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Protonation of metal–metal bonds: X-ray crystal structures of the complex salts $[\mathrm{Ru_2(CO)_4(\mu\text{-}H)(\mu\text{-}Cl)(\mu\text{-}P^tBu_2)(\mu\text{-}Ph_2PCH_2PPh_2)}][\mathrm{BF_4}]$ and $[\mathrm{M_2(CO)_4(\mu\text{-}H)_2(\mu\text{-}P^tBu_2)(\mu\text{-}Ph_2PCH_2PPh_2)}][\mathrm{BF_4}]$ (M = Fe, Ru)

Hans-Christian Böttcher *, Marion Graf, Kurt Merzweiler, Christoph Wagner

Institut für Anorganische Chemie der Martin-Luther-Universität Halle-Wittenberg, Kurt-Mothes-Straße 2, D-06120 Halle/Saale, Germany

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Dedicated to Professor Herbert Schumann on the occasion of his 65th birthday

Abstract

Addition of tetrafluoroboric acid to the coordinatively unsaturated species $[\mathrm{M_2(CO)_4(\mu\text{-}H)(\mu\text{-}P^tBu_2)(\mu\text{-}dppm)}]$ (*M*=*M*) (M = Fe, **1**; M = Ru, **2**; dppm = $\mathrm{Ph_2PCH_2PPh_2}$) in diethylether results in rapid protonation of the dimetal vector to give the corresponding complex salts $[\mathrm{M_2(CO)_4(\mu\text{-}H)_2(\mu\text{-}P^tBu_2)(\mu\text{-}dppm)}][\mathrm{BF_4}]$ (**1a** and **2a**) in nearly quantitative yield. In the same manner $[\mathrm{Ru_2(CO)_4(\mu\text{-}Cl)(\mu\text{-}P^tBu_2)(\mu\text{-}dppm)}]$ (**3**) is protonated to yield $[\mathrm{Ru_2(CO)_4(\mu\text{-}H)(\mu\text{-}Cl)(\mu\text{-}P^tBu_2)(\mu\text{-}dppm)}][\mathrm{BF_4}]$ (**3a**). In order to show the acid–base character of these reactions **1a**, **2a**, **3a** and $[\mathrm{Ru_2(CO)_4(\mu\text{-}H)(\mu\text{-}NO)(\mu\text{-}P^tBu_2)(\mu\text{-}dppm)}][\mathrm{BF_4}]$ (**4a**) were deprotonated by the base 1,8-diazabicyclo[5.4.0]undec-7-ene DBU to regenerate **1**, **2**, **3** and the novel complex $[\mathrm{Ru_2(CO)_4(\mu\text{-}NO)(\mu\text{-}P^tBu_2)(\mu\text{-}dppm)}]$ (**4**), respectively. The molecular structures of **1a**, **2a**, **3a** and **4** have been established by single-crystal X-ray structure analysis. Upon protonation in each case the metal–metal distance is reduced. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Iron; Ruthenium; Carbonyl; Phosphido-bridged; Crystal structure

1. Introduction

Organometallic transition metal dimers with formal metal–metal bond orders of two or higher constitute interesting species due to their high reactivity towards a great variety of substrates under mild conditions [1]. Recently we described the coordinatively unsaturated complexes $[\mathrm{M_2(CO)_4(\mu\text{-}H)(\mu\text{-}P^tBu_2)(\mu\text{-}dppm)}]$ (*M*=*M*) (M = Fe, **1**; M = Ru, **2**) [2]. As shown by crystal structure analysis both compounds exhibit short metal–metal distances and on the basis of the 18e rule the electron counting reveals these species to contain metal–metal double bonds. These observations prompted us to investigate the reactivity of **1** and **2** towards small molecules [2–4]. Above all, the fast reaction of **2** with the electrophile $\mathrm{NO^+}$ (from $[\mathrm{NO}][\mathrm{BF_4}]$) to yield $[\mathrm{Ru_2(CO)_4(\mu\text{-}H)(\mu\text{-}NO)(\mu\text{-}P^tBu_2)(\mu\text{-}dppm)}][\mathrm{BF_4}]$ (**4a**) indicates an enhanced basicity of this species [3]. Therefore, we were interested in other reactions of these complexes with electrophiles, and in this paper we describe reactions of **1** and **2** with strong acids (HCl, $\mathrm{HBF_4}$). Even electronically saturated species deriving from **2** exhibit a strong base character, and therefore $[\mathrm{Ru_2(CO)_4(\mu\text{-}Cl)(\mu\text{-}P^tBu_2)(\mu\text{-}dppm)}]$ (**3**) can be protonated by tetrafluoroboric acid to the corresponding complex salt $[\mathrm{Ru_2(CO)_4(\mu\text{-}H)(\mu\text{-}Cl)(\mu\text{-}P^tBu_2)(\mu\text{-}dppm)}][\mathrm{BF_4}]$ (**3a**). On the other hand, **4a** can be deprotonated by the base 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) to give the novel compound $[\mathrm{Ru_2(CO)_4(\mu\text{-}NO)(\mu\text{-}P^tBu_2)(\mu\text{-}dppm)}]$ (**4**).

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* Corresponding author: Tel.: +49-345-5525634; fax: +49-345-5527028.

E-mail address: boettcher@chemie.uni-halle.de (H.-C. Böttcher).

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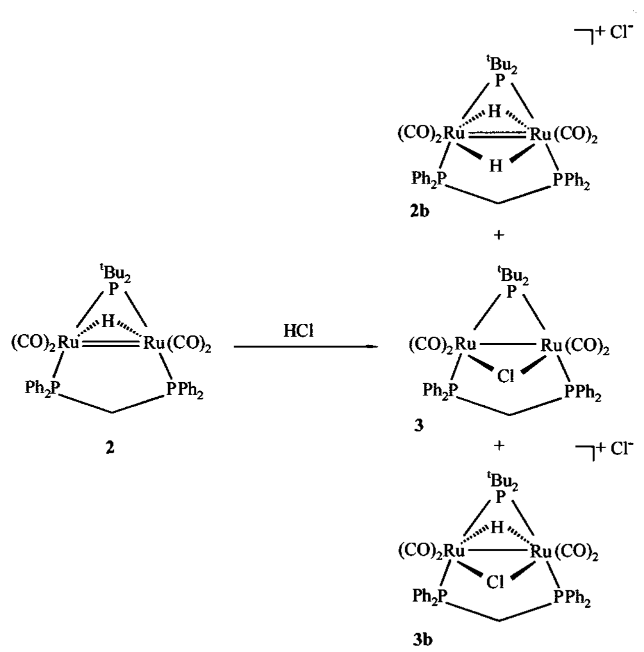
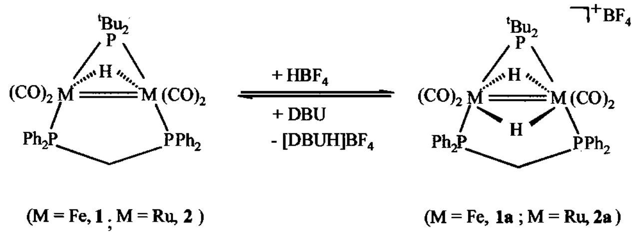
2. Results and discussion

2.1. Preparation and characterization of $[M_2(CO)_4(\mu\text{-}H)_2(\mu\text{-}P^tBu_2)(\mu\text{-}dppm)][BF_4]$ (M = Fe, **1a**; M = Ru, **2a**)

Treatment of solutions of **2** in THF or diethylether with hydrochloric acid (gaseous or aqueous) at room temperature results in a spontaneous reaction indicated by a rapid color change from deep violet to orange. Thereby a mixture of the protonated form of complex **2**, namely $[Ru_2(CO)_4(\mu\text{-}H)_2(\mu\text{-}P^tBu_2)(\mu\text{-}dppm)]Cl$ (**2b**) and $[Ru_2(CO)_4(\mu\text{-}Cl)(\mu\text{-}P^tBu_2)(\mu\text{-}dppm)]$ (**3**) is obtained (see Scheme 1). Compound **3** could be unambiguously identified by its spectroscopic data [3]. Furthermore, with an excess of hydrochloric acid the protonated form of **3**, namely $[Ru_2(CO)_4(\mu\text{-}H)(\mu\text{-}Cl)(\mu\text{-}P^tBu_2)(\mu\text{-}dppm)]Cl$ (**3b**), is obtained. However, the complex salt $[Ru_2(CO)_4(\mu\text{-}H)(\mu\text{-}Cl)(\mu\text{-}P^tBu_2)(\mu\text{-}dppm)][BF_4]$ (**3a**) can be prepared more conveniently by direct reaction of **3** with tetrafluoroboric acid (see below). Moreover, we found that **3** is formed by various reactions: if compound **2** is treated with chloride sources, e.g. $SnCl_2$ or $[Au(PPh_3)Cl]$, or even in the efficient synthesis using CCl_4 or $CHCl_3$ [3].



Scheme 1.



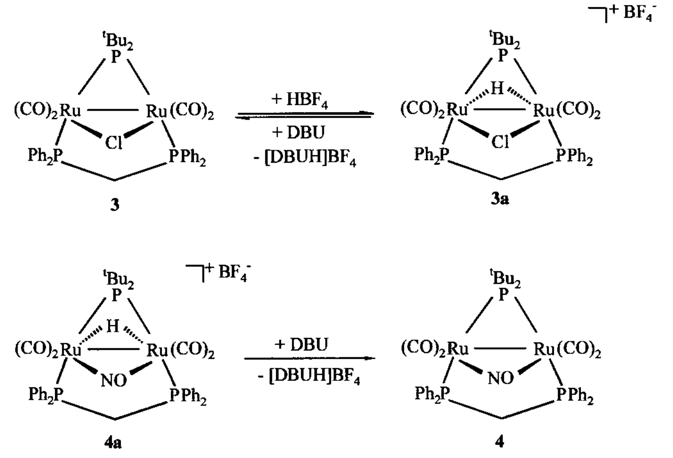
Scheme 2.

To obtain the protonated form of **2** directly, a reaction of the compound with HBF_4 in diethylether at room temperature has been investigated. Thus the corresponding complex salt **2a** was formed in a few seconds in nearly quantitative yield (Scheme 2). The product was obtained as an air-stable, slightly yellow powder which was recrystallized from acetone–diethylether. It should be noted that solutions of **2** are extremely sensitive to air, on the contrary solutions of **2a** are stable in air for a long time. Whereas **2** reacts immediately with HBF_4, the analogous reaction of **1** with the acid needs a few minutes for completion, probably for steric and electronic reasons, respectively, (the diruthenium centre is significantly more basic). **1a** was obtained in analytically pure form by recrystallization from acetone–diethylether as dark red–violet crystals.

On the other hand, a deprotonation of **1a** or **2a** was possible by the treatment of the corresponding complex with DBU in THF at room temperature (Scheme 2). The transformation back into **1** and **2** is visible by a color change of the solution from yellow to dark green and deep violet, respectively. The presence of the starting material was unambiguously indicated by NMR measurements. We note here that the coordinatively saturated species $[Ru_2(\mu\text{-}CO)(CO)_4(\mu\text{-}H)(\mu\text{-}P^tBu_2)(\mu\text{-}dppm)]$ [2] can also be protonated rapidly by HBF_4 as described. But the reaction yields compound **2a** in the same manner, i.e. during the protonation process there is an additional loss of one CO ligand from the starting complex. The compounds **1a** and **2a** have been fully characterized by their spectroscopic data and the molecular structures in the solid could be elucidated by X-ray crystal structure determination (see below).

2.2. Preparation and characterization of $[Ru_2(CO)_4(\mu\text{-}H)(\mu\text{-}Cl)(\mu\text{-}P^tBu_2)(\mu\text{-}dppm)][BF_4]$ (**3a**) and $[Ru_2(CO)_4(\mu\text{-}NO)(\mu\text{-}P^tBu_2)(\mu\text{-}dppm)]$ (**4**)

Since the reaction of **2** with hydrochloric acid under various conditions always yielded mixtures of **2b**, **3** and **3b** (**2b** and **3b** exclusively detected by NMR, not separated and isolated in this work), a more convenient synthesis for the complex cation of **3a** was found by treatment of **3** with tetrafluoroboric acid in diethylether at room temperature (Scheme 3). The reaction occurred spontaneously, and the salt $[Ru_2(CO)_4(\mu\text{-}H)(\mu\text{-}Cl)(\mu\text{-}P^tBu_2)(\mu\text{-}dppm)][BF_4]$ (**3a**) precipitated from the solution as slightly yellow powder in yields up to 90%. Compound **3a** was characterized by analytical and spectroscopic methods (see Section 4). A deprotonation of **3a** back into **3** was readily possible by the treatment



Scheme 3.

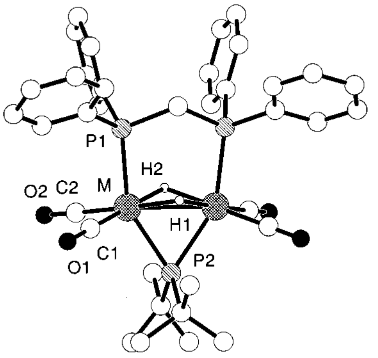


Fig. 1. A perspective view of the cations $[M_2(CO)_4(\mu\text{-H})_2(\mu\text{-P}^t\text{Bu}_2)(\mu\text{-dppm})]^+$ (M = Fe in **1a**; M = Ru in **2a**). The H-atoms are omitted for clarity (except hydrides).

Table 1
Selected bond lengths (Å) and angles (°) for complex salt **1a**

Fe–Fe′	2.4479(9)	Fe–P(2)	2.2644(9)
Fe–H(1)	1.71(3)	Fe–C(1)	1.767(4)
Fe–H(2)	1.68(4)	Fe–C(2)	1.771(4)
Fe–P(1)	2.2369(11)	P(2)–C(9)	1.834(3)
Fe–P(1)–Fe′	66.34(4)	P(1)–Fe–H(1)	75.4(13)
P(1)–Fe–P(2)	154.18(3)	P(2)–Fe–H(1)	82.6(14)
P(1)–Fe–C(1)	98.89(12)	H(1)–FeH(2)	81.1(17)
P(1)–Fe–C(2)	104.57(11)	P(2)–C(9)–P(1)	113.2(2)

Table 2
Selected bond lengths (Å) and angles (°) for complex salt **2a**

Ru–Ru′	2.6486(6)	Ru–C(1)	1.888(3)
Ru–H(1)	1.80(3)	Ru–C(2)	1.889(3)
Ru–P(1)	2.3681(8)	Ru–H(2)	1.78(3)
Ru–P(2)	2.3625(9)	P(1)–C(3)	1.833(2)
Ru–P(2)–Ru′	68.19(3)	P(2)–Ru–H(1)	73.8(13)
P(2)–Ru–C(1)	100.55(10)	H(1)–Ru–H(2)	79.2(15)
P(2)–Ru–C(2)	105.74(9)	C(2)–Ru–H(1)	174.8(11)
P(1)–Ru–P(2)	151.29(3)	C(1)–Ru–H(1)	98.5(11)
P(1)–Ru–H(1)	81.9(13)	P(1)–C(3)–P(1)′	116.6(2)

of the compound with DBU in THF at room temperature. The transformation was clearly indicated by NMR measurements.

In the context of the fast reaction of **2** with carbon monoxide yielding the coordinatively saturated species $[Ru_2(\mu\text{-CO})(CO)_4(\mu\text{-H})(\mu\text{-P}^t\text{Bu}_2)(\mu\text{-dppm})]$ [2], the corresponding reaction with nitric oxide (NO) was of interest. We found that **2** reacts spontaneously with NO. However a small excess of NO initiated a subsequent reaction which does not result in the assumed formation of $[Ru_2(CO)_4(\mu\text{-NO})(\mu\text{-P}^t\text{Bu}_2)(\mu\text{-dppm})]$ (**4**). On the other hand, reaction of **2** with diazald (*N*-methyl-*N*-nitroso-*p*-toluenesulfonamide) in refluxing THF yielded a mixture containing more than six products as indicated by ^{31}P-NMR measurements. Therefore, we devised a more convenient synthesis of **4** by deprotonation of the complex salt $[Ru_2(CO)_4(\mu\text{-H})(\mu\text{-NO})(\mu\text{-P}^t\text{Bu}_2)(\mu\text{-dppm})][BF_4]$ (**4a**) by DBU. Indeed **4a** reacted with the base in THF immediately with dissolution of the starting material and a color change from yellow to green yellow. Complex **4** was isolated from the reaction mixture in high yield (Scheme 3). The reaction could be monitored by ^{31}P{^{1}H}-NMR spectroscopy, i.e. **4a** exhibits the signal of the phosphido group more shifted to upfield, δ 184.7 (in comparison with the other similar constituted diruthenium species). The signal is shifted to downfield when **4** is formed (δ 219.9). A further indication is the disappearance of the hydride signal in the proton NMR spectrum (for **4a**: δ -8.12, m). Compound **4** was obtained in analytically pure form by recrystallization from dichloromethane–hexane and has been characterized by elemental analysis and spectroscopic means. Furthermore, the molecular structure of **4** was elucidated by a single-crystal X-ray analysis.

*2.3. Molecular structures of compounds **1a**, **2a**, **3a** and **4***

Compounds **1a** and **2a** crystallize from acetone–diethylether in the orthorhombic space group *Pcmn* with four molecules in the unit cell. A representation of the complex cations of **1a** and **2a**, respectively, is shown in Fig. 1 (M = Fe or Ru), selected bond lengths and angles are summarized in Tables 1 and 2. Both complexes are isostructural and exhibit a high molecular symmetry as observed for $[Ru_2(\mu\text{-CO})(CO)_4(\mu\text{-H})(\mu\text{-P}^t\text{Bu}_2)(\mu\text{-dppm})]$ [2], i.e. in these cationic structures the two hydrides, the phosphorus atom of the phosphido bridge, as well as the methylene carbon of the dppm ligand lie in a crystallographic mirror plane. Both **1a** and **2a** constitute complexes with 32 c.v.e. and in the sense of the EAN rule they should contain formal metal–metal double bonds. The M–M distances are in agreement with this (see Tables 1 and 2). The comparison of these M–M separations with those of the starting complexes shows a shortening of the metal–metal bond in each case; **1**: d(Fe–Fe) = 2.496(1); **2**: d(Ru–Ru) = 2.6974(4) Å. Normally a single, unsupported bridging hydride ligand causes a lengthening of a metal–metal bond. (Such a lengthening of a M–M bond upon protonation is expected due to the conversion of a 2c-2e bond to a 3c-2e bond.) However, in the present molecules the two-fold hydrido-bridged Ru–Ru bonds are shorter and a possible explanation of this may be that the (M–M) bond-lengthening influence of the second μ-H ligand is more than counterbalanced by the (M–M) bond-shortening effect of the $\mu\text{-}PR_2$ ligand [5].

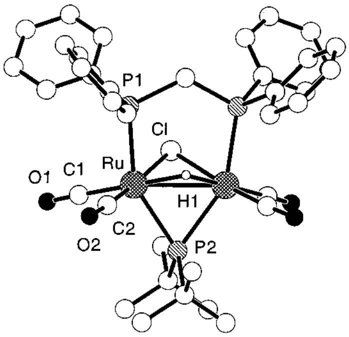


Fig. 2. A perspective view of the cation $[Ru_2(CO)_4(\mu\text{-}H)(\mu\text{-}Cl)(\mu\text{-}P^tBu_2)(\mu\text{-}dppm)]^+$ in **3a**. The H-atoms are omitted for clarity (except hydrides).

Table 3
Selected bond lengths (Å) and angles (°) for complex salt **3a**

Ru–Ru′	2.7608(5)	Ru–C(1)	1.903(3)
Ru–H(1)	1.78(2)	Ru–C(2)	1.855(2)
Ru–P(1)	2.4055(6)	Ru–Cl	2.4475(7)
Ru–P(2)	2.4088(7)	P(1)–C(3)	1.860(2)
Ru–P(2)–Ru′	69.93(2)	C(2)–Ru–Cl	174.22(8)
Ru–Cl–Ru′	68.67(2)	C(1)–Ru–Cl	93.38(8)
P(2)–Ru–C(2)	99.04(8)	P(1)–Ru–Cl	78.80(3)
P(2)–Ru–C(1)	102.40(8)	P(2)–Ru–Cl	85.01(3)
H(1)–Ru–Cl	86.00(1)	P(1)–C(3)–P(1)′	123.5(2)

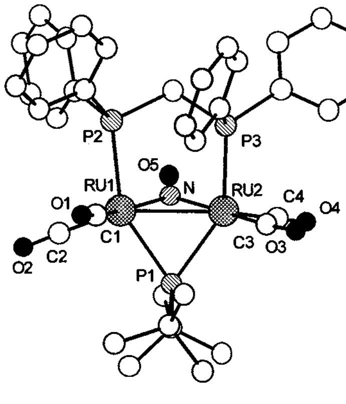


Fig. 3. The molecular structure of $[Ru_2(CO)_4(\mu\text{-}NO)(\mu\text{-}P^tBu_2)(\mu\text{-}dppm)]$ (**4**).

Table 4
Selected bond lengths (Å) and angles (°) for **4**

Ru(1)–Ru(2)	2.7552(8)	Ru(2)–N	2.004(2)
Ru(1)–C(1)	1.921(3)	Ru(1)–P(1)	2.3810(8)
Ru(1)–C(2)	1.900(3)	Ru(2)–P(1)	2.3797(8)
Ru(2)–C(3)	1.912(3)	Ru(1)–P(2)	2.3855(7)
Ru(2)–C(4)	1.898(3)	Ru(2)–P(3)	2.3435(7)
Ru(1)–N	2.000(2)	N–O(5)	1.214(3)
P(1)–Ru(1)–Ru(2)	54.62(2)	Ru(1)–P(1)–Ru(2)	70.73(2)
P(1)–Ru(2)–Ru(1)	54.659(19)	Ru(1)–N–O(5)	136.64(17)
P(1)–Ru(1)–P(2)	151.07(2)	Ru(2)–N–O(5)	134.53(17)
P(1)–Ru(2)–P(3)	141.91(2)	Ru(2)–Ru(1)–P(2)	96.55(2)
Ru(1)–N–Ru(2)	86.97(9)	Ru(1)–Ru(2)–P(3)	90.29(2)
P(1)–Ru(1)–N	78.00(6)	C(1)–Ru(1)–N	156.79(10)
P(1)–Ru(2)–N	77.96(6)	C(2)–Ru(1)–N	108.99(10)

Previously we found in a structural study of $[Fe_2(\mu\text{-}CO)(CO)_6(\mu\text{-}H)(\mu\text{-}P^tBu_2)]$ and its conjugate base $[Fe_2(\mu\text{-}CO)(CO)_6(\mu\text{-}P^tBu_2)]^-$ even such a bond-shortening effect of the $\mu\text{-}P^tBu_2$ ligand upon protonation [6]. The first example of a significant bond shortening of M–M bond on protonation has been described by Puddephatt and co-workers [7]. The conversion of $[CoRh(CO)_3(\mu\text{-}dppm)_2]$ to the corresponding cation $[CoRh(CO)_3(\mu\text{-}H)(\mu\text{-}dppm)_2]^+$ results in a shortening of the Co–Rh distance by 0.0372 Å. In our case this effect is still more significant (in each case about 0.048 Å). However, the bonding situation in **1a** and **2a**, respectively, is not comparable directly with the situation in the Co–Rh compound, because the M–M bond in the latter can be formulated as donor–acceptor bond.

The X-ray crystal structure data of **3a** (for the molecular structure details see Fig. 2 and for selected bond lengths and angles see Table 3) also reveal a shortening effect of the M–M bond upon protonation [**3**: d(Ru–Ru) = 2.7756(2) Å, molecule A; d(Ru–Ru) = 2.7858(1) Å, molecule B]; however, in comparison with the changes from **1** to **1a** and **2** to **2a**, respectively, the shortening effect is less significant. We assume that even in the case of the change from **3** to **3a** the phosphido bridging ligand seems to exert an influence on the Ru–Ru distance upon protonation.

Recently, the protonation of dinuclear iridium compounds containing formal metal–metal double bonds was described. Thus $[Ir_2Cp^*_2(CO)_2]$ ($Cp^* = C_5Me_5$) yields after protonation $[Ir_2Cp^*_2(CO)_2(\mu\text{-}H)]^+$ (*Ir=Ir*) and consequently $[Ir_2Cp^*_2(CO)_2(\mu\text{-}H)_2]^{2+}$ (*Ir=Ir*) by further protonation. Unfortunately, crystallographic data for the set of these compounds for comparative studies are not available. Moreover, in the starting complex the two carbonyl ligands are bridging, which was not proposed for the products, and therefore a direct comparison is not useful [8].

Compound **4** crystallizes from dichloromethane–hexane in the monoclinic space group $P2_1/n$ with four molecules in the unit cell. The molecular structure of **4** is shown in Fig. 3, selected bond lengths and angles are summarized in Table 4. The molecule consists of a diruthenium core bridged by a phosphido group, a dppm ligand and a nitrosyl group. The M–M distance of 2.7552(7) Å indicates a Ru–Ru single bond and agrees well with the Ru–Ru bonds found in the other similar constituted complexes [2–4]. A comparison of the structural data of **4** with the molecular structures of other diruthenium species with bridging NO ligands is complicated since X-ray crystal structure data of only one compound, namely [$Ru_2Cp^*_2(\mu\text{-}NO)_2Cl_2$] (**5**), are available. An inspection of these data yields a good agreement of the corresponding bond lengths and angles. Thus the following data of **5** agree well with those in **4** (see Table 4), for **5**: d(Ru–Ru) = 2.684(2), Ru–N(1) = 1.96, N(1)–O(1) = 1.21 Å; Ru(1)–N(1)–O(1) = 135.1(8)° [9].

3. Conclusions

The dimetal vector in the coordinatively unsaturated compounds [$M_2(CO)_4(\mu\text{-}H)(\mu\text{-}P^tBu_2)(\mu\text{-dppm})$] (M=Fe, **1**; M=Ru, **2**) is readily protonated by the strong acid HBF_4 to give the two-fold μ-hydrido bridged complexes [$M_2(CO)_4(\mu\text{-}H)_2(\mu\text{-}P^tBu_2)(\mu\text{-dppm})$][$BF_4$] (**1a**, **2a**) in almost quantitative yields. The hydrides in **1a** and **2a** are acidic, being rapidly deprotonated by the base DBU yielding the starting complexes **1** and **2**, respectively. An analogous reaction behaviour is observed for the compound [$Ru_2(CO)_4(\mu\text{-}Cl)(\mu\text{-}P^tBu_2)(\mu\text{-dppm})$] (**3**). The acid–base character of these reactions could be used for the synthesis of [$Ru_2(CO)_4(\mu\text{-}NO)(\mu\text{-}P^tBu_2)(\mu\text{-dppm})$] (**4**) via deprotonation of [$Ru_2(CO)_4(\mu\text{-}H)(\mu\text{-}NO)(\mu\text{-}P^tBu_2)(\mu\text{-dppm})$][$BF_4$] (**4a**) with the base DBU because attempts to prepare **4** in a clean reaction of **2** with nitric oxide or other sources of NO failed up to now.

4. Experimental

All reactions were performed under Ar atmosphere using conventional Schlenk techniques. Solvents were dried over sodium–benzophenone ketyl or molecular sieves and were distilled under Ar prior to use. Starting materials were either commercially available or were prepared as described before [2,3]. IR spectra were obtained using a Mattson 5000 instrument. The NMR spectra were recorded on Gemini 200 (Varian) or Unity 500 (Varian) spectrometers. Solvent signals (^1H) and 85% H_3PO_4 (^{31}P) were used as references. The mass spectra were obtained on the instrument AMD 402. Elemental analyses were carried out at the Microanalytical Laboratory of the Chemical Department, University of Halle.

*4.1. Synthesis of [$M_2(CO)_4(\mu\text{-}H)_2(\mu\text{-}P^tBu_2)(\mu\text{-dppm})$][$BF_4$] (M = Fe, **1a**; M = Ru, **2a**)*

In a typical reaction, a solution of [$M_2(CO)_4(\mu\text{-}H)(\mu\text{-}P^tBu_2)(\mu\text{-dppm})$] (380 mg, 0.50 mmol **1**; 420 mg, 0.50 mmol **2**) in 20 ml of Et_2O was treated with a few drops of tetrafluoroboric acid (aqueous, 40%) to give a dark redviolet precipitate after 10 min in the case of **1a** and a bright yellow precipitate immediately in the case of **2a**. The solid was filtered off and washed with 20 ml of Et_2O and dried in vacuo (380 mg **1a**, 90%, m.p. 170°C; 410 mg **2a**, 87%, m.p. 248°C).

1a: Anal. Found: C, 53.12; H, 5.37; P, 10.87. Calc. for $C_{37}H_{42}BF_4Fe_2O_4P_3$ (MW 842.16): C, 52.77; H, 5.03; P, 11.03% — ^{1}H-NMR ($CDCl_3$): δ 7.32 (m, 20H, C_6H_5), 3.51 (m, br, 2H, P–CH_2–P), 1.51 (d, 18H, $^tC_4H_9$, $^3J_{PH} = 12.3$ Hz), −21.48 (m, br, 2H, μ-H) — $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ 278.93 (t, br, μ-P, $^2J_{PP} = 79.0$ Hz), 63.10 (d, br, μ-dppm, $^2J_{PP} = 79.0$ Hz) — IR, (KBr, cm^{-1}) ν(CO) 2047s, 2025vs, 2003s, 1986vs — MS: 755 $[M - BF_4]^+$; 727 $[M - BF_4 - CO]^+$; 699 $[M - BF_4 - 2CO]^+$; 671 $[M - BF_4 - 3CO]^+$; 643 $[M - BF_4 - 4CO]^+$.

2a: Anal. Found: C, 47.43; H, 4.09; P, 10.32. Calc. for $C_{37}H_{42}BF_4O_4P_3Ru_2$ (MW 932.61): C, 47.65; H, 4.54; P, 9.96% — ^{1}H-NMR (CD_3COCD_3): δ 7.50 (m, 20H, C_6H_5), 3.89 (m, 2H, P–CH_2–P), 1.54 (d, 18H, $^tC_4H_9$, $^3J_{PH} = 15.5$ Hz), −13.48 (m, 2H, μ-H) — $^{31}P\{^1H\}$-NMR (CD_3COCD_3): δ 253.89 (t, μ-P, $^2J_{PP} = 146.4$ Hz), 46.46 (d, μ-dppm, $^2J_{PP} = 146.4$ Hz) — IR (KBr, cm^{-1}): ν(CO) 2067s, 2048vs, 2021s, 2002vs — MS: 846 $[M - BF_4]^+$; 818 $[M - BF_4 - CO]^+$; 790 $[M - BF_4 - 2CO]^+$; 762 $[M - BF_4 - 3CO]^+$; 734 $[M - BF_4 - 4CO]^+$.

*4.2. Synthesis of [$Ru_2(CO)_4(\mu\text{-}H)(\mu\text{-}Cl)(\mu\text{-}P^tBu_2)(\mu\text{-dppm})$][$BF_4$] (**3a**)*

A solution of [$Ru_2(CO)_4(\mu\text{-}Cl)(\mu\text{-}P^tBu_2)(\mu\text{-dppm})$] (440 mg, 0.50 mmol **3**) in 80 ml of Et_2O was treated with a few drops of tetrafluoroboric acid (aqueous, 40%) to give a pale yellow precipitate immediately. The solid obtained was filtered off and washed with 20 ml of Et_2O and dried in vacuo (440 mg, 92%, m.p. 220°C).

3a: Anal. Found: C, 46.32; H, 4.51; Cl, 3.96. Calc. for $C_{37}H_{41}BClF_4O_4P_3Ru_2$ (MW 967.05): C, 45.96; H, 4.27; Cl, 3.67% — ^{1}H-NMR ($CDCl_3$): δ 7.41 (m, 20H, C_6H_5), 2.78 (t, 2H, P–CH_2–P, $^2J_{PH} = 10.4$ Hz), 1.61 (d, 9H, $^tC_4H_9$, $^3J_{PH} = 14.6$ Hz), 1.50 (d, 9H, $^tC_4H_9$, $^3J_{PH} = 14.8$ Hz), −12.58 (dt, 1H, μ-H, $^2J_{PH} = 15.6$, 23.6 Hz) — $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ 261.10 (t, μ-P, $^2J_{PP} = 173.3$ Hz), 44.72 (d, μ-dppm, $^2J_{PP} = 173.3$ Hz) — IR (KBr, cm^{-1}): ν(CO) 2076s, 2065vs, 2017s, 1999vs — MS: 881 $[M - BF_4]^+$; 853 $[M - BF_4 - CO]^+$; 825 $[M - BF_4 - 2CO]^+$; 797 $[M - BF_4 - 3CO]^+$; 769 $[M - BF_4 - 4CO]^+$.

4.3. Synthesis of $[Ru_2(CO)_4(\mu\text{-}NO)(\mu\text{-}P^tBu_2)(\mu\text{-}dppm)]$ *(**4**) from **4a***

A slurry of $[Ru_2(CO)_4(\mu\text{-}H)(\mu\text{-}NO)(\mu\text{-}P^tBu_2)(\mu\text{-}dppm)][BF_4]$ (480 mg, 0.50 mmol **4a**) in 50 ml of THF was treated with 0.1 ml (excess) of DBU. The color of the solution turned spontaneously from slight yellow to green–yellow and the precipitate was dissolved immediately. After stirring for 30 min, the solvent was removed in vacuo. The residue was dissolved in 5 ml of CH_2Cl_2 and **4** was precipitated by the addition of 40 ml hexane. The green solid was filtered off and washed with 20 ml of hexane and dried in vacuo (340 mg, 78%, m.p. 182°C).

4: Anal. Found: C, 50.32; H, 4.58; N, 1.43; P, 10.25. Calc. for $C_{37}H_{40}NO_5P_3Ru_2$ (MW 873.79): C, 50.86; H, 4.61; N, 1.60; P, 10.63% — ^{1}H-NMR ($CDCl_3$): δ 7.24 (m, 20H, C_6H_5), 3.47 (m, 2H, P–CH_2–P), 1.92 (d, 9H, $^tC_4H_9$, $^3J_{PH} = 14.1$ Hz), 1.02 (d, 9H, $^tC_4H_9$, $^3J_{PH} = 13.8$ Hz) — $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ 219.96 (t, μ-P, $^2J_{PP} = 132.0$ Hz), 36.67 (d, μ-dppm, $^2J_{PP} = 132.0$ Hz) — IR (KBr, cm^{-1}): ν(CO) 1997s, 1972vs, 1943vs, 1926vs; ν(NO): 1648vs — MS: 844 $[M-NO]^+$; 816 $[M-NO-CO]^+$; 788 $[M-NO-2CO]^+$; 760 $[M-NO-3CO]^+$; 732 $[M-NO-4CO]^+$.

*4.4. Deprotonation of **1a**, **2a** and **3a***

210 mg **1a** (0.25 mmol), 230 mg **2a** (0.25 mmol) and 240 mg **3a** (0.25 mmol), respectively, were dissolved in 20 ml of THF and to the solution was added 0.1 ml of DBU (excess). The mixture immediately changed from dark red to deep green for **1a**, yellow to deep violet for **2a** and slight yellow to orange for **3a**, respectively. The solvent was removed under vacuum and ^{31}P-NMR investigations on the remaining residues ($CDCl_3$) indicated **1**, **2** and **3**, respectively, as the only phosphorus containing components.

5. X-ray crystal structure determinations

Crystal data, data collection and refinement parameters are summarized in Table 5. Crystals of **1a**, **2a** and **3a** suitable for X-ray diffraction studies were grown by slow diffusion of diethylether into acetone solutions of the compounds at room temperature. Crystals of **4** were obtained by diffusion of hexane into a dichloromethane solution of the complex. For data collection the diffractometer Stoe-Stadi (**1a**) and the Stoe-IPDS (**2a**, **3a**, and **4**) were used. The structures were solved by direct

Table 5
Crystal data and structure refinement for **1a**, **2a**, **3a** and **4** [a]

Identification code	**1a**	**2a**	**3a**·CH_3COCH_3	**4**·C_3H_7
Empirical formula	$C_{37}H_{42}BF_4Fe_2O_4P_3$	$C_{37}H_{42}BF_4O_4P_3Ru_2$	$C_{40}H_{47}BClF_4O_5P_3Ru_2$	$C_{40}H_{47}NO_5P_3Ru_2$
Formula weight	842.13	932.60	1025.09	916.88
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Monoclinic
Space group	*Pcmn*	*Pcmn*	*Pnma*	$P2_1/n$
Temperature (K)	293(2)	220(2)	220(2)	220(2)
Unit cell dimensions				
a (Å)	12.4058(14)	12.435(29	13.499(2)	14.121(3)
b (Å)	15.2987(13)	15.192(2)	17.058(2)	13.6666(18)
c (Å)	20.8229(16)	21.063(3)	18.828(3)	22.225(4)
β (°)	90	90	90	107.72(2)
U (Å^3)	3952.0(6)	3978.9(11)	4335.2(12)	4085.4(12)
D_{calc} (g cm^{-3})	1.415	1.553	1.570	1.479
μ (mm^{-1})	0.911	0.935	0.927	0.899
$F(000)$	1736	1872	2072	1840
Index ranges	$-14 \le h \le 14$, $-18 \le k \le 18$, $0 \le l \le 24$	$-14 \le h \le 14$, $-16 \le k \le 17$, $-24 \le l \le 24$	$-16 \le h \le 16$, $-20 \le k \le 20$, $-23 \le l \le 23$	$-17 \le h \le 15$, $-15 \le k \le 16$, $-27 \le l \le 27$
Reflections (measured/unique)	9394/3614	25 378/3448	29 209/4343	28 774/7901
Independent reflections [R_{int}]	0.0345	0.0619	0.0630	0.0491
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0391$, $wR_2 = 0.0830$	$R_1 = 0.0250$, $wR_2 = 0.0556$	$R_1 = 0.0299$, $wR_2 = 0.0733$	$R_1 = 0.0311$, $wR_2 = 0.0869$
R indices (all data)	$R_1 = 0.0669$, $wR_2 = 0.0960$	$R_1 = 0.0412$, $wR_2 = 0.0602$	$R_1 = 0.0318$, $wR_2 = 0.0746$	$R_1 = 0.0372$, $wR_2 = 0.0913$

[a] In each case the angles were $\alpha = \gamma = 90°$; $Z = 4$.

methods and refined on F^2 [10]. The hydride ligands have been found during the refinement by difference Fourier analysis. For **2a**, a disordering phenomenon was observed, i.e. for C(18) (^{t}Bu group) two alternative positions were found (relative site occupation factors refined to 0.6 and 0.4, respectively). Crystals of **4** were obtained with a half molecule of hexane per molecule.

6. Supplementary material

Crystallographic data for the structural analysis of **1a**, **2a**, **3a** and **4** has been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 151772, 151769, 151770 and 151771 for compounds **1a**, **2a**, **3a** and **4**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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