Activation of C–Cl Bonds: Synthesis and Structural Characterization of $[Ru_2(\mu\text{-}Cl)(\mu\text{-}P^tBu_2)(\mu\text{-}Ph_2PN(H)PPh_2)(CO)_4]$

Tobias Mayer and Hans-Christian Böttcher

Department Chemie, Ludwig-Maximilians-Universität, Butenandtstraße 5 – 13, D-81377 München, Germany

Reprint requests to Prof. Dr. Hans-Christian Böttcher.
Fax: (+49) (0)89 / 2180 77407.
E-mail: hans.boettcher@cup.uni-muenchen.de

Z. Naturforsch. **2013**, *68b*, 743 – 746
DOI: 10.5560/ZNB.2013-3029
Received January 28, 2013

Dedicated to Professor Heinrich Nöth on the occasion of his 85th birthday

The synthesis and structural characterization of the complex $[Ru_2(\mu\text{-}Cl)(\mu\text{-}P^tBu_2)(\mu\text{-}dppa)(CO)_4]$ (**4**, dppa = $Ph_2PN(H)PPh_2$) are reported. The title compound and two other related complexes were obtained in high yields by the reaction of the coordinatively unsaturated species $[Ru_2(\mu\text{-}H)(\mu\text{-}P^tBu_2)(\mu\text{-}P\hat{}P)(CO)_4]$ (P^P = dppa, **3**; P^P = $Ph_2PN(Ph)PPh_2$, **5**; P^P = $Ph_2PN(CH_2Ph)PPh_2$, **6**) with carbon tetrachloride. Single crystals of **4** grown from dichloromethane-acetone have been analyzed by X-ray crystallography.

Key words: Ruthenium, Phosphanido-bridged, Coordinative Unsaturation, X-Ray Diffraction

Introduction

Recently we reported the synthesis of some new coordinatively unsaturated diruthenium complexes $[Ru_2(\mu\text{-}H)(\mu\text{-}P^tBu_2)(\mu\text{-}P\hat{}P)(CO)_4]$ (P^P = diphosphanes and *N*-substituted bis(diphenylphosphanyl)amines) [1]. During studies of the reaction behavior of the parent compound $[Ru_2(\mu\text{-}H)(\mu\text{-}P^tBu_2)(\mu\text{-}dppm)(CO)_4]$ (**1**, dppm = $Ph_2PCH_2PPh_2$) we observed a spontaneous reaction with chlorinated solvents like chloroform and carbon tetrachloride giving the corresponding coordinatively saturated complex $[Ru_2(\mu\text{-}Cl)(\mu\text{-}P^tBu_2)(\mu\text{-}dppm)(CO)_4]$ (**2**) [2]. Furthermore this method was also successful for preparing the analogous diiron compound [3]. Sometimes a similar pattern of reactivity was reported in the literature especially for ruthenium complexes containing hydrido ligands [4 – 6]. Also for some other metal compounds the synthesis of chlorido complexes by reaction of the corresponding hydrido species with CCl_4 has been described [7 – 9]. Recently we reported the synthesis and the crystal structure of the new complex $[Ru_2(\mu\text{-}H)(\mu\text{-}P^tBu_2)(\mu\text{-}dppa)(CO)_4]$ (**3**, dppa = $Ph_2PN(H)PPh_2$) as well as the protonation reaction of the latter with HBF_4 [10]. The bridging diphosphane short-bite ligand dppa was of interest in some investigations on homo- and heteronuclear dimetal complexes of platinum [11, 12]. Furthermore, such P-N-P ligands are currently also of interest in studies on dinitrogen-molybdenum complexes [13]. The synthesis of the free ligand dppa from hexamethyldisilazane and chlorodiphenylphosphane has been described by Nöth and Meinel [14]. As a part of studies on the reaction behavior of compound **3** we describe here a convenient synthesis and the characterization of the chlorido-bridged compound $[Ru_2(\mu\text{-}Cl)(\mu\text{-}P^tBu_2)(\mu\text{-}dppa)(CO)_4]$ (**4**) and of two related complexes containing *N*-substituted bis(diphenylphosphanyl)amines.

Results and Discussion

As described for the coordinatively unsaturated complex **1** [2], we observed under similar conditions a spontaneous reaction of the related compound **3** with carbon tetrachloride. The electronically and coordinatively saturated species $[Ru_2(\mu\text{-}Cl)(\mu\text{-}P^tBu_2)(\mu\text{-}dppa)(CO)_4]$ (**4**) was obtained in high yield by dissolving $[Ru_2(\mu\text{-}H)(\mu\text{-}P^tBu_2)(\mu\text{-}dppa)(CO)_4]$ (**3**) at room temperature in carbon tetrachloride according to Eq. 1.

$$\underset{\mathbf{3}}{[Ru_2(\mu\text{-}H)(\mu\text{-}P^tBu_2)(\mu\text{-}dppa)(CO)_4]} + CCl_4 \rightarrow \underset{\mathbf{4}}{[Ru_2(\mu\text{-}Cl)(\mu\text{-}P^tBu_2)(\mu\text{-}dppa)(CO)_4]} + CHCl_3 \quad (1)$$

With respect to the diruthenium core in **3** (32 valence electron species), a substitution reaction of the $2e^-$ hydrido ligand by the $4e^-$ chlorido ligand with simultaneous electronic saturation according to the $18e^-$ rule occurred to give product **4** (34 valence electron species). The new compound **4** was obtained as yellow crystals in yields of about 76 % and was characterized by elemental analysis, IR, and ^1H and ^{31}P NMR spectroscopy (see Experimental Section), as well as by

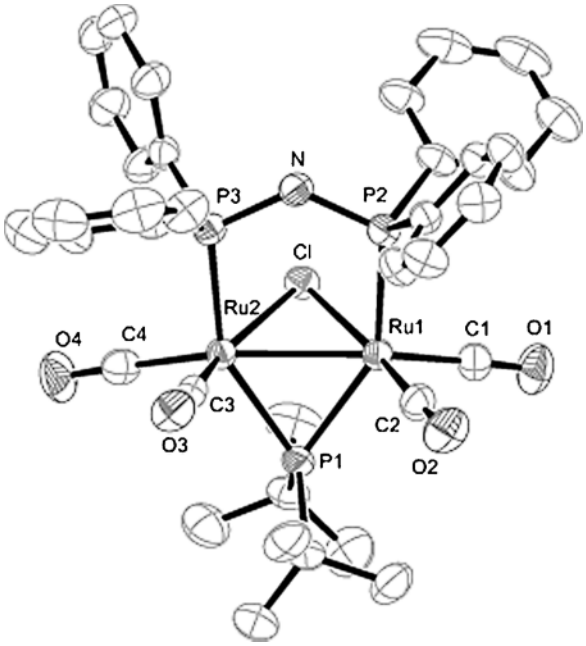

Fig. 1. Molecular structure of **4** in the crystal (the acetone solvate molecule and the H atoms have been omitted for clarity). Displacement ellipsoids are drawn at the 50 % probability level. Selected bond lengths (Å) and angles (deg): Ru1–Ru2 2.7037(4), Ru1–Cl 2.4432(9), Ru2–Cl 2.4871(9), Ru1–P1 2.4157(11), Ru2–P1 2.3971(10), Ru1–P2 2.3756(11), Ru2–P3 2.3361(10), P2–N 1.689(3), P3–N 1.684(4); Ru1–Cl–Ru2 66.51(2), Ru1–P1–Ru2 68.36(3), P2–N–P3 126.3(2).

single-crystal X-ray diffraction. Crystals of **4** (acetone solvate) belong to the monoclinic space group $P2_1/c$ with four molecules in the unit cell. A view of the molecule is shown in Fig. 1, and relevant bond lengths and angles are given in its caption.

The molecular structure of **4** is closely related to that of $[Ru_2(\mu\text{-Cl})(\mu\text{-P}^t\text{Bu}_2)(\mu\text{-dppm})(CO)_4]$ (**2**) [2]. A comparison of the structural parameters of both molecules in the crystal revealed a good agreement: Ru1-Ru2 2.7756(2), Ru1-Cl 2.4609(1), Ru2-Cl1 2.4653(2) Å; Ru1-Cl-Ru2 68.59(4) and Ru1-P1-Ru2 71.64(5)°. In the course of our investigations we examined furthermore the title reaction of two other coordinatively unsaturated complexes, $[Ru_2(\mu\text{-H})(\mu\text{-P}^t\text{Bu}_2)\{\mu\text{-Ph}_2\text{PN(Ph)PPh}_2\}(CO)_4]$ (**5**) and $[Ru_2(\mu\text{-H})(\mu\text{-P}^t\text{Bu}_2)\{\mu\text{-Ph}_2\text{PN(CH}_2\text{Ph)PPh}_2\}(CO)_4]$ (**6**). In both cases the corresponding chlorido-bridged complexes $[Ru_2(\mu\text{-Cl})(\mu\text{-P}^t\text{Bu}_2)\{\mu\text{-Ph}_2\text{PN(Ph)PPh}_2\}(CO)_4]$ (**7**) and $[Ru_2(\mu\text{-Cl})(\mu\text{-P}^t\text{Bu}_2)\{\mu\text{-Ph}_2\text{PN(CH}_2\text{Ph)PPh}_2\}(CO)_4]$ (**8**) were obtained in good yields. The new compounds were characterized by elemental analysis, IR and NMR spectroscopy (see Experimental Section). Moreover we were able to grow single crystals suitable for X-ray diffraction studies of compounds **7** and **8** from dichloromethane/ethanol. The molecular structures could be confirmed, but the collected crystal data were not of high quality.

In conclusion, we have shown that the very electron-rich metal centers in the coordinatively unsaturated hydrido complexes $[Ru_2(\mu\text{-H})(\mu\text{-P}^t\text{Bu}_2)(\mu\text{-P\^P})(CO)_4]$ (P^P = aminobiphosphanes) are capable of rupturing the strong C-Cl bonds in chlorinated solvents like CCl_4 to afford the corresponding chlorido-bridged derivatives in high yields.

Experimental Section

All manipulations were carried out under a dry argon atmosphere using standard Schlenk techniques. Solvents were dried according to standard procedures and stored under nitrogen. The starting compounds were prepared following methods reported in the literature: **3** [10], $[Ru_2(\mu\text{-H})(\mu\text{-P}^t\text{Bu}_2)\{\mu\text{-P\^P}\}(CO)_4]$ (P^P = $Ph_2PN(Ph)PPh_2$, **5**; $Ph_2PN(CH_2Ph)PPh_2$, **6**) [1]. IR spectra were recorded from solid samples with a JASCO FT/IR-460 plus spectrometer equipped with an ATR unit. The ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded using a Jeol Eclipse 270 instrument operating at 270 MHz (^1H) and 109 MHz (^{31}P), respectively. Elemental analyses (C, H, Cl, N) were performed at the Microanalytical Laboratory of the Department of Chemistry, LMU Munich, using a Heraeus Elementar Vario El instrument.

Synthesis of
*$[Ru_2(\mu\text{-Cl})(\mu\text{-P}^t\text{Bu}_2)\{\mu\text{-Ph}_2\text{PN(H)PPh}_2\}(CO)_4]$ (**4**)*

Compound **3** (211 mg, 0.25 mmol) was dissolved in carbon tetrachloride (10 mL) at room temperature. A spontaneous color change from deep-violet to yellow occurred. After stirring for 30 min the solvent was completely removed *in vacuo*. The residue was dissolved in dichloromethane (5 mL) and crystallized by adding ethanol (15 mL) affording **4** as yellow crystals. Yield 167 mg (76 %). – $^{31}P\{^1H\}$ NMR (CD_2Cl_2): $\delta = 275.0$ (t, $^2J_{PP} = 176.7$ Hz, μ-P^{t}Bu$_2$), 81.0 (d, $^2J_{PP} = 176.7$ Hz, μ-dppa). – ^1H NMR (CD_2Cl_2): $\delta = 7.84 – 7.25$ (m, 20H, C_6H_5), 3.85 – 3.81 (m, 1H, NH), 1.39 (d, 9H, $^3J_{PH} = 15.10$ Hz, ^{t}Bu), 1.25 (d, 9H, $^3J_{PH} = 15.10$ Hz, ^{t}Bu). – IR (solid, cm^{-1}): ν(CO) = 1989 (m), 1976 (s), 1937 (s), 1920 (vs). – $C_{36}H_{39}ClNO_4P_3Ru_2$ (880.22): calcd. C 49.12, H 4.47, Cl, 4.03, N 1.59; found C 49.36, H 4.25, Cl, 3.85, N 1.45.

Synthesis of
*[Ru_2(μ-Cl)(μ-P^{t}Bu$_2$){μ-$Ph_2PN(Ph)PPh_2$}(CO)$_4$] (**7**)*

Compound **5** (230 mg, 0.25 mmol) was dissolved in carbon tetrachloride (10 mL) whereupon a spontaneous color change from deep-violet to yellow occurred. After stirring for 30 min at room temperature the solvent was removed *in vacuo*, and the residue was dissolved in dichloromethane (5 mL) and crystallized by adding ethanol (15 mL) affording **7** as yellow crystals. Yield 148 mg (62 %). – ^{31}P{^{1}H} NMR (CD_2Cl_2): $\delta = 275.8$ (t, $^2J_{PP} = 176.0$ Hz, μ-P^{t}Bu$_2$), 99.3 (d, $^2J_{PP} = 176.0$ Hz, μ-P^P). – ^{1}H NMR (CD_2Cl_2): $\delta = 7.62 - 6.56$ (m, 25H, C_6H_5), 1.45 – 1.28 (m, 18H, ^{t}Bu). – IR (solid, cm^{-1}): ν(CO) = 2041 (s), 2025 (s), 1982 (s), 1963 (vs). – $C_{42}H_{43}ClNO_4P_3Ru_2$ (956.32): calcd. C 52.75, H 4.53, Cl, 3.71, N 1.46; found C 53.00, H 4.45, Cl, 3.95, N 1.53.

Synthesis of
*[Ru_2(μ-Cl)(μ-P^{t}Bu$_2$){μ-$Ph_2PN(CH_2Ph)PPh_2$}(CO)$_4$] (**8**)*

Compound **6** (234 mg, 0.25 mmol) was dissolved in carbon tetrachloride (10 mL) at room temperature. A spontaneous color change from deep-violet to yellow occurred. After stirring for 30 min the solvent was removed *in vacuo*. The residue was dissolved in dichloromethane (5 mL) and crystallized by adding ethanol (15 mL) affording **8** as yellow crystals. Yield 175 mg (72 %). – ^{31}P{^{1}H} NMR (CD_2Cl_2): $\delta = 266.9$ (t, $^2J_{PP} = 174.9$ Hz, μ-P^{t}Bu$_2$), 98.6 (d, $^2J_{PP} = 174.9$ Hz, μ-P^P). – ^{1}H NMR (CD_2Cl_2): $\delta = 7.70 - 6.55$ (m, 25H, C_6H_5), 4.44 (t, br, 2H, CH_2), 1.53 – 1.32 (m, 18H, ^{t}Bu). – IR (solid, cm^{-1}): ν(CO) = 2056 (s), 2037 (s), 1989 (s), 1970 (vs). – $C_{43}H_{45}ClNO_4P_3Ru_2$ (970.35): calcd. C 53.23, H 4.67, Cl, 3.65, N 1.44; found C 53.02, H 4.55, Cl, 3.39, N 1.36.

X-Ray crystal structure determination

Suitable single crystals of **4** (as the acetone solvate) were obtained from a mixture of dichloromethane and acetone at 4 °C overnight. A suitable crystal was selected by means of a polarization microscope, mounted on the tip of a glass fiber, and investigated on a Nonius KappaCCD diffractometer using MoK_α radiation ($\lambda = 0.71073$ Å). The structure was solved by Direct Methods (SHELXS-97) [15] and refined by full-matrix least-squares calculations on F^2 (SHELXL-97) [16]. Anisotropic displacement parameters were refined for all non-hydrogen atoms. Details of crystal data, data collection, structure solution, and refinement parameters of **4** are summarized in Table 1.

Table 1. Crystal data and structure refinement details for **4** · CH_3COCH_3.

Formula	$C_{39}H_{45}ClNO_5P_3Ru_2$
M_r	938.26
Crystal size, mm^3	0.25 × 0.12 × 0.09
Temperature, K	173(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a, Å	17.4818(3)
b, Å	13.0851(3)
c, Å	17.9062(4)
β, deg	92.5630(10)
V, Å^3	4091.97(15)
Z	4
$D_{calcd.}$, g cm^{-3}	1.52
μ(MoK_α), mm^{-1}	1.0
F(000), e	1904
θ range data collection, deg	3.19 – 27.62
hkl range	±22, −15 → 16, ±23
Refl. collected / independent / R_{int}	29532 / 9328 / 0.0485
R_1 / wR_2 [$I > 2\sigma(I)$]	0.0472 / 0.1091
R_1 / wR_2 (all data)	0.0605 / 0.1187
S	1.082
$\Delta\rho_{fin}$ (max / min), e Å^{-3}	1.053 / −1.052

CCDC 919461 (**4**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgement

The authors are grateful to the Department of Chemistry, Ludwig Maximilian University Munich, for support of this work. T. M. thanks Prof. P. Klüfers for financial support. A generous loan of hydrated ruthenium(III) chloride from Johnson Matthey plc, Reading, UK, is gratefully acknowledged. P. Mayer is thanked for collecting the X-ray crystal data.

[1] T. Mayer, E. Parsa, H.-C. Böttcher, *J. Organomet. Chem.* **2011**, *696*, 3415.
[2] H.-C. Böttcher, M. Graf, K. Merzweiler, C. Wagner, *Z. Anorg. Allg. Chem.* **2000**, *626*, 597.
[3] H.-C. Böttcher, M. Graf, K. Merzweiler, C. Wagner, *Inorg. Chim. Acta* **2003**, *350*, 399.
[4] J. D. Cotton, M. I. Bruce, F. G. A. Stone, *J. Chem. Soc. (A)* **1968**, 2162.
[5] M. J. A. Kraakman, C. J. Elsevier, V. W. de Haar, K. Vrieze, A. L. Spek, *Inorg. Chim. Acta* **1993**, *203*, 157.

[6] J. S. Field, R. J. Haines, M. W. Stewart, J. Sundermeyer, S. F. Woollam, *J. Chem. Soc., Dalton Trans.* **1993**, 947.
[7] P. Leoni, E. Grilli, M. Pasquali, M. Tomassini, *J. Chem. Soc., Dalton Trans.* **1986**, 1041.
[8] M. A. Esteruelas, A. V. Gómez, A. M. López, L. A. Oro, *Organometallics* **1996**, *15*, 878.
[9] G. Q. Li, J. Feldman, J. A. Krause, M. Orchin, *Polyhedron* **1997**, *16*, 2041.
[10] T. Mayer, H.-C. Böttcher, *Polyhedron* **2013**, *50*, 507.
[11] S. Todisco, V. Gallo, P. Mastroilli, M. Latronico, N. Re, F. Creati, P. Braunstein, *Inorg. Chem.* **2012**, *51*, 11549.
[12] S. J. Hoseini, M. Mohamadikish, K. Kamali, F. W. Heinemann, M. Rashidi, *Dalton Trans.* **2007**, 1697.
[13] T. Ogawa, Y. Kajita, Y. Wasada-Tsutsui, H. Wasada, H. Masuda, *Inorg. Chem.* **2013**, *52*, 182.
[14] H. Nöth, L. Meinel, *Z. Anorg. Allg. Chem.* **1967**, *349*, 225.
[15] G. M. Sheldrick, *Acta Crystallogr.* **1990**, *A46*, 467.
[16] G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112.