Journal of Organometallic Chemistry 696 (2011) 3415–3420

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Synthesis of electronically and coordinatively unsaturated complexes $[Ru_2(CO)_4(\mu\text{-}H)(\mu\text{-}P^tBu_2)(\mu\text{-}L_2)]$ (L_2 = biphosphanes)

Tobias Mayer, Edris Parsa, Hans-Christian Böttcher*

Department Chemie, Ludwig-Maximilians-Universität München, Butenandtstrasse 5-13, 81377 München, Germany

ARTICLE INFO

Article history:
Received 5 April 2011
Received in revised form
3 July 2011
Accepted 25 July 2011

Dedicated to Prof. Dirk Steinborn on the occasion of his 65th birthday.

Keywords:
Ruthenium
Carbonyl
Coordinative Unsaturation
Phosphanido-bridged
Crystal structure

ABSTRACT

A convenient synthesis and the characterization of six new electronically and coordinatively unsaturated complexes of the formula $[Ru_2(CO)_4(\mu\text{-}H)(\mu\text{-}P^tBu_2)(\mu\text{-}L_2)]$ (**2b**–**g**) (*Ru*=*Ru*) is described exhibiting a close relation to the known $[Ru_2(CO)_4(\mu\text{-}H)(\mu\text{-}P^tBu_2)(\mu\text{-}dppm)]$ (**2a**). The complexes **2b**–**g** were obtained in a kind of one-pot synthesis starting from $[Ru_3(CO)_{12}]$ and P^tBu_2H in the first step followed by the reaction with the bidentate bridging ligand in the second step. The method was developed for the following bridging ligands (μ-L_2): dmpm (**2b**, dmpm = $Me_2PCH_2PMe_2$), dcypm (**2c**, dcypm = $Cy_2PCH_2PCy_2$), dppen (**2d**, dppen = $Ph_2PC(=CH_2)PPh_2$), dppha (**2e**, dppha = $Ph_2PN(Ph)PPh_2$), dpppra (**2f**, dpppra = $Ph_2PN(Pr)PPh_2$), and dppbza (**2g**, dppbza = $Ph_2PN(CH_2Ph)PPh_2$). The molecular structures of all new complexes **2b**–**g** were determined by X-ray diffraction.

1. Introduction

Some years ago we described the synthesis and crystal structure of the electronically and coordinatively unsaturated complex $[Ru_2(CO)_4(\mu\text{-}H)(\mu\text{-}P^tBu_2)(\mu\text{-}dppm)]$ *(Ru*=*Ru)* (**2a**, dppm = $Ph_2PCH_2PPh_2$) [1]. The latter compound was obtained in a kind of one-pot synthesis from $[Ru_3(CO)_{12}]$ and P^tBu_2H affording the 32 VE complex $[Ru_2(CO)_4(\mu\text{-}H)(\mu\text{-}P^tBu_2)(P^tBu_2H)_2]$ (**1**) in situ [2], followed by the substitution of both secondary phosphanes towards dppm. Because of the unsaturated nature of the central $Ru_2(\mu\text{-}H)$ moiety compound **2a** showed an enhanced reactivity towards a great variety of small molecules under mild conditions. Thus reactions were obtained with molecules like CO and CH_2, respectively [1], CCl_4, S_8, NO^+, and CS_2 [3], phosphanes as well as phenylethyne [4]. The reaction with HBF_4 resulted in the protonation of the metal–metal bond [5], SO_2 added to the corresponding μ-SO_2 complex [6], and $P{\equiv}C^tBu$ resulted in the hydrodimetalation of the phosphaethyne [7]. Nitric oxide afforded in an unexpected reaction with the reductive dimerization of the latter, the hyponitrite species $[Ru_2(CO)_4(\mu\text{-}H)(\mu\text{-}P^tBu_2)(\mu\text{-}\eta^2\text{–}ONNO)]$ [8]. Especially in light of this reaction we are currently interested in some new similarly constituted diruthenium complexes to explore the influence of the ligand sphere on the course of the unusual reaction behavior towards NO. As a first step in this direction, herein we describe investigations on the synthesis and the structural characterization of some new electronically and coordinatively unsaturated complexes of the formula $[Ru_2(CO)_4(\mu\text{-}H)(\mu\text{-}P^tBu_2)(\mu\text{-}L_2)]$ (L_2 = biphosphane).

2. Experimental

2.1. General considerations

All manipulations were performed under an atmosphere of dry argon using conventional Schlenk techniques. Solvents were dried over sodium-benzophenone ketyl or molecular sieves and were distilled under argon prior to use. Chemicals were purchased commercially from Aldrich, the ligands dmpm, dcypm, and dppen from ABCR. The amino ligands dppha, dpppra, and dppbza were prepared by a modified literature procedure [9]. IR spectra were recorded as solid with a JASCO FT/IR-460 plus spectrometer. NMR spectra were obtained using Jeol Eclipse 270 and 400 instruments operating at 270 and 400 (^1H) and at 109 MHz and 161 MHz (^{31}P), respectively. Chemical shifts are given in ppm from $SiMe_4$ (^1H) or 85% H_3PO_4 ($^{31}P\{^1H\}$). Microanalyses (C, H, N) were performed by the Microanalytical Laboratory of the Department of Chemistry, LMU Munich, using a Heraeus Elementar Vario EI instrument.

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* Corresponding author. Tel.: +49 89218077422; fax: +49 89218077407.
E-mail address: hans.boettcher@cup.uni-muenchen.de (H.-C. Böttcher).

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doi:10.1016/j.jorganchem.2011.07.033

2.2. Synthesis of [$Ru_2(CO)_4(\mu$-H)(μ-P^{t}Bu$_2$)(μ-L_2)] (L_2 = dmpm, **2b**; dcypm, **2c**; dppen, **2d**)

A mixture of [$Ru_3(CO)_{12}$] (640 mg, 1.0 mmol) and PBu$^t_2$H (1 mL, 6.8 mmol) in THF (30 mL) was refluxed with stirring for 4 h. During this time the color of the solution changed from orange to deep red. After cooling to room temperature, the solvent was removed in vacuo and the excess phosphane was pumped off for about 30 min. The remaining residue was dissolved in 20 mL of toluene, the corresponding ligand L_2 (1.0 mmol) was added and the mixture refluxed with stirring for 5 h. After cooling to room temperature, the solvent was removed to dryness in vacuo. The remaining residue was crystallized from diethyl ether/ethanol and diethyl ether/hexane, respectively, affording deep violet crystals of **2b**–**d**. **2b**: Yield: 418 mg (70%). Anal. Calcd for $C_{17}H_{33}O_4P_3Ru_2$ (596.51): C, 34.23; H, 5.58. Found: C, 34.45; H, 5.72. IR (solid): ν(CO): 1951s, 1897vs, 1877vs, 1864s. ^{1}H NMR (CD_2Cl_2): δ 3.43 (t, 2H, $^2J_{PH}$ = 9.8 Hz, CH_2), 1.37 (d, 18H, $^3J_{PH}$ = 13.8 Hz, t-C_4H_9), 1.21 (d, 12H, $^2J_{PH}$ = 4.3 Hz, PCH_3), −9.40 (m, 1H, μ-H). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 279.9 (t, $^2J_{PP}$ = 137.9 Hz, μ-P^{t}Bu$_2$), 6.7 (d, $^2J_{PP}$ = 137.9 Hz, μ-dmpm).

2c: Yield: 539 mg (62%). Anal. Calcd for $C_{37}H_{65}O_4P_3Ru_2$ (868.98): C, 51.14; H, 7.54. Found: C, 51.01; H, 7.68%. IR (solid): ν(CO): 1994s, 1964vs, 1918vs. ^{1}H NMR (CD_2Cl_2): δ 1.81–1.14 (m, br, 46H, C_6H_{11} overlapped with P–CH_2–P), 1.34 (d, 18H, $^3J_{PH}$ = 13.9 Hz, t-C_4H_9), −9.10 (m, 1H, μ-H). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 290.6 (t, $^2J_{PP}$ = 134.4 Hz, μ-P^{t}Bu$_2$), 34.4 (d, $^2J_{PP}$ = 134.4 Hz, μ-dcypm). **2d**: Yield: 574 mg (67%). Anal. Calcd for $C_{38}H_{41}O_4P_3Ru_2$ (856.80): C, 53.27; H, 4.82. Found: C, 53.01; H, 4.69%. IR (solid): ν(CO): 1966s, 1942vs, 1932vs, 1913s. ^{1}H NMR (CD_2Cl_2): δ 7.41–7.17 (m, 20H, C_6H_5), 6.04 (t, 2H, = CH_2, $^3J_{PH}$ = 20.3 Hz), 1.49 (d, 9H, $^3J_{PH}$ = 14.4 Hz), 1.36 (d, 9H, $^3J_{PH}$ = 14.4 Hz), −14.24 (dt, 1H, $^2J_{PH}$ = 22.3 Hz, $^2J_{PH}$ = 16.3 Hz, μ-H). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 279.9 (t, $^2J_{PP}$ = 133.3 Hz, μ-P^{t}Bu$_2$), 44.3 (d, $^2J_{PP}$ = 133.3 Hz, μ-dppen).

2.3. Synthesis of [$Ru_2(CO)_4(\mu$-H)(μ-P^{t}Bu$_2$)(μ-L_2)] (L_2 = dppha, **2e**; dpppra, **2f**; dppbza, **2g**)

A mixture of [$Ru_3(CO)_{12}$] (640 mg, 1.0 mmol) and PBu$^t_2$H (1 mL, 6.8 mmol) in THF (30 mL) was refluxed with stirring for 4 h. After cooling to room temperature, the solvent was removed in vacuo. The remaining residue was dissolved in 20 mL of acetone, the corresponding ligand L_2 (1.0 mmol) was added and the mixture refluxed with stirring for 3 h. After cooling to room temperature, the solvent was removed to dryness in vacuo. The remaining residue was crystallized from dichloromethane/ethanol affording deep violet crystals of **2e**–**g**. **2e**: Yield: 673 mg (73%). Anal. Calcd for $C_{42}H_{44}NO_4P_3Ru_2$ (921.88): C, 54.72; H, 4.81; N, 1.52. Found: C, 54.51; H, 4.69; N, 1.47%. IR (solid): ν(CO): 1994s, 1972vs, 1932vs, 1922s. ^{1}H NMR (CD_2Cl_2): δ 7.57–7.29 (m, 20H, C_6H_5), 6.88–5.89 (m, 5H, NC_6H_5), 1.37 (d, 9H, $^3J_{PH}$ = 14.1 Hz, t-C_4H_9), 1.32 (d, 9H, $^3J_{PH}$ = 14.1 Hz, t-C_4H_9), −14.45 (dt, 1H, $^2J_{PH}$ = 21.8 Hz, $^2J_{PH}$ = 16.2 Hz, μ-H). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 286.3 (t, $^2J_{PP}$ = 144.7 Hz, μ-P^{t}Bu$_2$), 110.9 (d, $^2J_{PP}$ = 144.7 Hz, μ-dppha).

2f: Yield: 506 mg (57%). Anal. Calcd for $C_{39}H_{46}NO_4P_3Ru_2$ (887.86): C, 52.76; H, 5.22; N, 1.58. Found: C, 53.01; H, 4.95; N, 1.40%. IR (solid): ν(CO): 1994s, 1971vs, 1928vs, 1916s. ^{1}H NMR (CD_2Cl_2): δ 7.67–7.37 (m, 20H, C_6H_5), 3.63 (m, 2H, NCH_2), 2.78 (m, 2H, –CH_2CH$_3$), 1.31 (d, 9H, $^3J_{PH}$ = 14.1 Hz, t-C_4H_9), 1.26 (d, 9H, $^3J_{PH}$ = 14.1 Hz, t-C_4H_9), 0.13 (t, 3H, $^3J_{HH}$ = 7.3 Hz, CH$_2$CH_3), −14.79 (dt, 1H, $^2J_{PH}$ = 22.0 Hz, $^2J_{PH}$ = 16.5 Hz, μ-H). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 283.5 (t, $^2J_{PP}$ = 142.2 Hz, μ-P^{t}Bu$_2$), 108.1 (d, $^2J_{PP}$ = 142.2 Hz, μ-dpppra). **2g**: Yield: 608 mg (65%). Anal. Calcd for $C_{43}H_{46}NO_4P_3Ru_2$ (935.90): C, 55.18; H, 4.95; N, 1.50. Found: C, 54.91; H, 4.93; N, 1.38%. IR (solid): ν(CO): 1988s, 1971vs, 1926vs, 1893s. ^{1}H NMR (CD_2Cl_2): δ 7.68–7.30 (m, 20H, C_6H_5), 7.33–6.66 (m, 5H, CH$_2$C$_6H_5$), 4.34 (t, 2H, $^3J_{PH}$ = 7.3 Hz, CH_2), 1.39 (d, 18H, $^3J_{PH}$ = 14.5 Hz, t-C_4H_9), −14.72 (dt, 1H, $^2J_{PH}$ = 22.1 Hz, $^2J_{PH}$ = 16.2 Hz, μ-H). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 279.4 (t, $^2J_{PP}$ = 144.4 Hz, μ-P^{t}Bu$_2$), 111.6 (d, $^2J_{PP}$ = 144.4 Hz, μ-dppbza).

2.4. X-ray structural determination

Suitable single crystals for X-ray diffraction were selected by means of a polarization microscope, mounted on the tip of a glass fiber, and investigated on an Oxford XCalibur and a Bruker Nonius-Kappa CCD diffractometer, respectively, using Mo-Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods (SHELXS) [10] and refined by full-matrix least-squares calculations on F^2 (SHELXL-97) [11]. Details of the crystal data, data collection, structure solution, and refinement parameters of compounds **2b**–**g** are summarized in Table 1 and Table 2 respectively.

3. Results and discussion

3.1. Synthesis and characterization of compounds

Some time ago we investigated the reaction of [$Ru_3(CO)_{12}$] with P^{t}Bu$_2$H resulting in the electronically and coordinatively unsaturated complex [$Ru_2(CO)_4(\mu$-H)(μ-P^{t}Bu$_2$)(P^{t}Bu$_2$H)$_2$] ($Ru{=}Ru$) (**1**) [2]. An interesting feature of **1** affects its molecular fluxionality during the change from the solution into the solid state. Thus **1** exhibits in solution a symmetrical structure with exclusively terminal CO groups whereas **1** adopts in the crystal an asymmetrical framework containing a semibridging carbonyl ligand. Compound **1** reacted with dppm (dppm = $Ph_2PCH_2PPh_2$) in refluxing toluene with the substitution of both terminal phosphane ligands towards the bridging bidentate dppm resulting in [$Ru_2(CO)_4(\mu$-H)(μ-P^{t}Bu$_2$)(μ-dppm)] (**2a**) [1]. It should be noted here that the most important prerequisite for the isolation of **1** and the latter species **2a** is only

Table 1
Crystal data and structure refinement details for compounds **2b**–**d**.

Compound	2b	2c	2d
Empirical formula	$C_{17}H_{33}O_4P_3Ru_2$	$C_{37}H_{65}O_4P_3Ru_2$	$C_{38}H_{41}O_4P_3Ru_2$
Formula weight	596.48	868.94	856.76
Temperature (K)	200 (2)	200 (2)	173 (2)
Crystal system	monoclinic	orthorhombic	monoclinic
Space group	$P2_1/c$	$P2_12_12_1$	$P2_1/c$
a (Å)	16.436 (2)	11.4469 (5)	17.0748 (19)
b (Å)	8.9509 (9)	18.6483 (10)	16.2508 (15)
c (Å)	22.199 (4)	19.1508 (9)	13.8819 (7)
α (°)	90	90	90
β (°)	131.323 (11)	90	104.291 (6)
γ (°)	90	90	90
Volume (Å^3)	2456.7 (7)	4088.0 (3)	3732.7 (6)
Z	4	4	4
ρ_{calcd} (g cm^{-3})	1.613	1.412	1.525
μ/mm^{-1}	1.442	0.891	0.975
θ range for data collection (°)	3.79–26.32	3.71–26.31	4.33–26.32
Reflections measured	14196	31969	16024
R_{int}	0.0322	0.0631	0.0242
Observed reflections	3761	6189	5341
Reflections in refinement	4971	8311	7537
Parameters/restraints	249/0	425/0	434/0
R (F_{obs})	0.0385	0.0338	0.0303
R_w (F^2)	0.1012	0.0554	0.0686
S	1.121	0.848	0.914
Max electron density (e·Å^{-3})	2.089	0.598	0.778
Min electron density (e·Å^{-3})	−1.391	−0.432	−1.137

Table 2
Crystal data and structure refinement details for compounds **2e**–**g**.

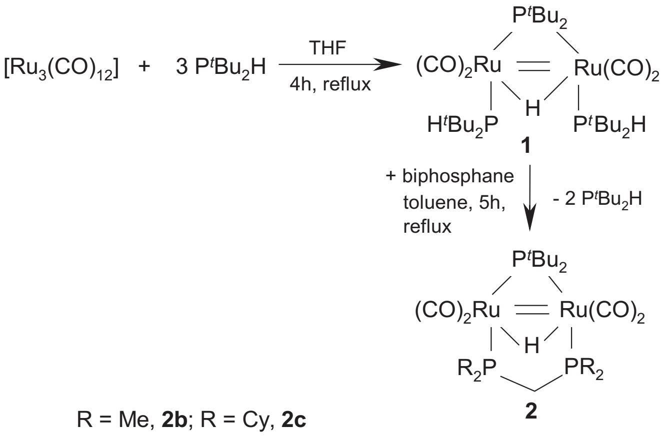
Compound	**2e**	**2f**	**2g**
Empirical formula	$C_{42}H_{44}NO_4P_3Ru_2$	$C_{39}H_{46}NO_4P_3Ru_2$	$C_{43}H_{46}NO_4P_3Ru_2$
Formula weight	921.83	887.82	935.86
Temperature (K)	173 (2)	173 (2)	173 (2)
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a (Å)	9.8265 (2)	9.6511 (18)	18.7391
b (Å)	18.7030 (4)	34.279 (4)	11.9867 (2)
c (Å)	22.8079 (4)	12.3799 (8)	18.7391 (2)
α (°)	90	90	90
β (°)	103.3440 (10)	103.882 (10)	94.417 (2)
γ (°)	90	90	90
Volume (Å^3)	4078.58 (14)	3976.0 (9)	4196.67 (9)
Z	4	4	4
ρ_{calcd} (g cm^{-3})	1.501	1.483	1.481
μ/mm^{-1}	0.899	0.919	0.875
θ range for data collection (°)	3.26–27.51	4.17–26.25	4.22–26.02
Reflections measured	32955	17170	27772
R_{int}	0.0797	0.0293	0.0456
Observed reflections	6870	5841	6390
Reflections in refinement	9361	7995	8100
Parameters/restraints	480/2	453/0	488/0
R (F_{obs})	0.0430	0.0296	0.0294
R_w (F^2)	0.1076	0.0607	0.0727
S	1.075	0.902	0.953
Max electron density (e·Å^{-3})	1.280	0.759	0.881
Min electron density (e·Å^{-3})	−0.890	−0.470	−0.670

given in the presence of the bulky μ-P^{t}Bu$_2$ group. This essential circumstance affects even all the other complexes described in this work. Some efforts to obtain analogously constituted complexes with less bulky substituents at the bridging phosphorus (e.g. Cy or Ph) failed. We assume that the peculiar sterical and electronical properties of the ^{t}Bu groups could be the reasonable explanation for this.

By using the same synthetic protocol as developed for the preparation of **2a**, now we were successful in the synthesis of the new compounds **2b**–**d**. Thus the *in situ*-prepared complex **1** reacted with the corresponding biphosphanes in refluxing toluene affording the unsaturated complexes [Ru$_2$(CO)$_4$(μ-H)(μ-P^{t}Bu$_2$)(μ-dmpm)] (**2b**; dmpm = $Me_2PCH_2PMe_2$), [Ru$_2$(CO)$_4$(μ-H)(μ-P^{t}Bu$_2$)(μ-dcypm)] (**2c**; dcypm = $Cy_2PCH_2PCy_2$), and [Ru$_2$(CO)$_4$(μ-H)(μ-P^{t}Bu$_2$)(μ-dppen)] (**2d**; dppen = $Ph_2PC(=CH_2)PPh_2$) in good yields. The first step of the one-pot synthesis occurs with a loss of carbon monoxide and an accompanying redox process including the oxidation of the formally zerovalent ruthenium with simultaneous formation of the hydrido ligand. The reaction sequence for the preparation of **2b** and **2c**, respectively, is illustrated in the Scheme. As a side product in the degradation reaction of the trinuclear ruthenium carbonyl the compound [Ru(CO)$_3$(P^{t}Bu$_2$H)$_2$] [2] could be identified which was omitted in the Scheme.

The complexes **2b**–**d** were obtained by this procedure as deep violet crystals in yields of about 70%. The crystalline compounds are moderately stable in air. Their solutions, however, are very sensitive towards atmospheric oxygen, i.e., they decompose within seconds while decolorizing the solutions. Unfortunately we have no evidence of what happens during this spontaneous decomposition reaction because no defined products could be identified by spectroscopic means in many attempts.

A small variation in the synthetic protocol was necessary for the synthesis of the compounds **2e**–**g** containing the aminophosphane ligands. In these cases the use of toluene as the solvent was not possible because decomposition to some extent was observed.



Scheme.

Therefore the use of acetone as the reaction medium was preferred, resulting in comparable yields as obtained during the synthesis of compounds **2b**–**d**. The reactions were conducted under similar conditions as applied to the preparation of compounds **2a**–**d** and the sequence of this one-pot synthesis was similar to that outlined in the Scheme.

Suitable crystals of all compounds **2b**–**g** for X-ray diffraction studies were obtained and their molecular structures could be determined (see below). Furthermore, the compounds **2b**–**g** were characterized by analytical and spectroscopic methods. The IR spectra (as solids) of all compounds show in each case four absorption bands that are characteristic of terminal carbonyl ligands (see Experimental). The ^{1}H NMR spectra of all new complexes include a characteristic resonance in the high field region (ca. −9 ppm, **2b** and **2c**; ca. −14 ppm, **2d**–**g**) as a doublet of triplets (or multiplet) with corresponding couplings to the bridging phosphorus nuclei. These signals can be attributed to the bridging hydrido ligands. The compounds **2b** and **2c** show the hydride resonance shifted to lower field values because of the higher electron density at the ruthenium atoms caused by the +I effect of the alkyl groups of the biphosphane ligands. Some remarks should be given concerning the signals of the *tert*-butyl groups of the bridging phosphanido ligands. By our long experience, in the room temperature ^{1}H NMR spectra these signals were observed as a set of two doublets in the case where three bridging ligands (μ-P^{t}Bu$_2$, μ-dppm, and a third ligand μ-X) are present in the molecule, e.g [1,3–7]. An exception in this light represent the compounds **2b**, **2c**, and **2g** which show in the room temperature ^{1}H NMR spectra only one doublet (18H) corresponding to the protons of the *tert*-butyl groups of the phosphanido bridge. The same observation was also made for the closely related compound [Fe$_2$(CO)$_4$(μ-H)(μ-P^{t}Bu$_2$)(μ-dppm)] [12], whereas for the closely related diruthenium complex **2a** however, the more frequently observed case of two doublets (each 9H) was found at room temperature. To bright more insight into this phenomenon, a dynamic NMR (*DNMR*) investigation of [Fe$_2$(CO)$_4$(μ-H)(μ-P^{t}Bu$_2$)(μ-dppm)] in the range from 25 °C to −80 °C was carried out in toluene as the solvent. Interestingly, this study afforded significant changes in the ^{1}H NMR spectra concerning the shape of the doublet belonging to the *tert*-butyl groups. Thus the ^{1}H NMR spectrum of the latter diiron complex showed at 25 °C a sharp doublet at δ 1.59 ($^3J_{PH}$ = 14.4 Hz). In the range from −20 to −40 °C these two signals broadened with a shoulder. At −50 °C the signal appeared only as one very broad signal with a shoulder which separated between −60 to −70 °C into two broad signal groups.

Finally at −80 °C, two broad signals (with some shoulder structure) were observed exhibiting chemical shifts at 1.79 and 1.53 ppm, respectively. These results hint to a stereodynamic behavior with respect to the rotation of the *tert*-butyl substituents about P–(*t*-C_4H_9) bonds on the one side *and* the rotation of the phosphanido ligand about the P–M bonds on the other side. At the moment we have no determined explanation which kind of stereodynamic processes are really responsible for this observation. In this light we have planned a broad *DNMR* investigation of a great number of our compounds containing the M(μ-P^tBu_2)-M moiety. The $^{31}P\{^1H\}$ NMR solution spectra of compounds **2b**–**f** indicate in each case the chemical equivalence of the two phosphorus nuclei of the bridging biphosphanes and aminobiphosphanes, respectively. This is confirmed by the observed triplet/doublet pattern in the spectra of all compounds (see Experimental).

In the case where the hydrido ligand is taken into account, by electron counting, 32 valence electrons (VE) result for these complexes. Therefore they are electronically unsaturated in the sense of the 18e rule. Moreover they are also coordinatively unsaturated because addition reactions of further ligands are possible. To obey the 18e rule, a dinuclear complex should exhibit an overall electron count of 34 VE. Therefore a formally Ru-Ru double bond can be assumed in all new complexes **2b**–**g**. The short Ru-Ru bond distances found in each case of all these new compounds (shorter than 2.7 Å) confirm this assumption. Furthermore, in light of the isolobal relationship between CH_2 and a fragment d^8–ML_4, these complexes can be formally considered as isolobal to ethylene.

3.2. Crystal and molecular structures of 2b–g

Suitable single crystals for the X-ray diffraction study of **2b** and **2c**, respectively, were grown from acetonitrile at 4 °C. Violet crystals of **2b** belonging to the monoclinic space group $P2_1/c$ were obtained. Fig. 1 shows a selected ORTEP view of the molecule of **2b**, selected bond lengths and angles are listed in Table 3. The molecular structure of **2b** is closely related to that of [$Ru_2(CO)_4$(μ-H)(μ-P^tBu_2)(μ-dppm)] (**2a**). The molecule consists of a diruthenium core bridged by a phosphanido ligand, a dppm group and a hydrido ligand. Both complexes **2a** and **2b** constitute complexes with 32 VE and, in the sense of the 18e rule, they should possess metal–metal double bonds as discussed before. The found short Ru–Ru distances are in good agreement with this. Thus for comparison purposes, for **2a** the Ru(1)–Ru(2) bond was found to be 2.6974(4) Å [1]. The short Ru(1)–Ru(2) separation in the molecule of **2b** confirms the reasonable assumption of a double bond between the ruthenium atoms.

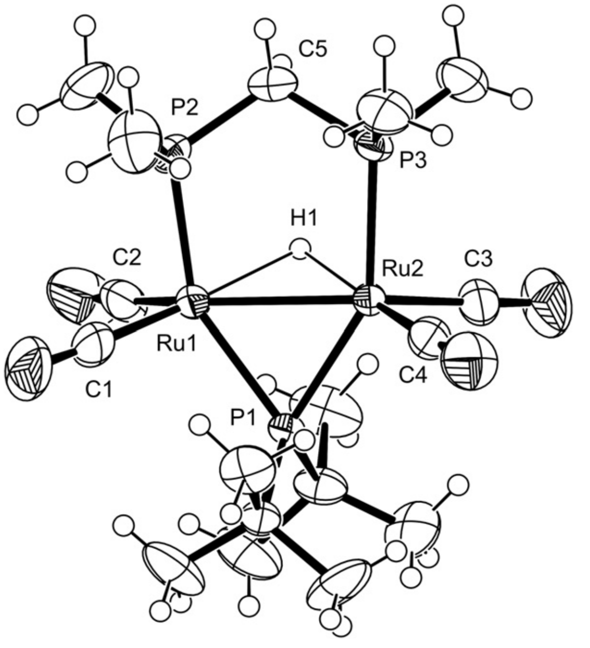


Fig. 1. ORTEP diagram and atom labeling scheme of compound **2b** with ellipsoids drawn at the 50% probability level.

Table 3
Selected bond lengths (Å) and angles (°) for compounds **2b**–**2d**.

	2b	2c	2d
Ru(1)–Ru(2)	2.683 (1)	2.703 (1)	2.692 (1)
Ru(1)–H(1)	1.94 (4)	1.83 (3)	1.90 (3)
Ru(2)–H(1)	1.92 (4)	1.88 (3)	1.88 (3)
Ru(1)–C(1)	1.836 (6)	1.856 (4)	1.872 (3)
Ru(1)–C(2)	1.886 (6)	1.873 (4)	1.880 (3)
Ru(2)–C(3)	1.871 (6)	1.880 (4)	1.883 (3)
Ru(2)–C(4)	1.852 (7)	1.852 (5)	1.856 (4)
Ru(1)–P(1)	2.334 (2)	2.331 (1)	2.316 (1)
Ru(2)–P(1)	2.341 (1)	2.331 (1)	2.323 (1)
Ru(1)–P(2)	2.324 (2)	2.355 (1)	2.346 (1)
Ru(2)–P(3)	2.339 (2)	2.387 (1)	2.360 (1)
C(5)–C(6)	–	–	1.324 (4)
Ru(1)–H(1)–Ru(2)	88.1 (23)	93.6 (16)	91.1 (16)
Ru(1)–P(1)–Ru(2)	70.07 (4)	70.88 (3)	70.92 (2)
P(2)–C(5)–P(3)	114.4 (4)	113.7 (2)	111.35 (14)

The compound **2c** crystallized in the orthorhombic space group $P2_12_12_1$ with four molecules in the unit cell. The molecular structure of **2c** (not depicted, selected bonding parameters see Table 3) is also closely related to those of **2a** and **2b**. The compound **2c** exhibits the longest Ru–Ru separation in this series of compounds **2a**–**g** adopting this similar arrangement of ligands. We assume that this is caused by steric effects of the bulky cyclohexyl groups. However, in comparison with the Ru–Ru single bond lengths of the related molecules [Ru_2(μ-CO)$(CO)_4$(μ-H)(μ-P^tBu_2)(μ-dppm)] (Ru–Ru, 2.768(1) Å) and [$Ru_2(CO)_4$(μ-CH_2)(μ-H)(μ-P^tBu_2)(μ-dppm)] (Ru–Ru, 2.784(1) Å) [1], which are electronically and coordinatively saturated complexes, the metal–metal bond in **2c** is short enough to be considered as a Ru–Ru double bond. The molecular structure of **2d** in the crystal is shown in Fig. 2, selected bond lengths are listed in Table 3. The compound crystallized from dichloromethane/methanol at room temperature in the monoclinic space group wit $P2_1/c$

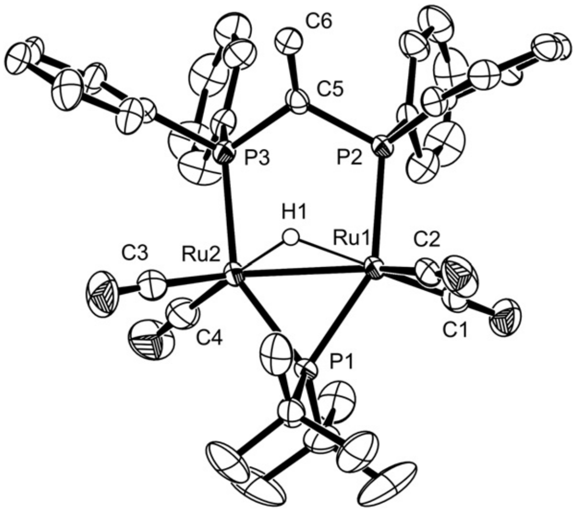


Fig. 2. ORTEP diagram and atom labeling scheme for **2d** with ellipsoids drawn at the 50% probability level. Hydrogen atoms (except hydride) were omitted for clarity.

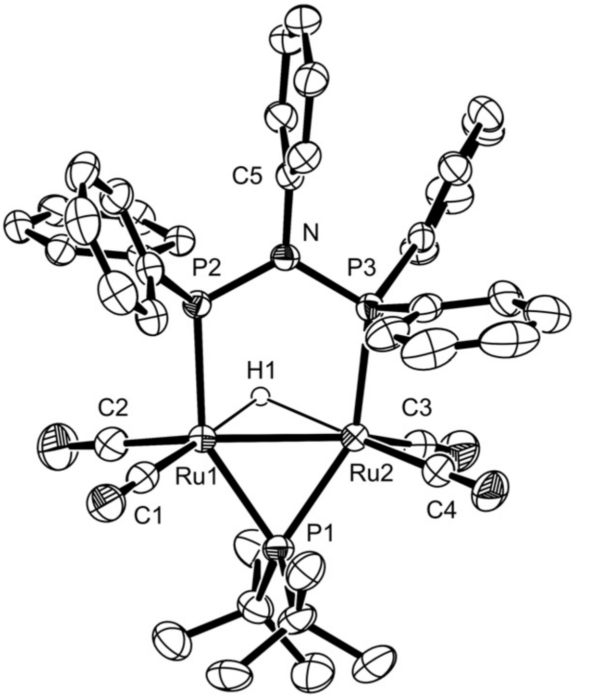


Fig. 3. ORTEP diagram and atom labeling scheme for **2e** with ellipsoids drawn at the 50% probability level. Hydrogen atoms (except hydride) were omitted for clarity.

with four molecules in the unit cell. As discussed before, the Ru(1)–Ru(2) bond in **2d** could even be considered as a double bond between both ruthenium atoms.

Good quality single crystals of the compounds **2e**–**g** containing the aminophosphane ligands were obtained from dichloromethane/ethanol at room temperature. Selected views of the molecular structures in the crystal of **2e** and **2f** are shown in the Figs. 3 and 4, respectively, selected bond lengths and angles of the compounds **2e**–**g** are summarized in the Table 4. The compounds **2e**–**g** crystallized all in the monoclinic space group $P2_1/c$ with four molecules in the unit cell. Their molecular structures are closely related to those of **2b**–**d**. Also in these molecules short Ru–Ru distances were found confirming the double bonding character as discussed above. With the observed values in the range from 2.652(1) to 2.668(1) Å they are shorter than the Ru–Ru separation found in the electronically and coordinatively unsaturated parent compound **2a** (Ru–Ru, 2.6974(4) Å [1]).

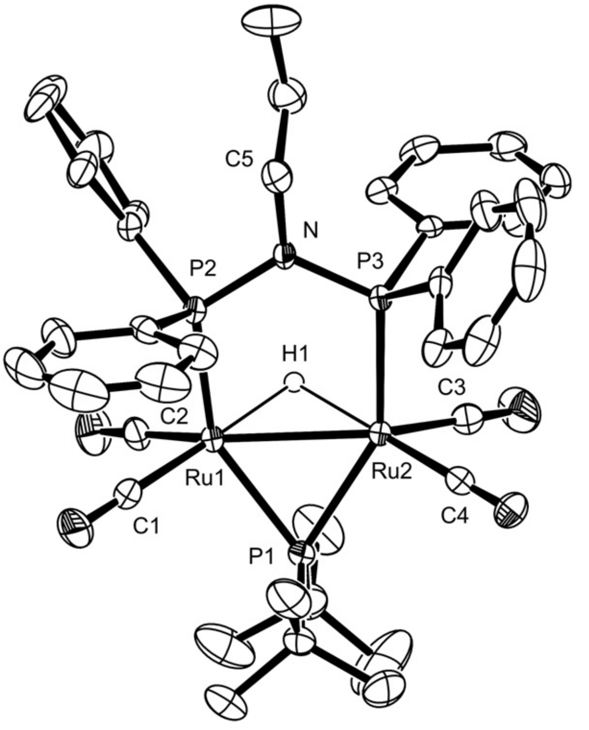


Fig. 4. ORTEP diagram and atom labeling scheme for **2f** with ellipsoids drawn at the 50% probability level. Hydrogen atoms (except hydride) were omitted for clarity.

Table 4
Selected bond lengths (Å) and angles (°) for compounds **2e**–**2 g**.

	2e	**2f**	**2g**
Ru(1)–Ru(2)	2.660 (1)	2.668 (1)	2.652 (1)
Ru(1)–H(1)	1.83 (2)	1.79 (3)	1.80 (3)
Ru(2)–H(1)	1.87 (2)	1.84 (3)	1.80 (3)
Ru(1)–C(1)	1.859 (4)	1.875 (3)	1.870 (3)
Ru(1)–C(2)	1.891 (5)	1.885 (3)	1.890 (3)
Ru(2)–C(3)	1.890 (4)	1.884 (4)	1.893 (3)
Ru(2)–C(4)	1.852 (4)	1.866 (3)	1.873 (3)
Ru(1)–P(1)	2.328 (1)	2.328 (1)	2.333 (1)
Ru(2)–P(1)	2.326 (1)	2.334 (1)	2.336 (1)
Ru(1)–P(2)	2.341 (1)	2.344 (1)	2.339 (1)
Ru(2)–P(3)	2.334 (1)	2.340 (1)	2.322 (1)
N–C(5)	1.450 (4)	1.500 (3)	1.494 (3)
Ru(1)–H(1)–Ru(2)	91.7 (15)	94.6 (17)	95.2 (20)
Ru(1)–P(1)–Ru(2)	69.73 (4)	69.83 (2)	69.21 (2)
P(2)–N–P(3)	120.08 (16)	119.36 (13)	118.27 (11)

4. Conclusions

Herein we described the synthesis and the X-ray crystal structures of six new electronically and coordinatively unsaturated complexes of the formula $[Ru_2(CO)_4(\mu\text{-}H)(\mu\text{-}P^tBu_2)(\mu\text{-}L_2)]$ ($Ru{=}Ru$) (**2b**–**g**) (L_2 = biphosphanes and aminobiphosphanes respectively). The molecular structures of **2b**–**g** are closely related to that of the known parent compound $[Ru_2(CO)_4(\mu\text{-}H)(\mu\text{-}P^tBu_2)(\mu\text{-dppm})]$ (**2a**). Furthermore, we have first evidences that these compounds show an unusual stereodynamic behavior concerning the signals of the *tert.*-butyl groups in the dynamic ^1H NMR spectra. For the near future, we have planned a broad *DNMR* investigation of a great number of compounds containing the $M(\mu\text{-}P^tBu_2)\text{-}M$ moiety to bring more insight into understanding of these phenomena.

Acknowledgments

The authors are grateful to the Department of Chemistry of the Ludwig Maximilian University Munich for supporting these investigations and the *Johnson Matthey plc*, Reading, UK, for a generous loan of hydrated $RuCl_3$. T. M. is thankful to Prof. P. Klüfers for financial support. Furthermore we thank P. Mayer for collecting the X-ray crystal data.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2011.07.033.

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