

Activation of C–Cl Bonds: Synthesis and Structural Characterization of $[\text{Ru}_2(\mu\text{-Cl})(\mu\text{-P}^i\text{Bu}_2)(\mu\text{-Ph}_2\text{PN}(\text{H})\text{PPh}_2)(\text{CO})_4]$

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The synthesis and structural characterization of the complex $[\text{Ru}_2(\mu\text{-Cl})(\mu\text{-P}^i\text{Bu}_2)(\mu\text{-dppa})(\text{CO})_4]$ (**4**, dppa = $\text{Ph}_2\text{PN}(\text{H})\text{PPh}_2$) are reported. The title compound and two other related complexes were obtained in high yields by the reaction of the coordinatively unsaturated species $[\text{Ru}_2(\mu\text{-H})(\mu\text{-P}^i\text{Bu}_2)(\mu\text{-P}^i\text{P})(\text{CO})_4]$ (P^iP = dppa, **3**; P^iP = $\text{Ph}_2\text{PN}(\text{Ph})\text{PPh}_2$, **5**; P^iP = $\text{Ph}_2\text{PN}(\text{CH}_2\text{Ph})\text{PPh}_2$, **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

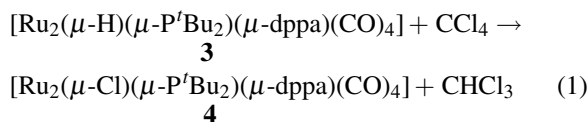
Introduction

Recently we reported the synthesis of some new coordinatively unsaturated diruthenium complexes $[\text{Ru}_2(\mu\text{-H})(\mu\text{-P}^i\text{Bu}_2)(\mu\text{-P}^i\text{P})(\text{CO})_4]$ (P^iP = diphosphanes and *N*-substituted bis(diphenylphosphanyl)amines) [1]. During studies of the reaction behavior of the parent compound $[\text{Ru}_2(\mu\text{-H})(\mu\text{-P}^i\text{Bu}_2)(\mu\text{-dppm})(\text{CO})_4]$ (**1**, dppm = $\text{Ph}_2\text{PCH}_2\text{PPh}_2$) we observed a spontaneous reaction with chlorinated solvents like chloroform and carbon tetrachloride giving the corresponding coordinatively saturated complex $[\text{Ru}_2(\mu\text{-Cl})(\mu\text{-P}^i\text{Bu}_2)(\mu\text{-dppm})(\text{CO})_4]$ (**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 hy-

drido 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 $[\text{Ru}_2(\mu\text{-H})(\mu\text{-P}^i\text{Bu}_2)(\mu\text{-dppa})(\text{CO})_4]$ (**3**, dppa = $\text{Ph}_2\text{PN}(\text{H})\text{PPh}_2$) 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 $[\text{Ru}_2(\mu\text{-Cl})(\mu\text{-P}^i\text{Bu}_2)(\mu\text{-dppa})(\text{CO})_4]$ (**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 $[\text{Ru}_2(\mu\text{-Cl})(\mu\text{-P}^i\text{Bu}_2)(\mu\text{-dppa})(\text{CO})_4]$ (**4**) was obtained in high yield by dissolving $[\text{Ru}_2(\mu\text{-H})(\mu\text{-P}^i\text{Bu}_2)(\mu\text{-dppa})(\text{CO})_4]$ (**3**) at room temperature in carbon tetrachloride according to Eq. 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

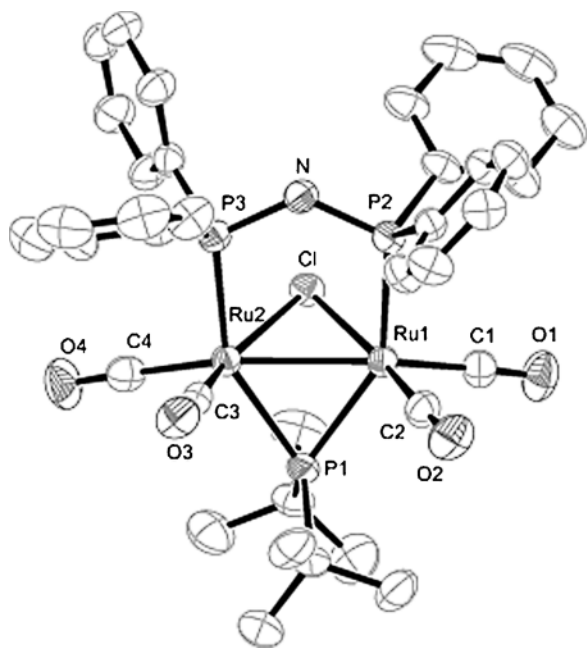


Fig. 1. Molecular structure of **4** in the crystal (the acetone solvate molecule and the H atoms have been omitted for clarity). Displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): Ru1–Ru2 2.7037(4), Ru1–Cl 2.4432(9), Ru2–Cl 2.4871(9), Ru1–P1 2.4157(11), 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 $[\text{Ru}_2(\mu\text{-Cl})(\mu\text{-P}^t\text{Bu}_2)(\mu\text{-dppm})(\text{CO})_4]$ (**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, $[\text{Ru}_2(\mu\text{-H})(\mu\text{-P}^t\text{Bu}_2)\{\mu\text{-Ph}_2\text{PN}(\text{Ph})\text{PPh}_2\}(\text{CO})_4]$ (**5**) and $[\text{Ru}_2(\mu\text{-H})(\mu\text{-P}^t\text{Bu}_2)\{\mu\text{-Ph}_2\text{PN}(\text{CH}_2\text{Ph})\text{PPh}_2\}(\text{CO})_4]$ (**6**). In both cases the corresponding chlorido-bridged complexes $[\text{Ru}_2(\mu\text{-Cl})(\mu\text{-P}^t\text{Bu}_2)\{\mu\text{-Ph}_2\text{PN}(\text{Ph})\text{PPh}_2\}(\text{CO})_4]$ (**7**) and $[\text{Ru}_2(\mu\text{-Cl})(\mu\text{-P}^t\text{Bu}_2)\{\mu\text{-Ph}_2\text{PN}(\text{CH}_2\text{Ph})\text{PPh}_2\}(\text{CO})_4]$ (**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 $[\text{Ru}_2(\mu\text{-H})(\mu\text{-P}^t\text{Bu}_2)(\mu\text{-P}^t\text{P})(\text{CO})_4]$ (P^tP = 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], $[\text{Ru}_2(\mu\text{-H})(\mu\text{-P}^t\text{Bu}_2)\{\mu\text{-P}^t\text{P}\}(\text{CO})_4]$ (P^tP = $\text{Ph}_2\text{PN}(\text{Ph})\text{PPh}_2$, **5**; $\text{Ph}_2\text{PN}(\text{CH}_2\text{Ph})\text{PPh}_2$, **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 $^{31}\text{P}\{^1\text{H}\}$ 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

$[\text{Ru}_2(\mu\text{-Cl})(\mu\text{-P}^t\text{Bu}_2)\{\mu\text{-Ph}_2\text{PN}(\text{H})\text{PPh}_2\}(\text{CO})_4]$ (**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%). – $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ = 275.0 (t, $^2J_{\text{PP}}$ = 176.7 Hz, $\mu\text{-P}^t\text{Bu}_2$), 81.0 (d, $^2J_{\text{PP}}$ = 176.7 Hz, $\mu\text{-dppa}$). – ^1H NMR (CD_2Cl_2): δ = 7.84–7.25 (m, 20H, C_6H_5), 3.85–3.81 (m, 1H, NH), 1.39 (d, 9H, $^3J_{\text{PH}}$ = 15.10 Hz, ^tBu), 1.25 (d, 9H, $^3J_{\text{PH}}$ = 15.10 Hz, ^tBu). – IR (solid, cm^{-1}): $\nu(\text{CO})$ = 1989 (m), 1976 (s), 1937 (s), 1920 (vs). – $\text{C}_{36}\text{H}_{39}\text{ClNO}_4\text{P}_3\text{Ru}_2$ (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

$[Ru_2(\mu-Cl)(\mu-P^tBu_2)\{\mu-Ph_2PN(Ph)PPh_2\}(CO)_4]$ (**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%). – $^{31}P\{^1H\}$ NMR (CD_2Cl_2): $\delta = 275.8$ (t, $^2J_{PP} = 176.0$ Hz, $\mu-P^tBu_2$), 99.3 (d, $^2J_{PP} = 176.0$ Hz, $\mu-P^tP$). – 1H NMR (CD_2Cl_2): $\delta = 7.62$ – 6.56 (m, 25H, C_6H_5), 1.45–1.28 (m, 18H, tBu). – IR (solid, cm^{-1}): $\nu(CO) = 2041$ (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

$[Ru_2(\mu-Cl)(\mu-P^tBu_2)\{\mu-Ph_2PN(CH_2Ph)PPh_2\}(CO)_4]$ (**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%). – $^{31}P\{^1H\}$ NMR (CD_2Cl_2): $\delta = 266.9$ (t, $^2J_{PP} = 174.9$ Hz, $\mu-P^tBu_2$), 98.6 (d, $^2J_{PP} = 174.9$ Hz, $\mu-P^tP$). – 1H 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, tBu). – IR (solid, cm^{-1}): $\nu(CO) = 2056$ (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 $MoK\alpha$ radiation ($\lambda = 0.71073$ Å). The structure

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	$0.25 \times 0.12 \times 0.09$
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
$\mu(MoK\alpha)$, mm^{-1}	1.0
$F(000)$, e	1904
θ range data collection, deg	3.19–27.62
hkl range	$\pm 22, -15 \rightarrow 16, \pm 23$
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), $e\ \text{\AA}^{-3}$	1.053 / –1.052

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.

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.

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