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Diazald: An entry to diruthenium complexes containing bridging nitrosyl ligands^{\Leftrightarrow}

Tobias Mayer, Peter Mayer, Hans-Christian Böttcher*

Department of Chemistry, Ludwig Maximilian University, Butenandtstraße 5–13, 81377 Munich, Germany

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ABSTRACT

Reactions of coordinatively unsaturated complexes $[Ru_2(\mu-P^tBu_2)(\mu-H)(\mu-PP)(CO)_4]$ (PP = bisphosphanes, *N*,*N*-substituted bis(diphenylphosphanyl)amines) with the nitrosylating reagent diazald (*N*-methyl-*N*-nitroso-*p*-toluenesulfonamide) were investigated. Thus a convenient synthesis affording a series of new diruthenium complexes containing bridging nitrosyl ligands of the general type $[Ru_2(\mu-P^tBu_2)(\mu-NO)(\mu-PP)(CO)_4]$ was developed and the crystal and molecular structures of five new compounds were determined. Contrary, this reaction principle does not work for the closely related complex $[Fe_2(\mu-P^tBu_2)(\mu-H)(\mu-dppm)(CO)_4]$ (dppm = Ph₂PCH₂PPh₂). In this case carbon monoxide was produced in side reactions and the known compound $[Fe_2(\mu-P^tBu_2)(\mu-H)(\mu-dppm)(\mu-CO)(CO)_4]$ was obtained as the main product. The molecular structure of the latter complex was also determined by X-ray diffraction.

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1. Introduction

Recently we reported the synthesis and X-ray crystal structures of some new coordinatively unsaturated complexes [Ru₂(µ- $P^{t}Bu_{2}(\mu-H)(\mu-PP)(CO)_{4}$ (PP = bisphosphanes or N,N-substituted bis(diphenylphosphanyl)amines) [1]. Because of the unsaturated character of the central $Ru_2(\mu-H)$ moiety these complexes exhibit an enhanced reactivity towards a great variety of small molecules under mild conditions [2–13]. During these investigations we found that the nitrosyl ligand can be introduced conveniently in the dimetal core of $[Ru_2(\mu-P^tBu_2)(\mu-H)(\mu-dppm)(CO)_4]$ (1, $dppm = Ph_2PCH_2PPh_2$) by the substitution of the hydrido ligand towards NO using the nitrosylating reagent diazald (N-methyl-Nnitroso-p-toluenesulfonamide). Thus the complex [Ru₂(µ- $P^{t}Bu_{2}(\mu-NO)(\mu-dppm)(CO)_{4}$ (2) was obtained in good yields [9]. The compound diazald was described in the literature as a useful selective nitrosylating agent especially in reactions with complexes containing hydrido ligands [14]. Now we examined this synthetic pathway for a series of other dinuclear unsaturated hydrido complexes and we describe therein the synthesis and the molecular structures of some new diruthenium complexes containing bridging nitrosyl ligands. Surprisingly this reaction principle was not successful in the case of the closely related

* Corresponding author. Tel.: +49 89218077422; fax: +49 89218077407. *E-mail address*: hans.boettcher@cup.uni-muenchen.de (H.-C. Böttcher). coordinatively unsaturated diiron complex $[Fe_2(\mu-P^tBu_2)(\mu-H)(\mu-dppm)(CO)_4]$ (3) [15].

2. Experimental

2.1. General considerations

All preparative operations were performed under a dry nitrogen atmosphere using conventional Schlenk techniques. Solvents were dried over sodium-benzophenone ketyl or molecular sieves. The compounds **1a**–**f** [1,12] and **3** [15] were prepared as reported in the literature. Chemicals were purchased commercially from Aldrich. IR spectra were recorded from solid samples with a JASCO FT/IR-460 plus spectrometer equipped with an ATR unit. NMR spectra were obtained using a Jeol Eclipse 270 instrument operating at 270 (¹H) and at 109 MHz (³¹P), respectively. Chemical shifts are given in ppm from SiMe₄ (¹H), and 85% H₃PO₄ (³¹P). Microanalyses (C, H, N) were performed by the Microanalytical Laboratory of the Department of Chemistry, LMU Munich, using a Heraeus Elementar Vario El instrument.

2.2. Synthesis of $[Ru_2(\mu-P^{f}Bu_2)(\mu-NO)(\mu-PP)(CO)_4]$ (PP = dmpm, **2a**; dcypm, **2b**; dppen, **2c**; dppa, **2d**; dpppra, **2e**; dpppha, **2f**)

A mixture of the corresponding diruthenium complex **1a–f** (0.5 mmol) and *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (322 mg, 1.5 mmol) in diethyl ether (40 mL) was stirred for 48 h at room





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temperature. During this time the color of the solution changed from violet to green. The resulting solution was evaporated to dryness under reduced pressure. The remaining residue was dissolved in toluene and filtered over alumina using toluene as the eluent. The solvent was removed in vacuo and the products were crystallized from acetone/water (1:3) affording deep green crystals.

2a: Yield: 234 mg (75%). Anal. Calcd for $C_{17}H_{32}NO_5P_3Ru_2$ (625.51): C, 32.64; H, 5.16; N, 2.24. Found: C, 32.41; H, 5.19; N, 2.02%. IR (solid): ν (CO): 1963s, 1916vs, ν (μ -NO): 1488s. ¹H NMR (270 MHz, CD₂Cl₂): δ 1.80 (d, ³*J*_{PH} = 14.0 Hz, 9H, ^tBu), 1.59 (m, 2H, CH₂), 1.56 (m, 6H, CH₃), 1.47 (m, 6H, CH₃), 0.88 (d, ³*J*_{PH} = 14.0 Hz, 9H, ^tBu). ³¹P{¹H} NMR (109 MHz, CD₂Cl₂): δ 207.7 (t, ²*J*_{PP} = 130.3 Hz, μ -P^tBu₂), 12.1 (d, ²*J*_{PP} = 130.3 Hz, μ -dmpm). Suitable single crystals of **2a** for X-ray diffraction were obtained from water/acetone at ambient temperatures by slow evaporation during 3 days.

2b: Yield: 278 mg (62%). Anal. Calcd for $C_{37}H_{64}NO_5P_3Ru_2$ (897.98): C, 49.49; H, 7.18; N, 1.56. Found: C, 49.36; H, 7.32; N, 1.34%. IR (solid): ν (CO): 1980s, 1949vs, 1920vs, 1904vs, ν (μ -NO): 1487s. ¹H NMR (270 MHz, CD₂Cl₂): δ 1.84 (d, ³*J*_{PH} = 13.6 Hz, 9H, ^tBu), 1.62–1.01 (m, 44H, Cy), 1.27 (m, 2H, CH₂), 0.94 (d, ³*J*_{PH} = 13.5 Hz, 9H, ^tBu). ³¹P {¹H} NMR (109 MHz, CD₂Cl₂): δ 216.4 (t, ²*J*_{PP} = 126.8 Hz, μ -P^tBu₂), 55.1 (d, ²*J*_{PP} = 126.8 Hz, μ -dcypm). Suitable single crystals of **2b** for X-ray diffraction were obtained by slow diffusion of ethanol into a dichloromethane solution at room temperature within 3 days.

2c: Yield: 319 g (72%). Anal. Calcd for $C_{38}H_{40}NO_5P_3Ru_2$ (885.80): C, 51.53; H, 4.55; N, 1.58. Found: C, 51.36; H, 4.82; N, 1.24%. IR (solid): ν (CO): 1972s, 1945vs, 1933vs, 1906s, ν (μ -NO): 1490s. ¹H NMR (270 MHz, CD₂Cl₂): δ 7.38–7.12 (m, 20H, Ph), 6.27 (t, ³J_{PH} = 20.5 Hz, 2H, C=-CH₂), 1.93 (d, ³J_{PH} = 14.0 Hz, 9H, ^tBu), 1.01 (d, ³J_{PH} = 14.0 Hz, 9H, ^tBu). ³¹P{¹H} NMR (109 MHz, CD₂Cl₂): δ 211.3 (t, ²J_{PP} = 127.9 Hz, μ -P^tBu₂), 41.7 (d, ²J_{PP} = 127.9 Hz, μ -dppen). Suitable single crystals of **2c** for X-ray diffraction were obtained from water/acetone at ambient temperatures by slow evaporation within 3 days.

2d: Yield: 284 mg (65%). Anal. Calcd for $C_{36}H_{39}N_2O_5P_3Ru_2$ (874.78): C, 49.43; H, 4.49; N, 3.20. Found: C, 49.36; H, 4.72; N, 3.44%. IR (solid): ν (CO): 2032m, 2007s, 1972vs, 1939s, ν (μ -NO): 1551vs. ¹H NMR (270 MHz, CD₂Cl₂): δ 7.47–7.31 (m, 20H, Ph), 1.54 (d, ³*J*_{PH} = 14.2 Hz, 9H, ^tBu), 1.05 (d, ³*J*_{PH} = 14.2 Hz, 9H, ^tBu). ³¹P{¹H} NMR (109 MHz, CD₂Cl₂): δ 224.1 (t, ²*J*_{PP} = 111.6 Hz, μ -P^tBu₂), 76.9 (d, ²*J*_{PP} = 111.6 Hz, μ -dppa). Suitable single crystals of **2d** for X-ray diffraction were obtained from water/acetone at ambient temperatures by slow evaporation within 3 days.

2e: Yield: 210 mg (46%). Anal. Calcd for $C_{39}H_{45}N_2O_5P_3Ru_2$ (916.86): C, 51.09; H, 4.95; N, 3.06. Found: C, 50.86; H, 4.82; N, 2.91%. IR (solid): ν (CO): 2026s, 1966s, 1944s, 1921vs, ν (μ -NO): 1615m. ¹H NMR (270 MHz, CD₂Cl₂): δ 7.63–7.31 (m, 20H, Ph), 3.70 (m, 2H, NCH₂), 2.55 (m, 2H, CH₂CH₃), 1.77 (d, ³*J*_{PH} = 14.0 Hz, 9H, ^tBu), 0.88 (d, ³*J*_{PH} = 14.0 Hz, 9H, ^tBu), 0.13 (m, 3H, CH₂CH₃). ³¹P{¹H} NMR (109 MHz, CD₂Cl₂): δ 213.9 (t, ²*J*_{PP} = 129.1 Hz, μ -P^tBu₂), 104.6 (d, ²*J*_{PP} = 129.1 Hz, μ -dpppra).

2f: Yield: 96 mg (20%). Anal. Calcd for $C_{42}H_{43}N_2O_5P_3Ru_2$ (950.88): C, 53.05; H, 4.56; N, 2.95. Found: C, 52.86; H, 4.82; N, 2.71%. IR (solid): ν (CO): 2026s, 1932s, ν (μ -NO): 1595m. ¹H NMR (270 MHz, CD₂Cl₂): δ 7.85–6.79 (m, 25H, Ph), 1.37 (d, ³J_{PH} = 14.5 Hz, 9H, ^tBu), 1.08 (d, ³J_{PH} = 13.2 Hz, 9H, ^tBu). ³¹P{¹H} NMR (109 MHz, CD₂Cl₂): δ 221.1 (t, ²J_{PP} = 133.8 Hz, μ -P^tBu₂), 104.7 (d, ²J_{PP} = 133.8 Hz, μ -dpppha). Suitable single crystals of **2f** for X-ray diffraction were obtained from water/acetone at ambient temperatures by slow evaporation within 3 days.

2.3. Reaction of $[Fe_2(\mu-P^tBu_2)(\mu-H)(\mu-dppm)(CO)_4](\mathbf{3})$ with diazald

Compound **3** (377 mg, 0.5 mmol) was dissolved in diethyl ether (30 mL), diazald (322 mg, 1.5 mmol) was added and the resulting solution stirred at room temperature. After 5 h the deep

green color of the solution was changed to red-brown. The solution was stirred for additional 15 h and the solvent was removed under reduced pressure. (During this procedure, the liquid in the vacuum trap adopted an orange color. In the liquid the presence of the volatile [Fe(CO)₂(NO)₂] was indicated by IR spectroscopy.) The remaining residue was extracted three times with 10 mL portions of diethyl ether. The combined extracts were filtered over a short column of alumina with diethyl ether as the eluent affording an orange-brown band. The investigation of this fraction by ³¹P NMR spectroscopy showed unambiguously the presence of complex 5 (traces) and 4, respectively [18,15]. Finally, compound 4 was obtained by crystallization from CH₂Cl₂/ethanol as orange-brown crystals suitable for X-ray diffraction. Yield: 172 mg (44%). Anal. Calcd for C₃₈H₄₁Fe₂O₅P₃ (782.36): C, 58.34; H, 5.28. Found: C, 58.12; H, 5.33%. ³¹P{¹H} NMR (109 MHz, CD₂Cl₂): δ 240.0 (t, ²J_{PP} = 42.8 Hz, μ -P^tBu₂), 74.2 (d, ²J_{PP} = 42.8 Hz, μ -dppm). The ¹H NMR and IR data were reported elsewhere [15].

2.4. X-ray structural determination

Suitable single crystals for X-ray diffraction of the compounds **2a–d** and **2f** were obtained as described in the experimental section. Crystals were selected by means of a polarization microscope, mounted on the tip of a glass fiber, and investigated on a Bruker Nonius-Kappa CCD diffractometer (**2a–c**, **2f**, and **4**) and on an Oxford XCalibur diffractometer (**2d**), respectively, using Mo-K α radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods (SHELXS) [16] and refined by full-matrix least-squares calculations on F^2 (SHELXL-97) [17]. The position of the hydrido ligand in compound **4** has been located from the difference map. Details of the crystal data, data collection, structure solution, and refinement parameters of the new compounds are summarized in Table 1 (**2a–c**) and Table 2 (**2d**, **2f**, and **4**), respectively.

Table 1

Crystal data and structure refinement details for compounds 2a-c.

Compound	2a	2b	2c · 1.5 acetone
Empirical formula	C17H32NO5P3Ru2	$C_{37}H_{64}NO_5P_3Ru_2$	C42.5H49NO6.5P3Ru2
Formula weight	625.9	897.94	972.88
Temperature (K)	173(2)	173(2)	173(2)
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	Pnma	$P2_1/c$	$P2_1/c$
a (Å)	14.9069(6)	18.1026(2)	16.6252(2)
b (Å)	14.9333(6)	18.2483(2)	13.6152(2)
<i>c</i> (Å)	11.1729(5)	12.78950(10)	18.7877(3)
α (°)	90	90	90
β (°)	90	104.1180(10)	93.2720(10)
γ (°)	90	90	90
Volume (Å ³)	2487.19(18)	4097.29(7)	4245.77(11)
Ζ	4	4	4
ρ_{calcd} (g cm ⁻³)	1.670	1.456	1.522
μ/mm^{-1}	1.433	0.894	0.872
θ range for data	3.29-27.48	3.21-27.56	3.18-27.49
collection (°)			
Reflections	16,607	35,193	32,845
measured			
R _{int}	0.1243	0.0343	0.0332
Observed reflections	2948	9423	9723
Reflections, unique	9076	18,382	17,748
Parameters/ restraints	156/0	453/0	524/0
$R(F_{obs})$	0.0421	0.0312	0.0279
$R_{\rm W}$ (F^2)	0.0956	0.0777	0.0605
S	1.060	1.039	1.067
Max electron	0.830	0.555	0.642
density (e Å ⁻³)			
Min electron density (e Å ⁻³)	-0.606	-0.516	-0.605

Table	2
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Crystal data and structure refinement details for compounds 2d, 2f, and 4.

Compound	2d	2f	4
Empirical formula	$C_{36}H_{39}NO_5P_3Ru_2$	$C_{42}H_{43}NO_5P_3Ru_2$	$C_{38}H_{41}Fe_2O_5P_3$
Formula weight	874.74	950.83	782.34
Temperature (K)	173(2)	173(2)	200(2)
Crystal system	triclinic	triclinic	triclinic
Space group	P 1	P 1	$P\overline{1}$
a (Å)	9.0261(8)	12.5167(4)	19.7861(4)
b (Å)	12.1578(18)	12.5406(4)	19.8314(4)
c (Å)	18.209(2)	15.1164(5)	20.6476(4)
α (°)	87.687(11)	80.081(2)	96.118(2)
β(°)	85.056(9)	67.870(2)	97.730(1)
γ (°)	69.726(12)	68.147(2)	110.239(1)
Volume (Å ³)	1867.3(4)	2038.62(11)	7429.7(3)
Ζ	2	2	8
ρ_{calcd} (g cm ⁻³)	1.556	1.549	1.399
μ/mm^{-1}	0.980	0.905	0.951
θ range for	4.19-26.25	3.29-27.50	3.19-25.74
data collection (°)			
Reflections measured	18,569	17,517	51,392
R _{int}	0.0618	0.0410	0.0763
Observed reflections	14,155	9225	16,977
Reflections, unique	6278	9343	27,540
Parameters/restraints	440/0	487/0	524/0
$R(F_{obs})$	0.0475	0.0385	0.0574
$R_{\rm W}$ (F^2)	0.1329	0.0883	0.1588
S	1.004	1.031	1.031
Max electron	1.110	0.763	0.692
density (e Å ⁻³)			
Min electron	-0.811	-0.630	-0.466
density (e Å ⁻³)			

3. Results and discussion

3.1. Preparation and characterization of new compounds 2a-f

Recently we found that the NO ligand can be introduced by hydride abstraction in the dimetal core of $[Ru_2(\mu-P^tBu_2)(\mu-H)(\mu-dppm)(CO)_4]$ (**1**, dppm = Ph₂PCH₂PPh₂) by the use of the nitrosylating reagent diazald (*N*-methyl-*N*-nitroso-*p*-toluenesulfona-mide). Thereby the nitrosyl-bridged complex $[Ru_2(\mu-P^tBu_2)(\mu-NO)(\mu-dppm)(CO)_4]$ (**2**) was obtained in good yield [9]. In this light we examined now this synthetic pathway for a series of other dinuclear unsaturated hydrido complexes $[Ru_2(\mu-P^tBu_2)(\mu-H)(\mu-PP)(CO)_4]$ (PP = dmpm, **1a**; dcypm, **1b**; dppen, **1c**; dppa, **1d**; dpppra, **1e**; dpppha, **1f**). Thus the latter compounds reacted with an excess diazald (molar ratio 1:3) in diethyl ether at room temperature during 48 h resulting in the corresponding nitrosyl-bridged complexes **2a**–**f** in good yields (see Scheme 1).

In each case the course of the reaction is accompanied by a color change from deep violet to green. As described for the parent complex **1**, the preparation of the nitrosyl-bridged species is also possible in refluxing dioxane as the solvent during shorter reaction times (2 h) [9]. We found, however, that the reaction at room



Ts = p-toluenesulfonyl

R = Me, X = CH₂, **1a**; R = Cy, X = CH₂, **1b**;

R = Ph: X = C=CH₂, 1c; X = NH, 1d; X = NPrⁿ, 1e; X = NPh, 1f

Scheme 1. Synthesis of nitrosyl-bridged complexes.

temperature over longer periods afforded the products in a cleaner manner. The new compounds 2a-f were characterized by standard spectroscopic methods (see Experimental section). In the IR spectra beside the characteristic carbonyl vibration bands in each case a band corresponding to the bridging nitrosyl ligand was found. For the complexes bearing the bisphosphane ligands (2a-c) this band is situated in the average at 1488 cm^{-1} whereas for the compounds containing the *N*.*N*-substituted bis(diphenylphosphanyl)amines (2d-f) this band was found in the average at 1587 cm⁻¹. This is in accordance with the higher electron-donating properties of the bisphosphane ligands. The same trend is observed for the CO stretching frequencies of the carbonyl ligands. At this point we have to correct the reported value for the $v(\mu$ -NO) band of the parent complex $[Ru_2(\mu-P^tBu_2)(\mu-NO)(\mu-dppm)(CO)_4]$ (1) [9]. There we reported $v(\mu-NO) = 1547 \text{ cm}^{-1}$ for the bridging nitrosyl ligand in **1**; however this was not correct. Now we have redetermined the $v(\mu$ -NO) band of compound **1** at 1467 cm^{-1} which is in very good agreement with the observed ones of the related complexes in the present work. The ³¹P{¹H} NMR spectra of the new compounds **2a**f showed in each case the typical doublet/triplet pattern indicating the symmetric arrangement of the phosphanido group together with the bridging µ-PP ligand. Suitable crystals of all new compounds **2a**–**f** for X-ray diffraction studies were obtained and their molecular structures could be confirmed (see below). The collected data for the compound **2e** were however only of lower quality, R_w $(F^2) = 0.2357$, therefore these data were not deposited with the CCDC.

In light of our interest in studies including the related diiron complexes we examined also the reaction of the coordinatively unsaturated complex $[Fe_2(\mu-P^tBu_2)(\mu-H)(\mu-dppm)(CO)_4]$ (3) [15] with diazald. Surprisingly the principle of the described title reaction was not successful in this case. Unexpectedly, the reaction resulted in the formation of the known carbonyl complex [Fe₂(µ- $P^{t}Bu_{2}(\mu-H)(\mu-dppm)(\mu-CO)(CO)_{4}$ [4] [15] as the main product (see Experimental section). In the past, during studies on the reaction behavior of **3**, we found that this compound reacted preferably with carbon monoxide, which was liberated in side reactions for example. Thus we found in reaction attempts between 3 and sulfur dioxide only the product of the CO addition (4) as the main product and not the corresponding μ -SO₂ complex as expected. In contrast to this the addition reaction of SO₂ was however successful in the case of the analogous ruthenium complex [6]. During the investigations described therein we studied in a similar manner the reaction of **3** with diazald (molar ratio of 1:3) in diethyl ether at room temperature. In contrast to the studies with the diruthenium species, we found that the reaction was completed during 5 h whereas the typical deep green color of the solution (3) was changed to yellow-brown. After stirring for additional 15 h the reaction mixture was filtered over alumina. An orange-brown band was separated using diethyl ether as the eluent. The investigation of this fraction by ³¹P{¹H} NMR spectroscopy in CD₂Cl₂ revealed only two products. A minor species (traces) exhibiting three signal groups of an ABX spin system at 309.9 ppm (m, µ- P^tBu_2), 66.1 (m, μ -dppm), and 62.0 (m, μ -dppm) with the corresponding couplings ${}^{2}J_{Ax} = 31.4$, ${}^{2}J_{Bx} = 68.0$, and ${}^{2}J_{AB} = 89.0$ Hz was unambiguously assigned to the complex $[Fe_2(\mu - P^tBu_2)(\mu - dppm)](\mu - dppm)](\mu - dppm)$ $CO)(CO)_3(NO)$ (5). The latter compound was yet described by us and its molecular structure was confirmed by crystal structure analysis [18]. This was the only detectable compound containing a nitrosyl ligand beside the bridging phosphanido group. The second product (major component, 44% yield) could be unambiguously assigned to $[Fe_2(\mu-P^tBu_2)(\mu-H)(\mu-dppm)(\mu-CO)(CO)_4]$ (4) by its known characteristic NMR data [15]. In the course of these investigations we were able to obtain orange-brown crystals of 4 suitable for an X-ray diffraction study and its molecular structure could be confirmed (see below). At this point some remarks on possible side reactions should be given. As observed in earlier studies on reactions of **3** with nitric oxide, we had to ascertain also in the present case a degradation of the diiron core of **3** during the reaction resulting in the formation of $[Fe(CO)_2(NO)_2]$. This species was trapped in the vacuum line as a red–orange liquid and characterized by its characteristic IR data. We have to assume that during this side reaction also carbon monoxide was liberated. To avoid the addition reaction of the liberated CO towards still unconsumed compound **3**, we carried out the reaction for a short time in refluxing dioxane with passing a vigorous stream of argon through the solution. However also in this reaction attempt only compound **4** (and **5** as a trace) could be detected by NMR spectroscopy.

3.2. Molecular structures of compounds 2a-d and 2f

Compound **2a** crystallized from acetone/water in the orthorhombic space group *Pnma* with four formulas in the unit cell. The asymmetric unit contained a half molecule of **2a**. A selected representation of the molecular structure is shown in Fig. 1, selected bond lengths and angles are summarized in the caption.

Compound **2b** crystallized from dichloromethane/ethanol in the monoclinic space group $P2_1/c$ with four formulas in the unit cell. The asymmetric unit contained one molecule of $[Ru_2(\mu-P^tBu_2)(\mu-NO)(\mu-dcypm)(CO)_4]$. Since the features of the molecular structure of **2b** are closely related to that of **2a** (except to the substituents on the bridging bisphosphane ligand) of an ORTEP representation of the molecule was disclaimed.

Compound **2c** crystallized from acetone/water as the acetone solvate (1.5 acetone) in the monoclinic space group $P2_1/c$ with four formulas in the unit cell. The asymmetric unit contained one molecule of **2c**. A selected view of the molecular structure is shown in Fig. 2, selected bond lengths and angles are given in the caption.

Compound **2d** crystallized from acetone/water in the triclinic space group $P\overline{1}$ with two formulas in the unit cell. The asymmetric unit contained one molecule of **2d**. A selected representation of the





Fig. 2. Molecular structure of **2c** in the crystal. Thermal ellipsoids were drawn at the 50% probability level. H atoms and the solvate molecules are omitted for clarity. Selected bond lengths (Å) and angles (°): Ru1–Ru2, 2.7847(2); Ru1–N, 2.0009(17); Ru2–N, 2.0070(17); N–O5, 1.221(2), Ru1–C1, 1.892(2); Ru1–C2, 1.917(2); Ru2–C3, 1.914(2); Ru2–C4, 1.896(2); Ru1–P1, 2.3751(6); Ru2–P1, 2.3801(5); Ru1–P2, 2.3493(6); Ru2–P5, 2.3721(6); C5–C6, 1.328(3). Ru1–N–Ru2, 88.02(7); Ru1–P1–Ru2, 71.69(2); P2–C5–P3, 115.82(11).

molecular structure is shown in Fig. 3, selected bond lengths and angles are summarized in the caption.

Compound **2f** crystallized from acetone/water in the triclinic space group $P\overline{1}$ with two formulas in the unit cell. The asymmetric unit contained one molecule of **2f**. A selected view of the molecular



Fig. 1. Molecular structure of **2a** in the crystal. Thermal ellipsoids were drawn at the 50% probability level. H atoms are omitted for clarity. Symmetry operation: ⁱx, $\frac{1}{2} - y$, *z*. Selected bond lengths (Å) and angles (°): Ru1–Ru1ⁱ, 2.7516(6): Ru1–N, 1.999(4); N–O3, 1.228(8), Ru1–C1, 1.898(6); Ru1–C2, 1.911(6); Ru1–P1, 2.3913(15); Ru1–P2, 2.3355(14); P2–C3, 1.838(4). Ru1–N–Ru1ⁱ, 87.0(2); Ru1–P1–Ru1ⁱ, 70.25(5); P2–C3–P2ⁱ, 116.4(2).

Fig. 3. Molecular structure of **2d** in the crystal. Thermal ellipsoids were drawn at the 50% probability level. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ru1–Ru2, 2.7426(7); Ru1–N1, 2.016(4); Ru2–N1, 2.015(4); N1–O5, 1.199(5), Ru1–C1, 1.898(5); Ru1–C2, 1.928(5); Ru2–C3, 1.913(6); Ru2–C4, 1.896(6); Ru1–P1, 2.4331(13); Ru2–P1, 2.4218(14); Ru1–P2, 2.4134(13); Ru2–P3, 2.4092(13), P2–N2, 1.605(4); P3–N2, 1.607(4). Ru1–N1–Ru2, 85.75(15); Ru1–P1–Ru2, 68.79(4); P2–N2–P3, 129.9(3).



Fig. 4. Molecular structure of **2f** in the crystal. Thermal ellipsoids were drawn at the 50% probability level. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ru1–Ru2, 2.7529(4); Ru1–N1, 1.990(2); Ru2–N1, 2.009(3); N1–O5, 1.224(3), Ru1–C1, 1.904(5); Ru1–C2, 1.918(4); Ru2–C3, 1.924(4); Ru2–C4, 1.899(3); Ru1–P1, 2.3747(9); Ru2–P1, 2.3788(10); Ru1–P2, 2.3431(10); Ru2–P3, 2.3433(10), P2–N2, 1.738(3); P3–N2, 1.719(3); N2–C5, 1.466(5). Ru1–N1–Ru2, 87.01(10); Ru1–P1–Ru2, 70.78(3); P2–N2–P3, 118.91(16).

structure is shown in Fig. 4, selected bond lengths and angles are summarized in the caption.

By electron counting the molecules of compounds **2a**–**d** and **2f** exhibit 34 valence electrons and therefore the Ru–Ru contacts can



Fig. 5. Molecular structure of **4** in the crystal. Thermal ellipsoids were drawn at the 50% probability level. H atoms are omitted for clarity (except bridging hydrido ligand). Selected bond lengths (Å) and angles (°): Fe1–Fe2, 2.5886(9); Fe1–H1, 1.63(5); Fe2–H1, 1.55(4); Fe1–P1, 2.2284(14); Fe2–P2, 2.2481(14); Fe1–P3, 2.2457(14); Fe2–P3, 2.2580(13); Fe1–C1, 1.757(5); Fe1–C2, 1.782(5); Fe2–C3, 1.747(5); 1.782(5); Fe2–C4, 1.806(5); Fe1–C5, 2.022(5); Fe2–C5, 1.933(5); P1–C21, 1.839(4); P2–C21, 1.842(4); C1–O1, 1.141(5); C2–O2, 1.160(5); C3–O3, 1.156(6); C4–O4, 1.155(6); C5–O5, 1.182(5), Fe1–P3–Fe2, 70.17(4); Fe1–P1–C21, 111.77(16); Fe2–P2–C21, 109.60(15); Fe1–C5–Fe2, 81.73(18); Fe2–C5–O5, 142.0(4); Fe1–C5–O5, 136.2(4).

be considered as single bonds in each case which is in good agreement with the observed Ru–Ru distances.

The crystal structure determination on crystals of **4** revealed that the compound belongs to the triclinic space group $P\overline{1}$ with four crystallographically independent molecules in the asymmetric unit. A selected view of one molecule of **4** is shown in Fig. 5. Molecules of compound **4** consist of a diiron core which is bridged by phosphanido, dppm, hydrido, and a carbonyl ligand. The coordination sphere around the two iron atoms is completed by four terminal carbonyl groups. Thus by electron counting the molecules exhibit 34 valence electrons and the Fe—Fe distance can be considered as a single bond.

The structural features of the pair of complexes **3** and **4** are comparable to the molecular structures of the closely related compounds $[Ru_2(\mu-P^tBu_2)(\mu-H)(\mu-dppm)(CO)_4]$ (**5**) and $[Ru_2(\mu-P^tBu_2)(\mu-H)(\mu-dppm)(\mu-CO)(CO)_4]$ (**6**) [2]. The metal–metal bond on going from **5** to **6** is elongated from 2.6974(4) to 2.768(1) Å, whereas the same trend is found on going from **3**, 2.496(1) Å [2], to 2.5886(9) Å in **4**. Thus the discussion of M–M double bonds in the unsaturated species $[M_2(\mu-P^tBu_2)(\mu-H)(CO)_4(\mu-dppm)]$ (M = Fe, Ru) seems to be reasonable.

4. Conclusions

In this paper we described the synthesis and structural characterization of six new dinuclear ruthenium complexes containing bridging nitrosyl ligands. They were prepared in the reaction of the coordinatively unsaturated complexes $[Ru_2(\mu-P^tBu_2)(\mu-H)(\mu-PP)(CO)_4]$ (PP = bisphosphanes, *N*,*N*-substituted bis(diphenylphosphanyl)amines) with the nitrosylating reagent diazald (*N*methyl-*N*-nitroso-*p*-toluenesulfonamide). The hydride abstraction reactions afforded the corresponding electronically saturated 34 VE species in good yields under mild conditions. In contrast to this the reaction principle does not work for the closely related complex $[Fe_2(\mu-P^tBu_2)(\mu-H)(\mu-dppm)(CO)_4]$. In this case carbon monoxide was liberated in side reactions, and thus the known compound $[Fe_2(\mu-P^tBu_2)(\mu-H)(\mu-dppm)(\mu-CO)(CO)_4]$ was obtained as the main product of the reaction. The molecular structure of the latter complex was confirmed by an X-ray diffraction study.

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Appendix A. Supplementary material

CCDC-941245 (**2a**), CCDC-941249 (**2b**), CCDC-941246 (**2c**), CCDC-941247 (**2d**), CCDC-941248 (**2f**), and CCDC-901382 (**4**) contain the supplementary crystallographic data for this paper. Copies of these data can be obtained from The Cambridge Crystallographic Data Centre via deposit@ccdc.cam.ac.uk or http:// www.ccdc.cam.ac.uk/.

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