

DOI: 10.1002/zaac.202100368

Triphenylmethyl Thionitrite: An Efficient NO Transfer Reagent During the Synthesis of a Triruthenium Nitrosyl Cluster

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Dedicated to Professor Wolfgang Beck on the Occasion of his 90th Birthday

The synthesis and structural characterization of the novel triruthenium nitrosyl cluster $[\text{Ru}_3(\mu\text{-NO})(\text{CO})_5(\mu\text{-H})(\mu\text{-PBU}^t_2)_2(\mu\text{-dppm})]$ (**2**) is described. Compound **2** was obtained by the reaction of the 46-valence electron cluster $[\text{Ru}_3(\mu\text{-CO})(\text{CO})_4(\mu_3\text{-H})(\mu\text{-H})(\mu\text{-PBU}^t_2)_2(\mu\text{-dppm})]$ (**1**) with nitric oxide and on the other hand in a more efficient way by the reaction of **1** with the nitrosyl transfer reagent triphenylmethyl thionitrite (TTN). The

reaction of **1** with NO was outlined in dichloromethane whereas the reaction with TTN was realized in THF. Both methods worked at ambient temperature affording compound **2** in high yield. Temporarily we found that the transformation of **1** with NO was accompanied by a fast side-reaction resulting in a further substitution of CO ligands. The molecular structure of **2** in the crystal was confirmed by single-crystal X-ray diffraction.

Introduction

In 1996 we described the electron-deficient 46VE cluster (VE = valence electrons) $[\text{Ru}_3(\mu\text{-CO})(\text{CO})_4(\mu_3\text{-H})(\mu\text{-H})(\mu\text{-PBU}^t_2)_2(\mu\text{-dppm})]$ (dppm = $\text{Ph}_2\text{PCH}_2\text{PPh}_2$, **1**) exhibiting an unusual bonding situation.^[1] Recently we confirmed the same situation in analogous triruthenium clusters containing *N,N*-bis(diphenylphosphanyl)-amines instead of the bridging dppm ligand.^[2] Whereas compound **1** showed no reactivity towards carbon monoxide (even under elevated pressure),^[1] now we observed that **1** reacts spontaneously with nitric oxide followed by a fast subsequent-reaction. Thus, for a better control of the stoichiometric reaction, we searched for an efficient nitrosyl transfer agent. Some time ago we successfully controlled the stoichiometry by the use of *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (diazald) for the synthesis of diruthenium complexes bearing bridging nitrosyl ligands.^[3] Therein, we examined a related NO transfer agent by the use of triphenylmethyl thionitrite (TTN) for preparing nitrosyl complexes as already described in the literature.^[4–8] Moreover, *S*-nitrosothiols play an important role in mediating the chemistry of the NO molecule in biochemical processes.^[7,8] For introducing the NO ligand in the triruthenium metal core of **1** in a clean way, we investigated

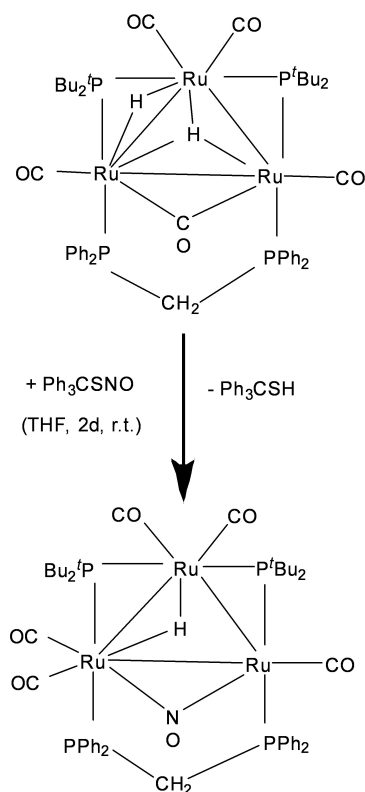
the reaction of the latter with triphenylmethyl thionitrite (Ph_3CSNO).

Results and discussion

The treatment of compound **1** in dichloromethane at ambient temperature with a slow stream of nitric oxide resulted in very fast color change from deep violet-brown to red-orange during one minute. The investigation of the reaction solution by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy indicated the complete disappearance of the characteristic signals belonging to the starting complex **1** and the formation of a new main species exhibiting four different signal groups in its corresponding spectrum. Furthermore, some minor signals hinted at the formation of a further side-product. By preliminary X-ray crystal-structure investigation results we obtained hints at the formation of a triruthenium cluster containing two NO ligands. The $^{31}\text{P}\{^1\text{H}\}$ NMR signals of this side-product belonged obviously to the product exhibiting two nitrosyl groups. To prevent its formation, we searched for another method to introduce the first NO ligand by a stoichiometric reaction. Thus, we treated compound **1** with equimolar amounts of TTN at room temperature in THF as the solvent. In that case, a significant color change similar to that observed from the above-mentioned treatment of **1** with NO gas, was clearly indicated after two days. Complete removal of the solvent and crystallization of the remaining residue from dichloromethane/methanol at room temperature yielded well-shaped dark red crystals suitable for a single-crystal X-ray diffraction study. The result of the analysis afforded a novel triruthenium nitrosyl cluster $[\text{Ru}_3(\mu\text{-NO})(\text{CO})_5(\mu\text{-H})(\mu\text{-PBU}^t_2)_2(\mu\text{-dppm})]$ (**2**), see Scheme 1. Compound **2** was obtained by the use of TTN as NO transfer reagent in high yield as the sole product. The investigation of the corresponding reaction solution by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy showed only a set of four signal groups belonging to one new product indicated by the

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Scheme 1. Synthesis of compound **2**.

different chemical shifts in comparison with the starting complex **1** and the corresponding coupling constants (see Supporting Information).

The new compound **2** was characterized by elemental analysis, mass spectrometry, infrared and NMR spectroscopy (see Experimental Section). In contrast to compound **1** which contains two different hydrido ligands, in **2** only one very complex multiplet at -18.00 ppm in the upfield region of the ^1H NMR spectrum was observed (see Supporting Information). That value hinted at a hydride in an edge-bridging coordination mode ($\mu\text{-H}$). In light of the valence electron counting (E.A.N. rule), compound **2** should contain only one hydride to reach the 48 VE corresponding to an electron-precise trinuclear metal cluster. Compound **2** crystallized from dichloromethane/methanol in the monoclinic space group $P2_1/n$ with four molecules in the unit cell. A view of the molecular structure of **2** in the crystal is shown in Figure 1, selected bond lengths and angles are listed in the caption. Molecules of **2** exhibit a triangular metal framework with three metal-metal bond lengths comparable to the starting compound **1**. This is somewhat surprising since the latter counts 46 VE whereas compound **2** exhibits 48 VE and three bonds in the range characteristically for electron-precise compounds should be expected. However, the Ru2-Ru3 distance in **2** is somewhat elongated in comparison to the other ones (compare caption in Figure 1). This was also observed in the case of the starting compound **1** [$3.1592(4)$ Å],^[1] and the related dppa analogue.^[2] A possible explanation could be that

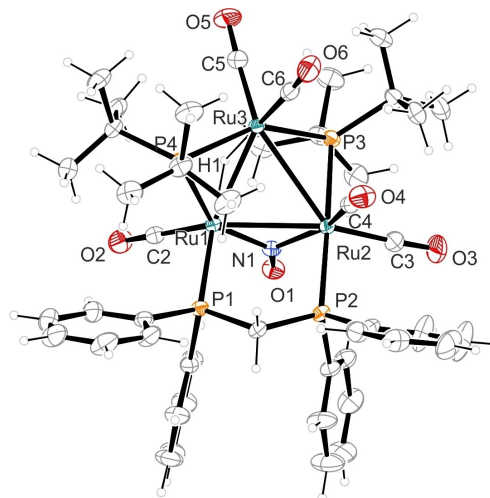


Figure 1. Molecular structure of **2** in the crystal (ORTEP drawing and atom labeling scheme with 50% probability level). Selected bond lengths (Å) and angles ($^\circ$): Ru1-Ru2, 2.8747(6); Ru1-Ru3, 2.7638(5); Ru2-Ru3, 3.0920(6); Ru1-P1, 2.3160(7); Ru2-P2, 2.3661(7); Ru1-P4, 2.4085(7); Ru3-P4, 2.3833(7); Ru2-P3, 2.4235(7); Ru3-P3, 2.3488(8); Ru1-H1, 1.78(2); Ru2-H1, 1.72(2); Ru1-N1, 1.9740(18); Ru2-N1, 2.0109(17); N1-O1, 1.221(2). Ru2-Ru1-Ru3, 66.48(1); Ru1-Ru2-Ru3, 55.04(1); Ru1-Ru3-Ru2, 58.48(1); Ru1-P4-Ru3, 70.45(2); Ru2-P3-Ru3, 80.75(2); Ru1-N1-Ru2, 92.34(7); Ru1-N1-O1, 133.92(14); Ru2-N1-O1, 133.74(14).

only one bridging ligand is present across that Ru–Ru bond. The bridging nitrosyl ligand was additionally confirmed by the presence of a strong vibration band in the IR spectrum at 1483 cm^{-1} (ATR). This is in accordance with observations in similarly constituted diruthenium complexes with bridging nitrosyl ligands in a closely related ligand environment.^[3]

Conclusions

The synthesis and the structural characterization of the novel nitrosyl cluster $[\text{Ru}_3(\mu\text{-NO})(\text{CO})_5(\mu\text{-H})(\mu\text{-PBUt}_2)_2(\mu\text{-dppm})]$ (**2**) was described. The compound was obtained by the direct reaction of the 46VE cluster $[\text{Ru}_3(\mu\text{-CO})(\text{CO})_4(\mu_3\text{-H})(\mu\text{-H})(\mu\text{-PBUt}_2)_2(\mu\text{-dppm})]$ (**1**) with nitric oxide. During the reaction a conversion of the electron-poor cluster **1** (46 VE) to the electron-precise compound **2** (48 VE) was realized. Because of a fast subsequent-reaction with an excess of NO gas, we examined the stoichiometric reaction of **1** with the nitrosyl transfer reagent trityl thionitrite resulting in compound **2** as the sole product in a clean manner. Therefore, the described method using TTN is clearly favored towards the use of gaseous nitric oxide in this case.

Experimental Section

General: All manipulations were performed under an atmosphere of dry nitrogen using conventional Schlenk techniques. The starting

Table 1. Experimental details of the crystal structure determination of **2**.

Compound	2
Formula	C ₄₆ H ₅₉ NO ₆ P ₄ Ru ₃
<i>M</i> /g mol ⁻¹	1149.03
<i>T</i> /K	173(2)
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> /Å	15.1443(13)
<i>b</i> /Å	15.4604(12)
<i>c</i> /Å	21.3235(17)
<i>α</i> /°	90
<i>β</i> /°	95.186(3)
<i>γ</i> /°	90
<i>V</i> /Å ³	4972.2(7)
<i>Z</i>	4
Density/g·cm ⁻³	1.535
<i>μ</i> /mm ⁻¹	1.073
<i>θ</i> range/°	3.005–29.57
Reflections, collected	131879
Reflections, independent	11488
<i>R</i> _{int}	0.0528
<i>wR</i> ₂ (all data)	0.0600
<i>R</i> ₁	0.0288
<i>S</i>	1.035
Δ <i>ρ</i> _{fin} (max/min)/e Å ⁻³	0.447/–0.451

complex **1** was prepared following the literature procedure.^[1] Trityl thionitrite (TTN) was synthesized by the published method.^[9] IR spectra were recorded from solids with a JASCO FT/IR-4600 spectrometer equipped with an ATR unit. NMR spectra were recorded in CD₂Cl₂ using a Jeol Eclipse 400 instrument operating at 400 MHz (¹H) and 161 MHz (³¹P). Chemical shifts are given in ppm relative to TMS (¹H) and 85% H₃PO₄ (³¹P). The Mass spectrum was measured using a Jeol Mstation JMS 700 spectrometer. Elemental analyses (C, H, N) were performed by the Microanalytical Laboratory of the Department of Chemistry, LMU Munich, using a Heraeus Elementar Vario EL instrument.

Synthesis of 2: To a solution of **1** (187 mg, 0.167 mmol) in 15 mL of dry THF trityl thionitrite (51 mg, 0.167 mmol) was added and the solution stirred for 2 days at room temperature. During that time the color of the solution changed from violet-brown to red-orange. The solution was reduced to dryness in vacuo and the remaining residue crystallized from CH₂Cl₂/MeOH. The resulting red crystals were collected by filtration, washed with cold methanol (10 mL) and dried in vacuo. Yield: 155 mg (81.0%). C₄₆H₅₉NO₆P₄Ru₃ (1149.08): C 47.75 (calcd. 48.08); H 5.31 (5.18); N 1.06 (1.22) %. **MS** (ESI): *m/z* = 1149 [M⁺]. **IR** (solid, ATR, cm⁻¹): CO: 1999 s, 1975 s, 1944 vs, 1920 vs, 1898 vs; μ-NO: 1483 s. **¹H NMR** (CD₂Cl₂, ppm): δ = 7.74–6.90 (m, 20H, C₆H₅), 3.90 (m, 1H, PCH₂P), 3.64 (m, 1H, PCH₂P), 1.49 (d, ³J_{PH} = 14.0 Hz, 9H, μ-PBu₁'), 1.40 (d, ³J_{PH} = 14.0 Hz, 9H, μ-PBu₁'), 1.17 (d, ³J_{PH} = 12.8 Hz, 9H, μ-PBu₂'), 1.16 (d, ³J_{PH} = 12.4 Hz, 9H, μ-PBu₂'), –18.00 (m, 1H, μ-H). **³¹P{¹H} NMR** (CD₂Cl₂, ppm): δ = 238.7 (dd, ²J_{PP} = 147.4 Hz, ²J_{PP} = 102.1 Hz, ³J_{PP} not observed, μ-P), 195.5 (ddd, ²J_{PP} = 102.4 Hz, ²J_{PP} = 12.5 Hz, ³J_{PP} = 4.5 Hz, μ-P), 32.2 (ddd, ²J_{PP} = 77.5 Hz, ²J_{PP} = 12.4 Hz, ³J_{PP} = 5.1 Hz, dppm), 20.1 (dd, ²J_{PP} = 147.4 Hz, ²J_{PP} = 78.2 Hz, ³J_{PP} not observed).

Crystal Structure Determination and Refinement: Crystals of **2** suitable for X-ray diffraction were obtained by crystallization from dichloromethane/methanol at ambient temperature. Crystals were selected by means of a Leika MZ6 polarization microscope, mounted on a MiTeGen MicroLoop and investigated with a Bruker

D8 Venture TXS diffractometer using Mo-Kα radiation (λ = 0.71073 Å). The structure was solved by direct methods (SHELXT)^[10] and refined by full-matrix least-squares calculations on *F*² (SHELXL-2016/6).^[11] Anisotropic displacement parameters were refined for all non-hydrogen atoms. The Ru-bound H-atoms have been located from the difference map. Details of the crystal data, data collection, structure solution, and refinement parameters of compound **2** are summarized in Table 1. Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge upon quoting the depository number CCDC-2112702 (**2**) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

Acknowledgements

The authors are grateful to the Department of Chemistry of the Ludwig Maximilians Universität Munich for financial support. Open Access funding enabled and organized by Projekt DEAL.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: Carbonyl complexes · Crystal structure · Ruthenium · Metal clusters · Nitrosyl ligand

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Manuscript received: December 3, 2021

Revised manuscript received: February 6, 2022