Activation of C–Cl Bonds: Synthesis and Structural Characterization of [Ru2(μ-Cl)(μ-PBu2)](μ-PhPN(H)PPh2)(CO)4

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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 [Ru2(μ-Cl)(μ-PBu2)](μ-dppa)(CO)4 (4, dppa = Ph2PN(H)PPh2) are reported. The title compound and two other related complexes were obtained in high yields by the reaction of the coordinatively unsaturated species [Ru2(μ-H)(μ-PBu2)(μ-P′)(CO)4] (P′ = dppa, 3; P′ = Ph2PN(Ph)PPh2, 5; P′ = Ph3PN(CH2Ph)PPh2, 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 [Ru2(μ-H)(μ-PBu2)(μ-P′)(CO)4] (P′ = diphosphines and N-substituted bis(diphenylphosphinyl)amines) [1]. During studies of the reaction behavior of the parent compound [Ru2(μ-H)(μ-PBu2)(μ-dppm)(CO)4] (1, dppm = Ph2PCH2PPh2) we observed a spontaneous reaction with chlorinated solvents like chloroform and carbon tetrachloride giving the corresponding coordinatively saturated complex [Ru2(μ-Cl)(μ-PBu2)(μ-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 CCl4 has been described [7 – 9]. Recently we reported the synthesis and the crystal structure of the new complex [Ru2(μ-H)(μ-PBu2)(μ-dppa)(CO)4] (3, dppa = Ph2PN(H)PPh2) as well as the protonation reaction of the latter with HBF4 [10]. The bridging diphasphane 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 [Ru2(μ-Cl)(μ-PBu2)(μ-dppa)(CO)4] (4) and of two related complexes containing N-substituted bis(diphenylphosphinyl)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 [Ru2(μ-H)(μ-PBu2)(μ-dppa)(CO)4] (4) was obtained in high yield by dissolving [Ru2(μ-H)(μ-PBu2)(μ-dppa)(CO)4] (3) at room temperature in carbon tetrachloride according to Eq. 1.

\[
[Ru2(\mu-H)(\mu-PBu2)(\mu-dppa)(CO)4] + CCl4 \rightarrow 3
\]

\[
[Ru2(\mu-Cl)(\mu-PBu2)(\mu-dppa)(CO)4] + CHCl3 \quad (1)
\]

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 31P NMR spectroscopy (see Experimental Section), as well as by
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 \([\text{Ru}_2(\mu-H)(\mu-P^3\text{Bu}_2)(\mu-P^3\text{P})(\text{CO})_4]\) \((\mu-P^3 = \text{aminobiphosphanes})\) are capable of rupturing the strong C–Cl bonds in chlorinated solvents like \(\text{CCl}_4\) 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: \(\text{3} \) [10], \([\text{Ru}_2(\mu-H)(\mu-P^3\text{Bu}_2)(\mu-P^3\text{P})(\text{CO})_4]\) \((\mu-P^3 = \text{Ph}_2\text{PN}(\text{Ph})\text{PPh}_2\) \(\text{5}; \text{Ph}_2\text{PN}(\text{CH}_2\text{Ph})\text{PPh}_2\) \(\text{6} \) [1]. IR spectra were recorded from solid samples with a JASCO FT/IR-460 plus spectrometer equipped with an ATR unit. The \(^1\text{H}\) and \(^{31}\text{P}^{[1]}\text{H}\) NMR spectra were recorded using a Jeol Eclipse 270 instrument operating at 270 MHz \((\text{H})\) and 109 MHz \((\text{P})\), respectively. Elemental analyses (\(\text{C, H, Cl, N}\) were performed at the Microanalytical Laboratory of the Department of Chemistry, LMU Munich, using a Heraeus Elementar Vario El instrument.

**Synthesis of**

\([\text{Ru}_2(\mu-CI)(\mu-P^3\text{Bu}_2)(\mu-\text{Ph}_2\text{PN}(\text{Ph})\text{PPh}_2)(\text{CO})_4]\) \(\text{4}\)

Compound \(\text{3} \) (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 \(\text{4}\) as yellow crystals. Yield 167 mg (76%). – \(^{31}\text{P}^{[1]}\text{H}\) NMR \((\text{CD}_2\text{Cl}_2\)\): \(\delta = 275.0 \) (t, \(^{2}\text{J}_{\text{PP}} = 176.7\) Hz, \(\mu-P^3\text{Bu}_2\)), 81.0 \(\) (d, \(^{2}\text{J}_{\text{PP}} = 176.7\) Hz, \(\mu-\text{dpmm}\) ). – \(^1\text{H}\) NMR \((\text{CD}_2\text{Cl}_2\)\): \(\delta = 7.84-7.25\) (m, 20H, \(\text{C}_8\text{H}_5\)), 3.85 – 3.81 (m, 1H, NH), 1.39 (d, 9H, \(^{3}\text{J}_{\text{PH}} = 15.10\) Hz, \(\text{Bu}\)), 1.25 (d, 9H, \(^{3}\text{J}_{\text{PH}} = 15.10\) Hz, \(\text{Bu}\)). – IR (solid, cm\(^{-1}\)): \(\nu(\text{CO}) = 1989\) (m), 1976 (s), 1937 (s), 1920 (vs). – \(\text{C}_{36}\text{H}_{45}\text{ClNO}_3\text{P}_2\text{Ru}_2\) \(\text{880.22}\). 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 [Ru₂(μ-Cl)[μ-P̂P̂Bu₂][μ-Ph₂PN(Ph)PPh₂](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%). – ³¹P[¹H] NMR (CD₂Cl₂): δ = 275.8 (t. J₂PP = 176.0 Hz, µ-P̂P₄Bu₂), 99.3 (d. J₂PP = 176.0 Hz, µ-P̂P₄P₄). – ¹H NMR (CD₂Cl₂): δ = 7.62 – 6.56 (m, 25H, C₆H₅), 1.45 – 1.28 (m, 18H, tBu), – IR (solid, cm⁻¹): ν(CO) = 2041 (s), 2025 (s), 1982 (s), 1963 (vs). – C₂H₅ClNO₃P₂Ru₂ (956.32): calcd. C 52.75, H 4.55, Cl 3.39, N 1.36. found C 53.02, H 4.55, Cl, 3.95, N 1.36.

Synthesis of [Ru₂(μ-Cl)[μ-P̂P̂Bu₂][μ-Ph₂PN(CH₂Ph)PPh₂](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%). – ³¹P[¹H] NMR (CD₂Cl₂): δ = 266.9 (t. J₂PP = 174.9 Hz, µ-P̂P₄Bu₂), 98.6 (d. J₂PP = 174.9 Hz, µ-P̂P₄P₄). – ¹H NMR (CD₂Cl₂): δ = 7.70 – 6.55 (m, 25H, C₆H₅), 4.44 (t, br, 2H, CH₂), 1.53 – 1.32 (m, 18H, tBu). – IR (solid, cm⁻¹): ν(CO) = 2056 (s), 2037 (s), 1989 (s), 1970 (vs). – C₂H₅ClNO₃P₂Ru₂ (956.32): calcd. C 52.75, H 4.45, Cl, 3.71, N 1.46; found C 53.00, H 4.45, Cl, 3.95, N 1.53.

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 spontaneous 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 MoKα radiation (λ = 0.71073 Å). The structure was solved by Direct Methods (SHELXS-97) [15] and refined by full-matrix least-squares calculations on F² (SHEXL-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 · CH₃COCH₃.

<table>
<thead>
<tr>
<th>Formula</th>
<th>C₅₇H₅₉ClNO₃P₂Ru₂</th>
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<tbody>
<tr>
<td>Mᵣ</td>
<td>938.26</td>
</tr>
<tr>
<td>Crystal size, mm³</td>
<td>0.25 × 0.12 × 0.09</td>
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<tr>
<td>Temperature, K</td>
<td>173(2)</td>
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<tr>
<td>Crystal system</td>
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<tr>
<td>Space group</td>
<td>P2₁/c</td>
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<tr>
<td>a, Å</td>
<td>17.4818(3)</td>
</tr>
<tr>
<td>b, Å</td>
<td>13.0851(3)</td>
</tr>
<tr>
<td>c, Å</td>
<td>17.9062(4)</td>
</tr>
<tr>
<td>β, deg</td>
<td>92.56(10)</td>
</tr>
<tr>
<td>V, Å³</td>
<td>4091.97(15)</td>
</tr>
<tr>
<td>Z</td>
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<tr>
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<tr>
<td>μ(MoKα), mm⁻¹</td>
<td>1.0</td>
</tr>
<tr>
<td>F(000), e</td>
<td>1904</td>
</tr>
<tr>
<td>θ range data collection, deg</td>
<td>±22. – 15 → 16, ±23</td>
</tr>
<tr>
<td>hkl range</td>
<td>±22. – 15 → 16, ±23</td>
</tr>
<tr>
<td>Refl. collected / independent / Rint</td>
<td>29532 / 9328 / 0.0485</td>
</tr>
<tr>
<td>R₁ / wR₁ [I &gt; 2σ(I)]</td>
<td>0.0472 / 0.1091</td>
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<tr>
<td>R₁ / wR₁ (all data)</td>
<td>0.0605 / 0.1187</td>
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<tr>
<td>S</td>
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<tr>
<td>Δρmax (max / min), e Å⁻³</td>
<td>1.053 / – 1.052</td>
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</table>

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.


