH}_2\text{P}$ ), 2.18 (m, 1H,  $\text{PCH}_2\text{P}$ ), 1.48 (d, 18H, <sup>3</sup>J<sub>PH</sub> = 13.8 Hz,  $\text{PC}_4\text{H}_9$ ), –12.30 (m, 1H,  $\mu\text{-H}$ ). <sup>31</sup>P{<sup>1</sup>H} NMR ( $\text{CDCl}_3$ ): 247.8 (dd, <sup>2</sup>J<sub>PP</sub> = 177.4 Hz, <sup>2</sup>J<sub>FP</sub> = 162.6 Hz,  $\mu\text{-P}^t\text{Bu}_2$ ), 46.0 (dd, <sup>2</sup>J<sub>FP</sub> = 162.6 Hz, <sup>2</sup>J<sub>PP</sub> = 72.1 Hz,  $\text{PC}_6\text{H}_5$ ), 35.6 (dd, <sup>2</sup>J<sub>PP</sub> = 72.1 Hz, <sup>2</sup>J<sub>FP</sub> = 177.9 Hz,  $\text{PC}_6\text{H}_5$ ).

**Computational Details.** The DFT calculations were performed using the Gaussian98 software package on the Silicon

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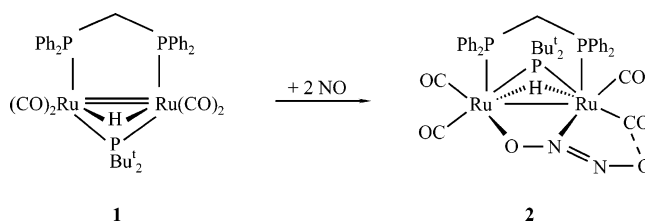
**Table 1. Details for the Crystal Structure Determination of Complex 2**

compd	2·solv <sup>a</sup>
formula	C <sub>37</sub> H <sub>41</sub> N <sub>2</sub> O <sub>6</sub> P <sub>3</sub> Ru <sub>2</sub> (without solvent)
fw	904.77
cryst size, mm	0.72 × 0.60 × 0.58
cryst syst	monoclinic
space group	P2 <sub>1</sub> /c (No. 14)
a, Å	19.3385(9)
b, Å	17.3924(8)
c, Å	26.0465(12)
β, deg	100.329(1)
V, Å <sup>3</sup>	8618.6(7)
Z	8
ρ <sub>calc</sub> , g cm <sup>-3</sup>	1.395
T, K	100(2)
μ(Mo Kα), mm <sup>-1</sup>	0.854
abs cor	multiscan
θ range for data collec (deg)	2.44–30.05
no. of rflns measd	126 453
no. of unique rflns	24 898 (R <sub>int</sub> = 0.0289)
no. of rflns, I > 2σ(I)	21 814
no. of params	907
R1, wR2 (I > 2σ(I))	0.0288, 0.0709
R1, wR2 (all data)	0.0337, 0.0732
residual electron density peaks (e/Å <sup>3</sup> )	+0.939, -0.813

<sup>a</sup> Compound is a disordered solvate containing proven CH<sub>2</sub>Cl<sub>2</sub> and likely ethanol in unknown quantities. The solvent content is not contained in the chemical formula and derived quantities.

Graphics Origin 2000 of the Vienna University of Technology.<sup>5</sup> The geometry and energy of the model complex were optimized at the B3LYP level<sup>6</sup> with the Stuttgart/Dresden ECP (SDD) basis set<sup>7</sup> to describe the electrons of the ruthenium atom. For all other atoms the 6–31g\*\* basis set was employed.<sup>8</sup> A vibrational analysis was performed to confirm that the structure has no imaginary frequency. The geometry was optimized without constraints (C<sub>i</sub> symmetry).

**X-ray Structure Determination.** Crystals of **2** in the form of a solvate, 2·solv, were obtained by slow diffusion of ethanol into a dichloromethane solution at room temperature. Due to a high solvent content the crystals are stable only in contact with mother liquor or at low temperatures. Crystal data and experimental details are given in Table 1. X-ray data were collected on a Bruker Smart CCD area detector diffractometer (graphite-monochromated Mo Kα radiation, λ = 0.71073 Å, 0.3° ω-scan frames covering a complete sphere of the reciprocal space, Bruker Kryoflex cooling unit). Corrections for Lorentz

**Scheme 1**

and polarization effects, for crystal decay, and for absorption were applied to the data. The structure was solved by direct methods using the program SHELXS97.<sup>9</sup> Structure refinement on *F*<sup>2</sup> was carried out with the program SHELXL97.<sup>10</sup> All non-hydrogen atoms were refined anisotropically. The hydride hydrogen was refined with a SADI distance restraint.<sup>10</sup> All other hydrogen atoms were inserted in idealized positions and were refined riding with the atoms to which they were bonded. It was found that the structure is built up from two crystallographically independent Ru complexes and that it contains large channels filled with considerable amounts of disordered solvent molecules. Three CH<sub>2</sub>Cl<sub>2</sub> molecules with approximately half-occupied positions were seen in difference Fourier maps, whereas the rest of the solvent was diffuse and would have to be modeled by over 20 additional peaks with concomitant critical parameter correlations (estimated solvent content two CH<sub>2</sub>Cl<sub>2</sub> molecules and one C<sub>2</sub>H<sub>5</sub>OH molecule per formula unit). Therefore, the contributions of all solvent molecules to the structure factors were *squeezed* with the program PLATON<sup>11</sup> followed by the final least-squares refinement of the structural backbone. Despite the crystallographically good accuracy of the structure, there are perceptible consequences of solvent disorder. Thus, both crystallographically independent Ru complexes possess regionally synchronous displacement anisotropies in different directions, which are attributed to local solvent influence.

## Results and Discussion

Recently we found that the reaction of [Fe<sub>2</sub>(CO)<sub>4</sub>(μ-H)(μ-PBu<sub>2</sub>)(μ-dppm)] with NO in toluene at -60 °C yields a variety of products with [Fe<sub>2</sub>(μ-CO)(CO)<sub>4</sub>(μ-H)(μ-PBu<sub>2</sub>)(μ-dppm)] as the only characterized main product. Presumably, the formation of CO by side reactions occurred, and subsequent addition to the coordinatively unsaturated species afforded the electron-precise diiron complex.<sup>2</sup> In contrast to this, the analogous reaction of [Ru<sub>2</sub>(CO)<sub>4</sub>(μ-H)(μ-PBu<sub>2</sub>)(μ-dppm)] (**1**) with nitric oxide resulted in the clean formation of the unprecedented complex [Ru<sub>2</sub>(CO)<sub>4</sub>(μ-H)(μ-PBu<sub>2</sub>)(μ-dppm)-(μ-η<sup>2</sup>-ONNO)] (**2**) in high yield (Scheme 1). Unfortunately, no intermediate products could be detected spectroscopically, and therefore the mechanism of the formation of **2** is currently unknown. It seems to be plausible that at low temperatures gaseous nitric oxide dimerizes to N<sub>2</sub>O<sub>2</sub>, which is subsequently reduced by the ruthenium(I) species, yielding the product **2** with the metals in the formal oxidation state +II. Complex **2** is stable to air in the solid state but decomposes slowly in solutions exposed to air. Moreover, within several days a slow decomposition by exposure to light is observed in the solid state as well as in solution. Under UV

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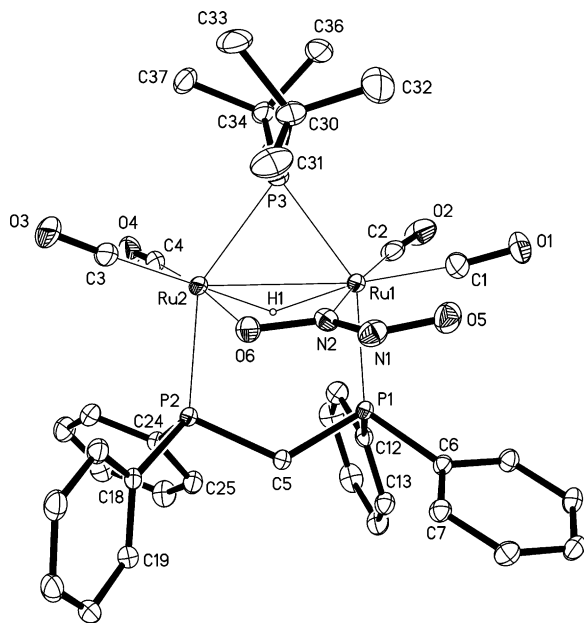
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**Figure 1.** Perspective view of the dimetal complex  $[\text{Ru}_2(\text{CO})_4(\mu\text{-H})(\mu\text{-P}^t\text{Bu}_2)(\mu\text{-dppm})(\mu\text{-}\eta^2\text{-ONNO})]$  (**2**) showing 40% thermal displacement ellipsoids (only one of two independent molecules in the unit cell for **2** is shown). For selected bond lengths and angles see Table 2.

irradiation compound **2** reacts at room temperature in THF within 4 h quantitatively back to **1** as the sole product. In contrast, an analogous photochemical treatment of **2** in  $\text{CH}_2\text{Cl}_2$  as the solvent yields a mixture of compounds containing  $[\text{Ru}_2(\text{CO})_4(\mu\text{-Cl})(\mu\text{-P}^t\text{Bu}_2)(\mu\text{-dppm})]$ <sup>12</sup> as the solely characterized product. The starting complex **1** could not be detected under these conditions.

Yellow crystals of **2**·solv were obtained by slow diffusion of ethanol into a  $\text{CH}_2\text{Cl}_2$  solution, and the molecular structure could be elucidated by single-crystal X-ray structure analysis. Consequently, compound **2** represents a diruthenium complex containing a  $\text{N}_2\text{O}_2$  ligand in an unprecedented coordination mode. The complex is diamagnetic, and its  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra show the chemical inequivalence of the two phosphorus nuclei of the bridging dppm ligand. They give rise to two signals (dd) with corresponding couplings to the P nucleus of the phosphido bridge (dd). The  $^1\text{H}$  NMR spectroscopic data of **2** include a characteristic resonance at  $-12.30$  ppm as a multiplet attributable to a bridging hydride ligand. The infrared spectrum of **2** (KBr) exhibits three absorption bands in the region characteristic of terminal carbonyl ligands. Furthermore, one band at  $1742\text{ cm}^{-1}$  is indicative of a carbonyl group in a bridging position.

The result of the structural identification of **2** by X-ray crystallography is depicted in Figure 1. The molecule consists of a dinuclear metal core bridged by a hydride, a phosphido group, a dppm moiety, and an unusual  $\text{N}_2\text{O}_2$  ligand. The coordination spheres of the two Ru are completed by four carbonyl ligands, and therefore by electron counting **2** exhibits 34 cluster valence electrons. The most remarkable feature of the molecule is clearly the  $\text{N}_2\text{O}_2$  ligand. This group is a 4-electron hyponitrite ligand,  $(\text{ONNO})^{2-}$ , in the *trans* configura-

tion. The coordination to the dimetal core is accomplished "side-on" by only one NO fragment, and both ruthenium atoms can be considered as being in the formal oxidation state +II.

Although the knowledge regarding the structural, mechanistic, and derivative chemistry of hyponitrites has improved significantly in recent years with particular emphasis on simple inorganic salts (e.g. *cis*- $\text{Na}_2\text{N}_2\text{O}_2$  and *trans*- $\text{Na}_2\text{N}_2\text{O}_2 \cdot 5\text{H}_2\text{O}$ ) and salts with organic amines or esters of hyponitric acid,<sup>13</sup> the knowledge of transition-metal hyponitrites is still in its infancy, as there are so far only four examples of structurally characterized transition-metal hyponitrite complexes. Two of these concern  $[\text{Pt}(\eta^2\text{-O}_2\text{N}_2)(\text{PPh}_3)_2]$ <sup>14</sup> and  $[\text{Ni}(\eta^2\text{-O}_2\text{N}_2)(\text{dppf})]$ <sup>15</sup> (*dppf* = 1,1'-bis(diphenylphosphanyl)ferrocene), which contain chelating bidentate *cis*-hyponitrite groups that are exclusively O-bonded to the metal atoms. In two earlier crystallographic studies the *cis*-hyponitrite complex  $[(\text{H}_3\text{N})_5\text{Co}(\text{O})\text{NOC}(\text{NH}_3)_5]^{4+}$  as the mixed nitrate/bromide and the *trans*-hyponitrite compound  $[(\text{ON})_2\text{Co}(\mu\text{-ONO})\text{Co}(\text{NO})_2(\mu\text{-ONNO})]$ , a remarkable neutral tetranuclear Co complex, have been described.<sup>15,16</sup> In the dinuclear Co complex the two metal atoms are asymmetrically bridged through the *cis*-hyponitrite dianion via N and O in the 1,3-positions (O–N–N–O bond lengths of 1.29, 1.25, and 1.32 Å). Only in the tetranuclear Co complex does the bonding situation of the *trans*-hyponitrite resemble in part that of our novel ruthenium complex **2**, because the centrosymmetric hyponitrite bridges two pairs of adjacent Co atoms via its two N–O entities, thus forming an essentially planar Co–O–N(Co)–N(Co)–O–Co arrangement with O–N–N–O bond lengths of 1.316, 1.265, and 1.316 Å. In comparison with all these examples, the ruthenium complex **2** stands out by its highly asymmetric coordination with only one N–O group bonded to the two Ru atoms, whereas the second N–O group is a spectator. The O–N–N–O bond lengths of the two independent molecules in **2**·solv average 1.356(2), 1.264(2), and 1.317(2) Å (for the individual values see Table 2) and thus exhibit a clear-cut elongation for the N–O moiety chelating Ru in comparison with its noncoordinated N–O counterpart. The first two bond lengths (long O–N and N–N) also compare well with recent accurately determined *trans*-hyponitrites, e.g. with  $\text{Na}_2\text{N}_2\text{O}_2 \cdot 5\text{H}_2\text{O}$ , where O–N–N–O bond lengths within a centrosymmetric and Na–O-bonded *trans*-hyponitrite were found to be 1.362(1), 1.256(2), and 1.362(2) Å.<sup>13b</sup> In comparison with all other known solid-state structures of hyponitrites the free termination of the ONNO group in the Ru complex is unusual and should be prone to further interactions, because the terminal oxygen O(5) is certainly distinctly charged. In fact, there is a long-range interaction to the carbon C(1) of the next-neighboring

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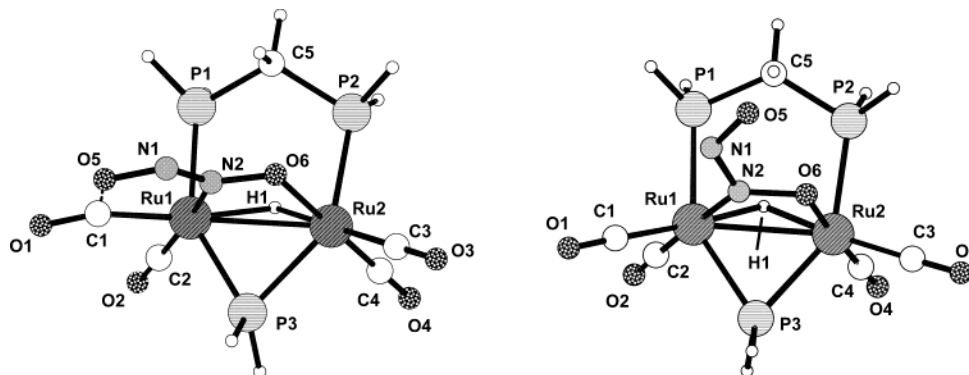
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**Figure 2.** Optimized geometries for *trans*-[Ru<sub>2</sub>(CO)<sub>4</sub>(μ-H)(μ-PH<sub>2</sub>)(μ-H<sub>2</sub>PCH<sub>2</sub>PH<sub>2</sub>)(μ-η<sup>2</sup>-ONNO)] (**2a**) and *cis*-[Ru<sub>2</sub>(CO)<sub>4</sub>(μ-H)(μ-PH<sub>2</sub>)(μ-H<sub>2</sub>PCH<sub>2</sub>PH<sub>2</sub>)(μ-η<sup>2</sup>-ONNO)] (**2b**) calculated at the B3LYP (Ru, sdd; C, H, N, O, P, 6-31g\*\*) level of theory.

**Table 2.** Observed Parameters and Computational Results (in Å and deg) for Complex **2** and the Model Compounds **2a** and **2b**

	<b>2·solv</b> (obsd)		<b>2a</b>	<b>2b</b>
	complex 1	complex 2		
Ru(1)–Ru(2)	2.8479(2)	2.8373(2)	2.891	2.889
Ru(1)–N(2)	2.060(2)	2.062(2)	2.062	2.118
Ru(1)–C(1)	1.944(2)	1.920(3)	2.022	1.918
Ru(1)–C(2)	1.883(2)	1.894(3)	1.901	1.907
Ru(1)–H(1)	1.743(9)	1.743(9)	1.819	1.779
Ru(2)–O(6)	2.125(2)	2.123(1)	2.174	2.099
Ru(2)–C(3)	1.909(2)	1.909(2)	1.928	1.919
Ru(2)–C(4)	1.874(2)	1.862(2)	1.879	1.900
Ru(2)–H(1)	1.743(9)	1.743(9)	1.777	1.781
N(2)–O(6)	1.357(2)	1.355(2)	1.336	1.384
N(1)–N(2)	1.261(2)	1.267(2)	1.256	1.317
N(1)–O(5)	1.313(3)	1.321(2)	1.351	1.251
C(1)···O(5)	2.062(3)	2.244(4)	1.573	
N(1)–N(2)–O(6)	115.5(2)	114.9(2)	118.3	118.3
N(2)–N(1)–O(5)	112.5(2)	112.4(2)	111.8	117.4
Ru(1)–C(1)–O(1)	158.9(2)	164.7(3)	140.8	178.5

CO group. This interaction is geometrically indicated by the short distances C(1)···O(5) of 2.062(3) Å in complex **1** and 2.244(4) Å in complex **2**. Although these distances exceed C–O single bonds by more than 0.6 Å, they are on the other hand too short for being merely van der Waals contacts. Further evidence for this comes from solid-state IR spectroscopy, which shows an IR band of 1742 cm<sup>−1</sup> indicative of a bridging CO group, and this can only be attributed to C(1)–O(1) with its long C(1)···O(5) interaction. For comparison, the CO stretching frequencies of the “normal” terminal CO ligands are found in the range of 2028–1965 cm<sup>−1</sup> (see the Experimental Section). Further aspects of this feature are addressed in the discussion of the DFT calculations. Another interesting point is the comparatively large difference in the C(1)···O(5) distances of the two independent Ru complexes. Looking for an explanation, we found out that the environments of the two oxygen atoms O(5) and O(5)’ are different, with O(5)’ having adjacent solvent neighbors but not O(5). It is therefore reasonable to assume that for O(5)’ hydrogen bond interactions to CH<sub>2</sub>Cl<sub>2</sub> and/or ethanol are responsible for this feature. Interestingly, in CH<sub>2</sub>Cl<sub>2</sub> solution this C(1)···O(5) interaction should obviously be interrupted, since the corresponding IR band is absent in the spectrum and only two absorptions for terminal carbonyls are observed.

DFT calculations were carried out to determine the structure and the relative stability of the two model complexes *trans*-[Ru<sub>2</sub>(CO)<sub>4</sub>(μ-H)(μ-PH<sub>2</sub>)(μ-H<sub>2</sub>PCH<sub>2</sub>PH<sub>2</sub>)(μ-η<sup>2</sup>-ONNO)] (**2a**) and the corresponding isomer *cis*-[Ru<sub>2</sub>(CO)<sub>4</sub>(μ-H)(μ-PH<sub>2</sub>)(μ-H<sub>2</sub>PCH<sub>2</sub>PH<sub>2</sub>)(μ-η<sup>2</sup>-ONNO)] (**2b**). In addition, the possibility of a hypothetical ONON ligand instead of the hyponitrite ONNO has also been investigated on the basis of the model complex [Ru<sub>2</sub>(CO)<sub>4</sub>(μ-H)(μ-PH<sub>2</sub>)(μ-H<sub>2</sub>PCH<sub>2</sub>PH<sub>2</sub>)(μ-η<sup>2</sup>-ONON)] (**2c**). According to the calculations, the geometry of **2a** is in very good agreement with the X-ray structural data of **2**, despite the absence of substituents in the model complex. Table 2 compares salient geometric data of the two independent *trans*-hyponitrite complexes in **2·solv** found by the X-ray crystal structure analysis with the computational results for **2a** and **2b**. The optimized geometries for **2a** and **2b** are shown in Figure 2. The largest deviation is observed for the intramolecular distance C(1)···O(5). Therefore, in the model complex **2a** a bonding contact may be envisaged, while for the real structure of **2** we would interpret this as a “noticeable bonding interaction”, additionally by consideration of a space-filling model of the critical part Ru<sub>2</sub>(CO)<sub>2</sub>(μ-H)(μ-ONNO) of the complex. (For the second independent molecule in the unit cell of **2** the contact C(1)’–O(5)’ = 2.244(4) Å was found, and normally this is still longer than a bonding distance.) It is worth noting that the isomeric *cis* complex **2b**, which has not been observed in the solid state, lacks a C···O interaction and is 8.8 kcal/mol less stable than the *trans* isomer **2a**. This barrier may be even lower in solution. However, DFT computational methods are not well set for taking into account solute–solvent interactions, especially if large organometallic molecules such as **2** are involved. Such calculations are beyond our present computational abilities. The latter result may suggest that perhaps in solution a fast equilibrium between these two isomers is present, being in line with the solution IR data, where indeed only absorptions for terminal carbonyls were observed. On the other hand, for the hypothetical complex **2c** (with an ONON ligand), despite several attempts, we were unable to locate a stationary point, suggesting that **2c** is a stable entity.

The bonding characteristics of the N<sub>2</sub>O<sub>2</sub> group found by X-ray structure analysis substantiate this arrangement unambiguously as a *trans*-hyponitrite ligand. The N(1)–N(2) distance shows a double-bond character and is comparable with the N–N bonds in the *cis*-hyponitrite

ligands of  $[\text{Pt}(\eta^2\text{-O}_2\text{N}_2)(\text{PPh}_3)_2]$  ( $\text{N}(1)\text{--}\text{N}(2) = 1.21(5) \text{ \AA}$ )<sup>14</sup> and  $[\text{Ni}(\eta^2\text{-O}_2\text{N}_2)(\text{dppf})]$  ( $\text{N}(1)\text{--}\text{N}(2) = 1.236(6) \text{ \AA}$ ).<sup>13</sup> Furthermore, the N–O distances agree well for all these compounds and are comparable with those found for  $[(\text{H}_3\text{N})_5\text{CoN}(\text{O})\text{NOC}(\text{NH}_3)_5]^{4+}$  and  $[(\text{ON})_2\text{Co}(\mu\text{-ONO})\text{-Co}(\text{NO})_2]_2(\mu\text{-ONNO})$ .<sup>15,16</sup> The planarity within the hyponitrite ligand of **2** is well documented by the torsion angle  $\text{O}(5)\text{--}\text{N}(1)\text{--}\text{N}(2)\text{--}\text{O}(6) = -176.0(2)^\circ$ , and taken together, the hyponitrite ligands in the former complexes were also found to be planar.

Currently, there seems to be an increased electron density on the noncoordinating oxygen atom of the hyponitrite ligand in **2**, manifested by the close intramolecular contact to one carbonyl carbon, and consequently we have to prove the reactivity of this ligand toward electrophiles.

### Conclusion

We described the reaction of the coordinatively unsaturated complex  $[\text{Ru}_2(\text{CO})_4(\mu\text{-H})(\mu\text{-P}^t\text{Bu}_2)(\mu\text{-dppm})]$  (**1**) with nitric oxide. The reaction does not result in a simple addition of NO, affording  $[\text{Ru}_2(\text{CO})_4(\mu\text{-NO})(\mu\text{-P}^t\text{Bu}_2)(\mu\text{-dppm})]$ ; rather, in a clean manner a reductive dimerization of NO occurs and thus the unprecedented

*trans*-hyponitrite compound  $[\text{Ru}_2(\text{CO})_4(\mu\text{-H})(\mu\text{-P}^t\text{Bu}_2)(\mu\text{-dppm})(\mu\text{-}\eta^2\text{-ONNO})]$  (**2**) is formed in high yield. The advantage of the synthesis consists of the use of nitric oxide as the source for the hyponitrite formation, whereas for other preparations of hyponitrites, e.g. for the complexes  $[\text{M}(\eta^2\text{-O}_2\text{N}_2)\text{L}_2]$  ( $\text{M} = \text{Ni}, \text{Pt}$ ;  $\text{L} = \text{phosphines}$ )<sup>13</sup> diazenium diolates,  $\text{RN}_2\text{O}_2^-$ , are necessary for their synthesis. Since **2** exhibits a very close intramolecular contact between one C atom of a carbonyl group and the noncoordinating O atom of the hyponitrite ligand, the latter should be a center of high nucleophilicity. Currently we are exploring the chemical transformation of **2** to confirm such a pattern of reactivity.

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**Supporting Information Available:** Listings of atomic coordinates, anisotropic temperature factors, and bond lengths and angles for **2**·solv. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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