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Synthesis and Molecular Structure of $[Ru_3(CO)_{10}(\mu-dppa)]$ (dppa = Ph₂PN(H)PPh₂) Provided by Its Dioxane Solvate

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Dedicated to Prof. Herbert W. Roesky on the Occasion of his 85th Birthday

Abstract. The sodium benzophenone ketyl-induced reaction of $[Ru_3(CO)_{12}]$ with bis(diphenylphosphanyl)amine Ph₂PN(H)PPh₂ (dppa) in THF resulted in the formation of the expected metal cluster $[Ru_3(CO)_{10}(\mu$ -dppa)] (1) in high yield. 1 was fully characterized by spectroscopic means and crystals of the compound suitable for X-ray diffraction were obtained from dichloromethane/dioxane. The molecu-

lar structure of **1** as its dioxane solvate was determined by X-ray crystallography. The compound crystallized in a new crystal structure of $[Ru_3(CO)_{10}(\mu$ -dppa)] in the triclinic space group $P\overline{1}$, whereas that compound was described in an earlier report crystallizing from chloroform in the monoclinic space group $P2_1/c$.

Introduction

The chemistry of clusters $[M_3(CO)_{10}(\mu-dppm)]$ (M = Ru, Os; dppm = bis(diphenylphosphanyl)methane with respect to activating and maintaining the trinuclear core of these complexes is well established.^[1] Recently the interest of the reactivity of $[Ru_3(CO)_{10}(\mu-dppm)]$ was, for example, also directed on the activation of main-group element species.^[2] The compounds $[M_3(CO)_{10}(\mu$ -dppm)] were obtained by replacing two equatorial carbonyl groups by the small bite-angle diphosphane ligand dppm.^[3–5] As a very efficient preparation method of the triruthenium metal cluster, the benzophenone ketylinduced substitution method of carbonyls was established, which was well described in the case of the preparation of [Ru₃(CO)₁₀(µ-dppm)] starting from [Ru₃(CO)₁₂].^[4] Although many different methods are known to substitute carbonyl groups in metal complexes with various - especially P-donor ligands, direct syntheses from the triruthenium dodecacarbonyl precursor is often complicated. The formation of numerous side products in case of thermal driven reactions with phosphane ligands make chromatographic workups often inevitable.^[6]

The compound $[Ru_3(CO)_{10}(\mu-dppa)]$ (1) [dppa = bis(diphenylphosphanyl)amine] was described in the literature by usingthe sodium benzophenone ketyl-induced CO substitutionmethod, however, the preparation protocol was not reported in

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a deeper detail.^[7] Furthermore, the authors obtained the species $[Ru_3(CO)_{10}(\mu$ -dppa)] and $[Ru_3(CO)_8(\mu$ -dppa)_2] as a mixture of both complexes (30 and 60%), whereas the mixture had to be separated by chromatographic workup.^[7] Finally, these authors obtained single-crystals of $[Ru_3(CO)_{10}(\mu$ -dppa)] from chloroform suitable for X-ray diffraction and determined its molecular structure. We prepared compound **1** in nearly quantitative yield by the before-mentioned ketyl-induced substitution method since it proved as excellent starting material for further investigations in the field of triruthenium metal clusters. During these studies, crystals of **1** as dioxane solvate suitable for an X-ray diffraction study were obtained exhibiting a new crystal and molecular structure of the title compound. On these findings we report in this communication.

Results and Discussion

Using the sodium benzophenone ketyl-induced preparation method,^[4] we reacted $[Ru_3(CO)_{12}]$ with equimolar amounts of dppa in THF and obtained compound **1** in nearly quantitative yield [Equation (1)]:

$$\begin{aligned} \text{Ru}_{3}(\text{CO})_{12}] + \text{Ph}_{2}\text{PN}(\text{H})\text{PPh}_{2} \\ \rightarrow 2\text{CO} + [\text{Ru}_{3}(\text{CO})_{10}\{\mu\text{-Ph}_{2}\text{PN}(\text{H})\text{PPh}_{2}\}] \ (1) \end{aligned} \tag{1}$$

From the reaction solution an orange-brown powder was obtained which was characterized by ¹H, ³¹P{¹H}, ¹³C{¹H} NMR, and IR spectroscopy as well as elemental analysis. The observed NMR spectroscopic data agreed very well with the reported ones.^[7] Thus, the proton NMR spectrum of **1** showed the triplet-signal of the NH proton at 4.7 ppm (²J_{PH} = 4.9 Hz, CDCl₃) beside the signals for the aromatic protons in the characteristic region. The two chemically equivalent P nuclei resonated in the ³¹P{¹H} NMR spectrum as singlet at δ = 69.6 ppm (CDCl₃).^[7] For our compound **1** compare these data in the Experimental Section. Furthermore, a ¹³C{¹H} NMR spectrum of **1** in CD₂Cl₂ was recorded exhibiting the following reso-

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nances: $\delta = 209.2$ (s, broad; assigned to the carbonyl ligands in proximity to the P atoms), and four signal groups at 139.1, 131.1, 130.4, and 128.8 which were assigned to carbon C atoms of the aromatic rings on phosphorus. The infrared spectrum of our compound **1** (ATR, solid) showed a comparable pattern as observed for $[Ru_3(CO)_{10}(\mu$ -dppm)]^[4] indicating the presence of only terminal carbonyl ligands.

Red-orange crystals of **1** suitable for X-ray diffraction were obtained by the slow diffusion method from dichloromethane/ dioxane at room temperature overnight. Thus **1** crystallized as dioxane solvate in the triclinic space group $P\bar{1}$ with two molecules in the unit cell. A view of the molecular structure of **1** in the crystal is depicted in Figure 1, selected bond lengths and angles are given in the caption.



Figure 1. ORTEP plot of the molecular structure of **1** in the crystal (Ellipsoids are drawn with 50% probability level). Selected bond lengths (Å) and angles (°): Ru1–Ru2, 2.8390(4); Ru1–Ru3, 2.8710(4); Ru2–Ru3, 2.8271(4); Ru3–P1, 2.3188(6); Ru2–P2, 2.3027(6); P1–N1, 1.6920(18); P2–N1, 1.6922(18); N1–H1, 0.8800. Ru2–Ru1–Ru3, 59.35(1); Ru1–Ru3–Ru2, 59.76(1); Ru1–Ru3–P1, 146.34(2); Ru2–Ru3–P1, 87.88(2); Ru3–Ru2–P2, 92.70(2); P1–N1–P2, 123.27(11); Ru3–P1–N1, 111.96(7); Ru2–P2–N1, 112.21(6); P2–N1–H1, 118.00. N1–H1•••O11: 2.925(2); 162.00°.

Molecules of **1** exhibit a triangular metal core with three ruthenium-ruthenium bonds whose lengths are comparable to similarly constituted clusters such as $[Ru_3(CO)_{10}(\mu\text{-dppm})]$. The literature known parameters are: Ru1–Ru2, 2.834(1), Ru1–Ru3, 2.841(1), and Ru2–Ru3, 2.860(1) Å.^[8] In $[Ru_3(CO)_{10}(\mu\text{-dppm})]$ as well as in **1** the edge bridged by the bidentate phosphane ligand was found as slightly shorter than the other two. The same observation was made for the originally reported structure of $[Ru_3(CO)_{10}(\mu\text{-dppa})]$ for which the corresponding bond lengths were found: Ru1–Ru1a, 2.8287(11) (bridged by dppa), Ru1a–Ru2, 2.8545(10), and Ru1–Ru2, 2.8546(10) Å.^[7]

In general, the molecules of both crystal modifications exhibit very similar geometric and bonding parameters. Thus for $[Ru_3(CO)_{10}(\mu$ -dppa)]^{[7]} the following data were reported: P1–N1, 1.688(4) and Ru1–P1, 2.307(2) Å, as well as P1–N1–P1a, 127.1(5)°. For 1·C₄H₈O₂ these parameters can be compared by

using the caption in Figure 1. Furthermore, the corresponding parameters agree very well with the observed ones for diruthenium complexes bridged by dppa.^[9,10] The ability to form intermolecular hydrogen-bridge bondings of the NH group of dppa was already found in the compound $[Ru_2(CO)_4(\mu-dppa)]$ $(\mu-H)(\mu-NO)(\mu-PBu_2^t)]BF_4$ where the tetrafluoridoborate as the counterion functioned as the hydrogen-bridge bonding acceptor part.^[10] The same behavior was observed in crystals of $1 \cdot C_4 H_8 O_2$ where the NH group of dppa formed a strong hydrogen bond towards a co-crystallized dioxane molecule resulting from the crystal growing process. During the slightly bent (162.00°) intermolecular hydrogen bridge N1-H1--O11 the following distances were found: 0.8800, 2.0800, and 2.925(2) Å. The fortunate circumstance of the dioxane solvate formation in crystals of 1 allowed us to obtain a better wR_2 value during the structure refinement as reported for the same compound in an earlier report.^[7]

Conclusions

The herein reported investigations describes the convenient high-yield synthesis of the trimetal cluster $[Ru_3(CO)_{10}(\mu-dppa)]$ (1) obtained by the sodium benzophenone ketyl-induced substitution of two carbonyl ligands in $[Ru_3(CO)_{12}]$ towards the small bite-angle PNP ligand bis(diphenylphosphanyl)amine (dppa). A crystal structure determination of 1 on its dioxane solvate was carried out, whereas crystals of the compound exhibited a strong hydrogen-bridge bonding between the NH function of the dppa ligand as the hydrogen-bridge bonding donor and one oxygen atom of the dioxane molecule as the hydrogen-bridge bonding acceptor in the solid. Thus a new crystal and molecular structure of the title compound was found, and the fortunate circumstance of the dioxane solvate formation in the crystal allowed us to reach a more better wR_2 value during the structure refinement as reported for the chloroform solvate of $[Ru_3(CO)_{10}(\mu-dppa)]$ in the earlier report.^[7]

Experimental Section

General: All preparative work was carried out under a dry nitrogen atmosphere using standard Schlenk techniques. Chemicals were purchased from Sigma/Aldrich and used as received. IR spectra were recorded from solids with a JASCO FT/IR-4600 spectrometer equipped with an ATR unit. NMR spectra were recorded using a Jeol Eclipse 400 instrument operating at 400 MHz (¹H), 100 MHz (¹³C), and at 162 MHz (³¹P). Chemical shifts are given in ppm relative to TMS (¹H, ¹³C) and 85 % H₃PO₄ (³¹P). Elemental analyses were performed by the Microanalytical Laboratory of the Department of Chemistry, LMU Munich, using a Heraeus Elementar Vario EL instrument.

Synthesis of 1: $[Ru_3(CO)_{12}]$ (320 mg, 0.5 mmol) and dppa (193 mg, 0.5 mmol) were placed in a Schlenk tube and 30 mL of deoxygenated THF were added. The mixture was stirred and warmed to about 50 °C to dissolve the metal carbonyl. At this point some drops of a sodium benzophenone ketyl solution were added, while a strong carbon monoxide evolution was registered and the solution rapidly darkened to orange-brown. After stirring for 30 min at room temperature the resulting dark red-brown solution was reduced to about 1 mL in vacuo. Addition of 20 mL of methanol afforded orange-red crystals, which

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Table 1. Experimental details of the crystal structure determination of the solvate $1 \cdot C_4 H_8 O_2$.

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	$1 \cdot C_4 H_8 O_2$
Formula	$C_{38}H_{29}NO_{12}P_2Ru_3$
$M/g \cdot mol^{-1}$	1056.77
Т /К	101(2)
Crystal system	triclinic
Space group	$P\bar{1}$
a /Å	10.9105(5)
b /Å	13.2013(7)
c /Å	14.8450(8)
a /°	101.639(2)
β /°	90.323 (2)
γ /°	109.795(2)
$V/Å^3$	1946.10(8)
Z	2
Density /g·cm ⁻³	1.787
μ /mm ⁻¹	1.284
θ range /°	2.946-29.58
Reflections, collected	49448
Reflections, independent	9861
R _{int}	0.0383
wR_2 (all data)	0.0586
R_1	0.0261
S	1.061
$\Delta \rho_{\rm fin}$ (max/min) /e·Å ⁻³	0.513/ -0.487

were collected by filtration, washed with cold methanol (5 mL) and dried in vacuo. Yield: 475 mg (98.0%). $C_{34}H_{21}NO_{10}P_2Ru_3$ (968.70): C 41.79 (calcd. 42.16); H 2.59 (2.19); N 1.34% (1.45)%. **IR** (solid, ATR): $\tilde{v} = 2075$ s, 2009 s, 1990 s, 1983 s, 1947 vs, 1939 vs. cm⁻¹. ¹**H NMR** (CD₂Cl₂): $\delta = 7.47-7.41$ (m, 20 H, Ph), 4.60 (t, ²*J*_{PH} = 5.0 Hz, 1 H). ³¹P{¹H} NMR (CD₂Cl₂): $\delta = 65.9$ (s). ¹³C{¹H} NMR (CD₂Cl₂): $\delta = 209.2$ (s, broad; CO ligands in proximity to P), 139.1 (m, *X*-part of *AA'X* spectrum, *N* = 52.0 Hz, *C_{ipso}*, Ph), 131.1 (s, *C_{para}*, Ph), 130.4 (m, *N* = 14 Hz, *C_{ortho}*, Ph), 128.8 (m, *N* = 11 Hz, *C_{meta}*, Ph).

Crystal Structure Determination and Refinement: Crystals of **1** as dioxane solvate suitable for X-ray diffraction were obtained by the diffusion method from dichloromethane/dioxane at room temperature overnight. Crystals were selected by means of a Leika MZ6 microscope with polarization filter, mounted on a MiTeGen MicroLoop, and investigated with a Bruker D8 Venture TXS diffractometer with rotating anode using Mo-K*a* radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods (SHELXT)^[11] and refined by full-matrix least-squares calculations on F^2 (SHELXL-2014/7).^[12] Anisotropic displacement parameters were refined for all non-hydrogen atoms. Details

of the crystal data, data collection, structure solution, and refinement parameters of compound 1 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 on quoting the depository number CCDC-2034499 for **1** (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk)

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