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Electronic Supplementary Information

Stabilisaton effects of phosphane ligands in the homogeneous approach of sunlight induced hydrogen production

C. M. Strabler^{a,b}, S. Sinn^b, R. Pehn^a, J. Pann^a, J. Dutzler^a, W. Viertl^a, J. Prock^a, K. Ehrmann^a, A. Weninger^a, H. Kopacka^a, L. De Cola^{*,b} and P. Brüggeller^{*,a}

^aUniversity of Innsbruck, Institute of General, Inorganic and Theoretical Chemistry, Innrain 80-82, CCB – Centre of Chemistry and Biomedicine, 6020 Innsbruck, Austria

^bISIS & icFRC, Université de Strasbourg & CNRS, 8 rue Gaspard Monge, 67000 Strasbourg, France

Corresponding author e-mail: peter.brueggeller@uibk.ac.at

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1. Hydrogen measurements

All the sunlight induced water splitting experiments were realised in so called Schlenk tubes in an argon atmosphere. For the irradiation of the Schlenk tubes different kinds of light sources were tested, like: different kinds of LEDs and a medium pressure mercury lamp. The produced hydrogen in the gas phase was analysed by means of a micro gas chromatograph of the company Inficon (Inficon 3000 μ -GC) that was equipped with a 5 Å molecular sieve column, followed by a thermal conductivity detector with Argon as carrier gas. To guarantee an exact and reproducible measurement, the pipe between the micro gas chromatograph and the Schlenk tube is rinsed with Argon every time. After a defined time period (different timescale, based on the irradiation source) the production of elementary palladium as colloid was visible. In control experiments elemental mercury was added. However, its influence on the hydrogen production was negligible, indicating that colloidal palladium did not produce any hydrogen under these conditions.

The temperature of the solution was equilibrated during the preparation and after the irradiation with water at 20 °C. The reduced pressure (argon atmosphere at 800 mbar) was involved in the calculation and the measurements were performed three times to receive statistically robust values of produced hydrogen.

2. Compounds for the investigation of the electron transfer in the intramolecular system



Figure 1: The four complexes to investigate the influence of the two metal centres (osmium and palladium) in $[Os(bpy)_2(dppcb)Pd(dppm)](PF_6)_4$ (OsPd), $[Os(bpy)_2(dppcb)Os(bpy)_2](PF_6)_4$ (OsOs), $[Os(bpy)_2(cis-dppen)](PF_6)_2$ (Os) and $[Pd(dppm)(dppcb)Pd(dppm)](PF_6)_4$ (PdPd), where OsOs and Os have been prepared according to ref. 31 and 32 of the manuscript, respectively. A detailed synthetic protocol including PdPd will be given elsewhere.

Kinetic constants of the (non)-radiative pathway

The kinetic constants of the radiative decay of the osmium based complexes are with $16.81*10^4$ s⁻¹ of Os, $16.61*10^4$ s⁻¹ of *meso*-OsOs and $18.21*10^4$ s⁻¹ of *rac*-OsOs in the same range. The kinetic constants of the nonradiative decay are quite different. The constant of the *rac*-form is with $3.87*10^6$ s⁻¹ significantly higher than of the two other complexes with $2.78*10^6$ s⁻¹ for the monometallic complex (Os) and with $2.74*10^6$ s⁻¹ for the *meso*-form. At ambient temperature the *rac*-form of the homodimetallic complex (OsOs) loses more energy during nonradiative pathways. However the excited state lifetimes at 77 K of all three complexes are quite similar with $3.74 \ \mu s$ of Os, $3.62 \ \mu s$ of the *meso*-form and and $3.59 \ \mu s$ of the *rac*-form of OsOs. Based on folding-effects of the cyclobutane ring system at ambient temperature the excited state lifetime of *rac*-OsOs is shorter. The phosphorescence quantum yields of the two different diastereomers of $[Os(bpy)_2(dppcb)Os(bpy)_2](PF_6)_4$ (*rac* and *meso*) (SI Figure 2) are quite different. The value of *meso*- $(\Delta\Lambda/\Lambda\Delta)$ - $[Os(bpy)_2(dppcb)Os(bpy)_2](PF_6)_4$ is $4.5 \ \%$. The *meso* form has the same

luminescence quantum yield as the monometallic complex $[Os(bpy)_2(cis-dppen)](PF_6)_2$. The *rac* form has a slightly lower luminescence quantum yield, because the excited state of it is able to lose energy *via* nonradiative decay more rapidly. This could be explained by their different single crystal X-ray structures, leading to variations in the available vibrations.³¹ The excited state lifetimes of the two OsOs modifications are also quite different (see manuscript).



Figure 2: The two different diastereomers of the homodimetallic Os complex, the meso isomer has two similar osmium metal centres, whereas the rac isomer has two different osmium metal centres – see ref. 31.

3. Crystal structure of OsPd



Figure 3: The palladium moiety of the OsPd dyad, showing the slightly distorted square planar coordination of the Pd(II) centre. For the phenyl groups of dppcb only the ipso carbon atoms are shown for clarity.



Figure 4: The osmium moiety of the OsPd dyad, showing the distorted octahedral coordination of the Os(II) centre.

bond	bond length [Å]	bond	bond length [Å]
Os1 N1	2.078(10)	P2 C41	1.826(15)
Os1 N2	2.091(11)	P2 C2	1.850(13)
Os1 N3	2.094(10)	P3 C51	1.815(14)
Os1 N4	2.115(10)	P3 C61	1.801(13)
Os1 P1	2.323(3)	P3 C3	1.870(13)
Os1 P2	2.328(3)	P4 C71	1.796(14)
Pd1 P3	2.310(3)	P4 C81	1.795(13)
Pd1 P4	2.309(3)	P4 C4	1.852(14)
Pd1 P5	2.363(4)	P5 C5	1.834(14)
Pd1 P6	2.363(4)	P6 C5	1.857(13)
P1 C11	1.820(13)	C1 C2	1.593(17)
P1 C21	1.819(14)	C1 C3	1.545(17)
P1 C1	1.882(12)	C2 C4	1.578(18)
P2 C31	1.852(15)	C3 C4	1.574(17)

Table 1: chosen bond lengths of OsPd

Table 2: chosen bond angles of OsPd

angle	bond angle [°]	angle	bond angle [°]
N1 Os1 N2	77.0(5)	P3 Pd1 P5	102.85(12)
N1 Os1 N3	159.3(4)	P3 Pd1 P6	172.29(13)
N1 Os1 N4	87.1(4)	P4 Pd1 P5	168.00(13)
N2 Os1 N3	88.7(4)	P4 Pd1 P6	101.61(13)
N2 Os1 N4	83.6(4)	P5 Pd1 P6	70.55(13)
N3 Os1 N4	76.4(4)	C11 P1 Os1	125.3(5)
N1 Os1 P1	105.0(3)	C21 P1 Os1	110.2(5)
N2 Os1 P1	177.6(3)	C31 P2 Os1	120.8(5)

89.7(3)	C41 P2 C2	103.3(7)
97.8(3)	C1 P1 Os1	111.6(4)
93.7(3)	C2 P2 Os1	110.9(4)
94.6(3)	C3 P3 Pd1	110.8(4)
102.4(3)	C4 P4 Pd1	111.0(4)
177.9(3)	C5 P5 Pd1	91.7(4)
83.91(12)	C5 P6 Pd1	91.1(4)
84.22(12)	C1 C2 C3	90.5(8)
	89.7(3) 97.8(3) 93.7(3) 94.6(3) 102.4(3) 177.9(3) 83.91(12) 84.22(12)	89.7(3)C41 P2 C297.8(3)C1 P1 Os193.7(3)C2 P2 Os194.6(3)C3 P3 Pd1102.4(3)C4 P4 Pd1177.9(3)C5 P5 Pd183.91(12)C5 P6 Pd184.22(12)C1 C2 C3

4. Syntheses of the compounds of the intermolecular system

[Cu(Xanthphos)(Bathocuproine)]PF₆

This synthesis is adapted from M. Beller and co-workers.¹

62.77 mg Bathocuproine (n = 0,1745 mmol) and 17,28 mg CuCl (n = 0,1745 mmol) were mixed in 30 ml of degassed dichloromethane and the red solution was stirred for 1 h. Meanwhile 99,95 mg of Xanthphos (n = 0,1745 mmol) and 55,56 mg TIPF₆ (n = 0,1745 mmol) were dissolved in 30 ml of degassed tetrahydrofuran and stirred for 1 h. The red solution, containing [CuCl(Bathocuproine)] was added to the solution containing the phosphane ligand and the solution was stirred over night at room temperature. Afterwards, TICl as precipitation was filtered off and the solution was concentrated to 5 ml and the product was precipitated with 30 ml of n-hexane, filtered off and dried under vacuum. Yield = 87 % as yellow solid.

¹H NMR (300 MHz, CD₂Cl₂)

δ (ppm): 7.71 (s, 2H), 7.59 (d, J=7.5 Hz, 2H), 7.50-7.39 (m, 12H), 7.19-7.04 (m, 12H), 6.99-6.87 (m, 12H), 2.23 (s, 6H), 1.67(s, 6H)

¹³C NMR (75 MHz, CD₂Cl₂)

$$\begin{split} &\delta \text{ (ppm): } 158.2, 155.5, 155.2, 155.0, 150.4, 143.9, 136.1, 133.9, 133.3, 133.1, 132.9, 131.7, 131.4, 131.1, \\ &130.3, 130.0, 129.2, 129.0, 128.8, 128.4, 128.2, 128.1, 127.7, 125.4, 125.1, 123.3, 121.4, 121.2, 121.1, \\ &36.0, 28.4, 27.2 \end{split}$$

³¹P NMR (121 MHz, CD₂Cl₂)

δ (ppm): -11.74 (s, br, 2P)

ESI-HRMS m/z: calculated for [C₆₅H₅₂CuN₂OP₂]⁺: 1001.28454; found: 1001.28318, [M]⁺

[Co(DO)(DOH)pnBr₂]

The synthesis is described in the literature.²

[Co(DO)(DOH)pn(PPh₃)]

This synthesis is adapted from V. Artero and co-workers.²

20.0 mg of $[Co(DO)(DOH)pnBr_2]$ (n = 4.4x10⁻⁵ mol) were dissolved in 4 ml MeOH and 0.4 ml of a KOH solution (c = 1 mol/L) and 8.3 mg NaBH₄ (n = 2.2x10⁻⁴ mol) were added to the solution and the solution was stirred for 3 h. The produced black precipitation was filtered off, washed 3 times with 15 ml of n-hexane and the solution was dried under vacuum. Yield = 71.4%. (Found: C 62.03, H 6.15, N 9.90, O 5.77, C₂₉H₃₄CoN₄O₂P (560.50) requires C 62.14, H 6.11, N 10.00, O 5.71%.)

¹H NMR (300 MHz, CD₂Cl₂):

 $\delta \text{ (ppm): 7.29 (m, 15H_{Phenyl}), 2.38 (m, 4H_{Imin}), 1.33 (m, 12H_{Me}), 1.21 (m, 2H_{methylen}).}$

¹³C NMR (75 MHz, CD₂Cl₂):

 δ (ppm): solubility is too low.

³¹P NMR (121 MHz, CD₂Cl₂):

δ (ppm): 45.60 (s, br, 1P).

Single crystals suitable for an X-ray structure analysis with the composition $[Co(DO)(DOH)pn(PPh_3)]$ were obtained by slow evaporation of a CH_2Cl_2 solution of $[Co(DO)(DOH)pn(PPh_3)]$ in the presence of n-hexane under an Ar atmosphere at room temperature. They are extremely air sensitive and have been protected by apiezon grease during the preparation procedure.

[Co(DO)(DOH)pn(PMePh₂)]

20.0 mg of $[Co(DO)(DOH)pnBr_2]$ (n = 4.4x10⁻⁵ mol) were dissolved in 4 ml MeOH and 0.4 ml of a KOH solution (c = 1 mol/L) and 150 µL of a PMePh₂ solution (c = 0.295 µmol/L in MeCN, n = 4.4x10⁻⁵ mol) were added to the solution above. This solution was stirred for 3 h. The solvent was completely removed and 5 ml water were added. The produced dark green residue was filtered off, washed 3 times with 15 ml H₂O and 3 times with 15 ml of n-hexane and the dark green powder was dried under vacuum. Yield = 67.3%. (Found: C 57.75, H 6.51, N 11.15, O 6.50, C₂₄H₃₂CoN₄O₂P (498.44) requires C 57.83, H 6.47, N 11.24, O 6.42%.)

¹H NMR (300 MHz, CD₂Cl₂):

δ (ppm): 7.32 (m, 10H_{Phenyl}), 2.35 (m, 4H_{Imin}), 1.31 (m, 12H_{Me}), 1.18 (m, 2H_{methylen}), 0.83 (m, 3 H_{P-Me}).

¹³C NMR (75 MHz, CD₂Cl₂):

 δ (ppm): solubility is too low.

³¹P NMR (121 MHz, CD₂Cl₂):

δ (ppm): 35.18 (s, br, 1P).

Single crystals suitable for an X-ray structure analysis with the composition $[Co(DO)(DOH)pn(PMePh_2)]$ were obtained by slow evaporation of a CH_2Cl_2 solution of $[Co(DO)(DOH)pn(PMePh_2)]$ in the presence of n-hexane under an Ar atmosphere at room temperature. They are extremely air sensitive and have been protected by apiezon grease during the preparation procedure.

5. Hydrogen production with different phosphane ligands

All the solutions for the hydrogen production were irradiated with a Hg-medium pressure lamp for 15 h.

At different pH-values

Table 3: hydrogen production with 60 μmol/L PS X, 90 μmol/L Co-WRC and 180 μmol/L either PPh₃, PMePh₂ or PMe₂Ph at different pH-Values from 6.5 to 12.5 in a mixture of H₂O:ACN:TEA (4.5:4.5:1).

		TON (PS X)	
pH-Value	PPh₃	PMePh ₂	PMe₂Ph
6,5	0	0	0
7,0	171	156	164
7,5	298	276	271
8,0	422	421	437
8,5	533	534	538
9,0	601	597	602
9,5	654	644	652
10,0	681	671	675
10,5	731	709	712
11,0	770	738	745
11,5	715	715	710
12,0	545	539	547
12,5	263	228	240

With PMe₂Ph

Table 4: different solutions for the sunlight induced hydrogen production with PS X as photosensitiser and Co-WRC as water reduction catalyst and PMe₂Ph as phosphane ligand in a mixture of H₂O:ACN:TEA (4.5:4.5:1).

Entry	24	PS X	Co-WRC	Phosphane	TON	TON
	рп	µmol/L	μmol/L	µmol/L	PS X	Co-WRC
1	10	60	90	90	623	415
2	10	60	90	180	675	439
3	11	60	90	90	717	478
4	11	60	90	180	739	493
5	11	60	60	120	496	496
6	11	120	60	120	245	490
7	11	60	120	240	825	413
8	11	60	90	270	739	493
9	11	60	90	450	730	487
10	11	30	45	90	563	376
11	11	15	22.5	45	445	297
12	11	90	135	270	664	443
13	11	120	180	360	611	407

With P(*n*Bu)₃

Table 5: different solutions for the sunlight induced hydrogen production with PS X as photosensitiser and Co-WRC as waterreduction catalyst and $P(nBu)_3$ as phosphane ligand in a mixture of $H_2O:ACN:TEA$ (4.5:4.5:1).

Entry	۶U	PS X	Co-WRC	Phosphane	TON	TON
	рп	µmol/L	μmol/L	µmol/L	PS X	Co-WRC
1	10	60	90	90	573	382
2	10	60	90	180	622	415
3	11	60	90	90	646	431
4	11	60	90	180	762	508
5	11	60	60	120	390	390
6	11	120	60	120	186	372
7	11	60	120	240	829	415
8	11	60	90	270	715	477
9	11	60	90	450	781	521
10	11	30	45	90	527	351
11	11	15	22.5	45	459	306
12	11	90	135	27	643	429
13	11	120	180	360	645	430

With P(*t*Bu)₃

Table 6: different solutions for the sunlight induced hydrogen production with PS X as photosensitiser and Co-WRC as waterreduction catalyst and $P(tBu)_3$ as phosphane ligand in a mixture of $H_2O:ACN:TEA$ (4.5:4.5:1).

Entry	nЦ	PS X	Co-WRC	Phosphane	TON	TON
Liitiy	рп	µmol/L	μmol/L	µmol/L	PS X	Co-WRC
1	10	60	90	90	416	277
2	10	60	90	180	499	333
3	11	60	90	90	515	343
4	11	60	90	180	611	407
5	11	60	60	120	297	297
6	11	120	60	120	144	288
7	11	60	120	240	665	333
8	11	60	90	270	553	369
9	11	60	90	450	627	418
10	11	30	45	90	424	283
11	11	15	22.5	45	330	220
12	11	90	135	27	515	343
13	11	120	180	360	518	345

With P(2-An)₃

Table 7: different solutions for the sunlight induced hydrogen production with PS X as photosensitiser and Co-WRC as water
reduction catalyst and P(2-An) ₃ , where An is anisyl, i.e. methoxyphenyl, as phosphane ligand in a mixture of H ₂ O:ACN:TEA
(4.5:4.5:1).

Entry	nU	PS X	Co-WRC	Phosphane	TON	TON
	рп	µmol/L	μmol/L	µmol/L	PS X	Co-WRC
1	10	60	90	90	446	298
2	10	60	90	180	485	323
3	11	60	90	90	504	336
4	11	60	90	180	593	396
5	11	60	60	120	288	288
6	11	120	60	120	161	323
7	11	60	120	240	646	323
8	11	60	90	270	547	365
9	11	60	90	450	609	406
10	11	30	45	90	412	275
11	11	15	22.5	45	357	238
12	11	90	135	27	500	333
13	11	120	180	360	503	335

With P(4-An)₃

Table 8: different solutions for the sunlight induced hydrogen production with PS X as photosensitiser and Co-WRC as waterreduction catalyst and $P(nBu)_3$ as phosphane ligand in a mixture of $H_2O:ACN:TEA$ (4.5:4.5:1).

Entry	nН	PS X	Co-WRC	Phosphane	TON	TON
	рп	μmol/L	μmol/L	µmol/L	PS X	Co-WRC
1	10	60	90	90	551	367
2	10	60	90	180	598	399
3	11	60	90	90	688	458
4	11	60	90	180	733	488
5	11	60	60	120	375	375
6	11	120	60	120	199	398
7	11	60	120	240	798	399
8	11	60	90	270	768	512
9	11	60	90	450	751	501
10	11	30	45	90	563	375
11	11	15	22.5	45	441	294
12	11	90	135	27	684	456
13	11	120	180	360	620	414

6. Emission spectra of the quenching investigations

Description of the measurements

Emission and excitation spectroscopy

Luminescence spectra were measured with a spectrophotometer. Light is generated with an excitation source (xenon lamp), passes through a monochromator and is directed to a reference detector and to the sample. Emission of the sample, collected at 90° with respect to the incident light, passes through another monochromator (emission monochromator) before reaching the detector. The excitation spectra are corrected for source intensity (lamp and excitation grating) and for detector spectral response and emission grating by standard correction curves (emission monochromator and Photomultiplier, PM). Steady-state emission spectra were recorded on a Horiba Jobin Yvon IBH FL-322 Fluorolog 3 spectrometer equipped with a 450 W xenon arc lamp, double-grating excitation, and emission monochromator (2.1 nm/mm of dispersion; 1200 grooves/mm) and a TBX-04 single photoncounting detector.

Quantum yield measurements

Absolute photoluminescent quantum yields (PLQY) were measured by using an integrating sphere (IS). Light from a xenon lamp is monochromatised at the selected wavelength and guided by an optical fiber into the IS. The emitted light from the sample is collected by a detector after passing through another optical fiber and a second monochromator. In this method, the reference (pure solvent in a quartz cuvette) is first measured and then the sample in the same solvent is also analysed. The software eventually corrects the quantum yields for the reference to give absolute quantum yields.

$$\Phi = \frac{N_{emission}}{N_{absorption}} = \frac{\int \frac{\lambda}{hc} \{I_{em}^{S}(\lambda) - \frac{\lambda}{hc} \{I_{em}^{R}(\lambda)\} d\lambda}{\int \frac{\lambda}{hc} \{I_{exc}^{S}(\lambda) - \frac{\lambda}{hc} \{I_{exc}^{R}(\lambda)\} d\lambda}$$

Where, $N_{absorption}$ is the number of photons absorbed by the sample, $N_{emission}$ is number of photons emitted by the sample, I_{em} stands for intensity of the emission, I_{ex} is intensity of the excitation light. The superscripts are, S: sample and R: reference, *h* is planck's constant, λ is the wavelength and *c* is the velocity of light. The quantum yield measurements were performed by using an absolute photoluminescence quantum yield spectrometer Quantaurus C11347 (Hamamatsu, Japan) exciting the sample every 10 nm in a range of λ exc = 300-450 nm.

Excited state lifetime measurements

Time-resolved experiments, such as the excited state lifetime determination, were carried out by timecorrelated single-photon counting (TCSPC). The pulsed light source is either a flash lamp or a laser. Each pulse gives an electrical signal to the START input of the time-to-amplitude converter (TAC). When a photon is emitted after the excitation pulse the detector gives an electrical response, which is then directed as a STOP signal to the TAC. The START pulse has initiated the charging of the capacitor, while the STOP pulse terminates it. Therefore, the final voltage is proportional to the time between the START and the STOP pulses and is stored in a histogram. The x-axis in the histogram is the time difference between START and STOP signal and the y-axis shows the number of photons detected for this time difference. The large number of repetitive measurements gives a good statistical fit for the time distribution of emitted photons.

Time-resolved measurements were performed using either the time-correlated single-photon counting (TCSPC) electronics PicoHarp300 or the Multi-Channel Scaling (MCS) electronics NanoHarp

250 of the PicoQuant FluoTime 300 (PicoQuant GmbH, Germany), equipped with a PDL 820 laser pulse driver. Different pulsed lasers were used to excite the sample and mounted directly on the sample chamber at 90°:

- LDH-P-C-375 (λexc= 375 nm, pulse FWHM <70 ps, repetition rate 200 kHz 40 MHz)
- LDH-D-C-405 (λexc= 405 nm, pulse FWHM <50 ps, repetition rate 200 kHz 40 MHz)

The photons were collected by a PMA-C-192 photomultiplier (PMT) single-photon-counting detector. The data were acquired by using the commercially available software EasyTau (PicoQuant GmbH, Germany), while data analysis was performed using the commercially available software FluoFit (PicoQuant GmbH, Germany).

The quality of the fit was assessed by minimising the reduced χ^2 function and by visual inspection of the weighted residuals. For multi-exponential decays, the intensity, namely I(t), has been assumed to decay as the sum of individual single exponential decays:

$$I(t) = \sum_{i=1}^{n} a_i e^{\frac{t}{t_i}}$$

The percentages to the pre-exponential factors, ai, are listed upon normalisation.

Results

In pure ACN



Figure 5: Quenching of the intensity (left) and Stern Volmer plot (right) with the green triangles for the intensity measurements and the orange diamonds for the lifetime measurements

In a solution of ACN:TEA (9:1)



Figure 6: Quenching of the intensity (left) and Stern Volmer plot (right) with the green triangles for the intensity measurements and the orange diamonds for the lifetime measurements



In a solution of ACN:H₂O:TEA (4,5:4,5:1)

Figure 7: Quenching of the intensity (left) and Stern Volmer plot (right) with the green triangles for the intensity measurements and the orange diamonds for the lifetime measurements in the irradiation solution



In a solution of ACN:H₂O:TEA (4,5:4,5:1) with the addition of 2 eq. of PPh₃ calculated to the concentration of the water reduction catalyst

Figure 8: Quenching of the intensity (left) and Stern Volmer plot (right) with the green triangles for the intensity measurements and the orange diamonds for the lifetime measurements in the irradiation solution

7. CV spectra of Co-WRC at different Conditions



Figure 9: CV measurements of Co-WRC in ACN with the addition of TEA (black curve), the addition of 2 eq. of PPh_3 (red curve) and the addition of 2 eq. of $P(2-An)_3$ (blue curve).

8. Selected bond lengths and bond angles of the Co-complexes

[Co(DO)(DOH)pn(PPh₃)]

Bond lengths in [Å]

bond	bond length [Å]	bond	bond length [Å]
Co1-N1	1.864(2)	01-H1	1.12(3)
Co1-N2	1.901(2)	O2-N4	1.364(3)
Co1-N3	1.899(2)	O2-H1	1.33(3)
Co1-N4	1.869(2)	N1-C2	1.323(4)
Co1-P1	2.2514(11)	N2-C3	1.315(4)
P1-C11	1.831(3)	N2-C5	1.468(3)
P1-C21	1.842(3)	N3-C7	1.467(3)
P1-C31	1.844(3)	N3-C8	1.322(3)
01-N1	1.358(3)	N4-C10	1.330(3)

Table 9: chosen bond lengths

Bond angles in [°]

Table 10: chosen bond angles

angle	bond angle [°]	angle	bond angle [°]
N1-Co1-N2	80.89(10)	C11-P1-C31	103.60(12)
N1-Co1-N3	154.10(9)	C21-P1-C31	98.19(12)
N1-Co1-N4	92.83(10)	C11-P1-Co1	108.35(9)
N2-Co1-N3	94.36(10)	C21-P1-Co1	119.85(9)
N2-Co1-N4	154.77(9)	C31-P1-Co1	121.45(9)
N3-Co1-N4	80.64(10)	N1-01-H1	102.4(14)
N1-Co1-P1	95.12(8)	N4-O2-H1	102.1(12)
N2-Co1-P1	96.75(7)	C2-N1-O1	116.8(2)
N3-Co1-P1	110.74(7)	C2-N1-Co1	118.11(19)
N4-Co1-P1	108.18(7)	01-N1-Co1	124.92(18)
C11-P1-C21	102.93(12)		

[Co(DO)(DOH)pn(PMePh₂)]

Bond lengths in [Å]

bond	bond length [Å]	bond	bond length [Å]
Co1-N1	1.863(3)	01-H1	1.04(3)
Co1-N2	1.883(3)	O2-N4	1.361(3)
Co1-N3	1.888(3)	O2-H1	1.42(3)
Co1-N4	1.856(3)	N1-C2	1.322(4)
Co1-P1	2.2113(9)	N2-C3	1.331(4)
P1-C11	1.824(3)	N2-C5	1.457(4)
P1-C21	1.814(3)	N3-C7	1.473(4)
P1-C31	1.821(3)	N3-C8	1.324(4)
01-N1	1.361(3)	N4-C10	1.324(4)

Table 11: chosen bond lengths

Bond angles in [°]

Table 12: chosen bond angles

angle	bond angle [°]	angle	bond angle [°]
N1-Co1-N2	80.97(12)	C11-P1-C31	101.60(15)
N1-Co1-N3	159.24(11)	C21-P1-C31	104.30(16)
N1-Co1-N4	95.50(12)	C11-P1-Co1	116.66(10)
N2-Co1-N3	96.48(11)	C21-P1-Co1	113.73(10)
N2-Co1-N4	163.15(11)	C31-P1-Co1	113.28(11)
N3-Co1-N4	80.95(12)	N1-01-H1	103.8(17)
N1-Co1-P1	98.24(8)	N4-02-H1	102.1(13)
N2-Co1-P1	103.80(8)	C2-N1-O1	117.0(3)
N3-Co1-P1	102.36(8)	C2-N1-Co1	118.4(2)
N4-Co1-P1	93.00(8)	01-N1-Co1	124.3(2)
C11-P1-C21	105.83(14)		

9. Bond lengths and angles of the molecular structure vs. calculated structure

[Co(DO)(DOH)pn(PPh₃)]

Table 13: Comparison of the theoretical bond lengths and the bond lengths from the x-ray measurement

Bond	Bond lengths [Å] X-ray structure	Bond lengths [Å] theor. calc.
Co1-N1	1.864	1.882
Co1-N2	1.901	1.915

Co1-N3	1.899	1.907
Co1-N4	1.869	1.859
Co1-P	2.251	2.243

Table 13: Comparison of the bond angles of the x-ray measurements and the theoretical calucation

Angle	Bond angles [°]	Bond angles [°]
	X-ray structure	theor. calc.
N1-Co1-N2	80.9	80.9
N2-Co1-N3	94.4	93.6
N3-Co1-N4	80.6	81.5
N1-Co1-N4	92.8	92.7
N1-Co1-P	95.1	97.7
N2-Co1-P	96.8	98.1
N3-Co1-P	110.7	108.8
N4-Co1-P	108.2	106.3

Calculated and measured UV-Vis spectra of [Co(DO)(DOH)pn(PPh₃)]



Figure 10: UV-Vis spectrum of [Co(DO)(DOH)pn(PPh₃)] in ACN (black line) and calculated oscillator strengths (blue bars).

References

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