

# Tricarbonylrhenium(I) Complexes with Tridentate Schiff Bases

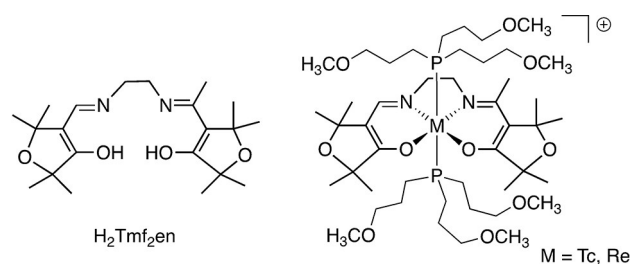
Sarah Hildebrandt<sup>+, [a]</sup>, Adelheid Hagenbach,<sup>[a]</sup> and Ulrich Abram<sup>\*[a]</sup>

Potentially tridentate, phosphine-containing Schiff bases with *P,N,O* and *P,N,P* donor sets have been prepared from 2-(diphenylphosphino)benzaldehyde, salicylaldehyde, 2-aminophenol and 2-((diphenylphosphino)phenyl)methylamine and reacted with  $(\text{NEt}_3)_2[\text{Re}(\text{CO})_3\text{Br}_3]$  in methanol. Deprotonation and the formation of neutral  $[\text{Re}(\text{CO})_3(\text{L})]$  complexes with tridentate coordination of the Schiff bases has been obtained

for the salicylidene derivatives, while the potential *P,N,P* ligand  $\text{L}^3$  forms  $[\text{Re}(\text{CO})_3\text{Br}(\text{L}^3)]$  with the Schiff base in a bidentate bonding mode. The formation of a cationic  $[\text{Re}(\text{CO})_3(\text{L}^3)]^+$  complex with tripodal coordination of the organic ligand could be achieved by the addition of  $\text{Ag}(\text{PF}_6)$  to the reaction mixture. The obtained rhenium(I) complexes were studied spectroscopically and by X-ray diffraction.

## Introduction

Schiff bases are flexible and easily tunable ligand systems and form stable complexes with almost all transition metal ions. Consequently, their complexes found applications in many fields such as catalysis, magnetochemistry or as model compounds in bioinorganic chemistry.<sup>[1–6]</sup> In the latter research area, Schiff bases and related ligand systems have not only be used as mimics for metalloenzymes, but also as metal-based radiopharmaceuticals. An illustrative example is the myocardial imaging agent  $^{99\text{m}}\text{Tc}$ -furifosmin, a technetium(III) complex with the tetradentate Schiff base 4,4'-[(1*E*,1'*E*)-[ethane-1,2-diylbis(azanilylidene)]bis(methanylylidene)]bis(2,2,5,5-tetramethyl-2,5-dihydrofuran-3-ol) ( $\text{H}_2\text{Tmf}_2\text{en}$ ),<sup>[7]</sup> which has also been found suitable for the imaging of glioma and multidrug-resistant tumors.<sup>[8,9]</sup>



Such a behavior makes the structurally analogous rhenium complexes of this type interesting for cancer treatment. Rhenium possesses two  $\beta$ -emitting isotopes, which can be used for nuclear medical therapy:  $^{186}\text{Re}$  and  $^{188}\text{Re}$ .<sup>[9,10]</sup> The latter one can be obtained for clinical use from a so-called  $^{188}\text{W}/^{188}\text{Re}$  nuclide generator, which makes it readily available at the clinical site.<sup>[11,12]</sup> Very recently,  $\text{Re}(\text{V})$  and  $\text{Re}(\text{III})$  complexes with the Schiff base  $\text{H}_2\text{tmf}_2\text{en}$  have been synthesized and structurally characterized.<sup>[13]</sup>

Potentially tridentate Schiff bases become interesting, since they can match the available coordination positions of the  $\{\text{M}(\text{CO})_3\}^+$  cores ( $\text{M} = \text{Re, Tc}$ ) and, thus, provide a maximum of stability for the corresponding complexes.<sup>[14–27]</sup> Such a stability, preferably accompanied by a kinetic inertness, is a fundamental requirement for use of corresponding tricarbonyl complexes in nuclear medical applications.

We have prepared a small series of Schiff bases from 2-(diphenylphosphino)benzaldehyde, salicylaldehyde, 2-aminophenol and 2-((diphenylphosphino)phenyl)methylamine (see Figure 1). The products can potentially act as tridentate ligands and the two salicylidene derivatives ( $\text{HL}^1$  and  $\text{HL}^2$ ) may deprotonate during the complex formation. Keeping in mind that there exist appropriate procedures for normal-pressure syntheses of  $[\text{M}(\text{CO})_3(\text{H}_2\text{O})_3]^+$  ( $\text{M} = ^{188}\text{Re}, ^{99\text{m}}\text{Tc}$ ) complexes,<sup>[28,29]</sup> the aim of the present study is to explore complex formation tendencies of these ligands with the corresponding tricarbonyl cores.

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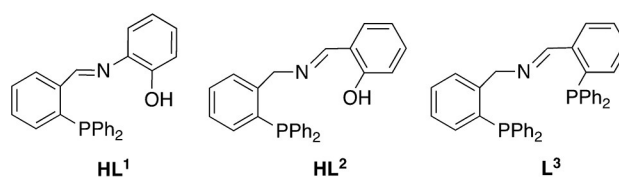


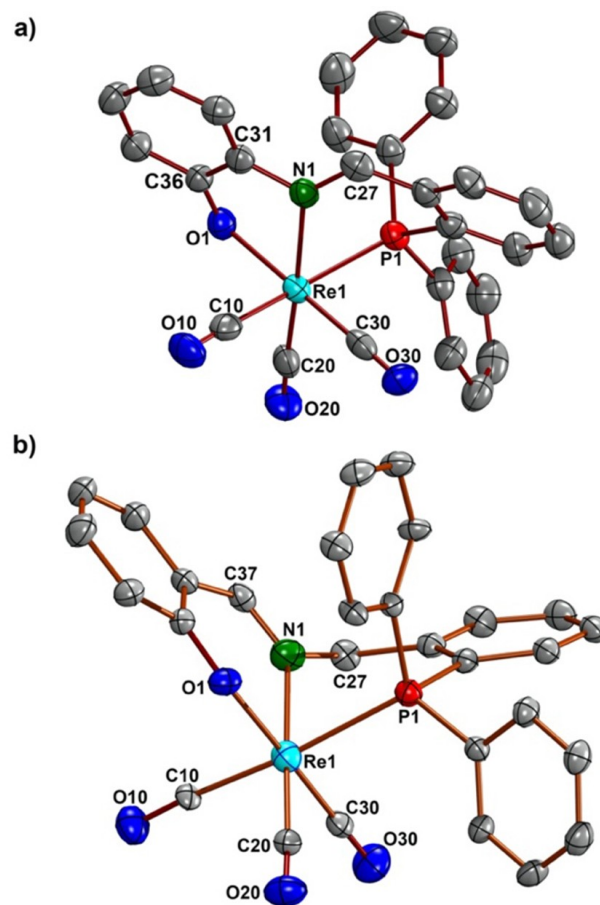
Figure 1. Schiff bases used in this study.

## Results and Discussion

$(\text{NEt}_4)_2[\text{Re}(\text{CO})_3\text{Br}_3]$  is a suitable starting material to mimic reactions of  $(\text{NEt}_4)_2[{}^{99}\text{Tc}(\text{CO})_3\text{Cl}_3]$  and the nuclear medically relevant cations  $[\text{M}(\text{CO})_3(\text{H}_2\text{O})_3]^+$  ( $\text{M} = {}^{99\text{m}}\text{Tc}$  or  ${}^{188}\text{Re}$ ). Reactions of  $(\text{NEt}_4)_2[\text{Re}(\text{CO})_3\text{Br}_3]$  with the Schiff bases  $\text{HL}^1$  or  $\text{HL}^2$  in methanol give yellow to orange-red solids of the composition  $[\text{Re}(\text{CO})_3(\text{L})]$  (Scheme 1). The organic ligands undergo deprotonation without the addition of a supporting base and coordinate in a tripodal fashion. The products can be recrystallized from methanol and are readily soluble in organic solvents such as  $\text{CHCl}_3$  or  $\text{CH}_2\text{Cl}_2$ . Their IR spectra show each three  $\nu_{\text{CO}}$  bands in the range between  $1878$  and  $2016\text{ cm}^{-1}$ . Their positions at lower wavenumbers than in non-coordinated carbon monoxide ( $2143\text{ cm}^{-1}$ ) confirm the  $\pi$ -back donation, which is commonly observed for electron-rich metal ions such as the  $d^6$  system of the present study. The presence of three IR-active modes is typical for facial tricarbonyl complexes with a low-symmetric coordination sphere. The positions at lower wavenumbers than in non-coordinated carbon monoxide ( $2143\text{ cm}^{-1}$ ) confirm the  $\pi$ -back donation, which is commonly observed for electron-rich metal ions such as the  $d^6$  system of the present study. The presence of three IR-active modes is typical for facial tricarbonyl complexes with a low-symmetric coordination sphere. The  ${}^1\text{H}$  and  ${}^{13}\text{C}$  NMR spectra of the products are unexceptional and the  ${}^{31}\text{P}$  spectra show resonances at  $31.7\text{ ppm}$  ( $[\text{Re}(\text{CO})_3(\text{L}^1)]$ ) and  $37.1\text{ ppm}$  ( $[\text{Re}(\text{CO})_3(\text{L}^2)]$ ), which is in the expected range for coordinated phosphines.

Single crystal X-ray studies on both compounds confirm the tripodal coordination of the deprotonated Schiff bases. Ellipsoid representations of the two structures are given in Figure 2. Table 1 contains selected bond lengths and angles of the neutral complexes.

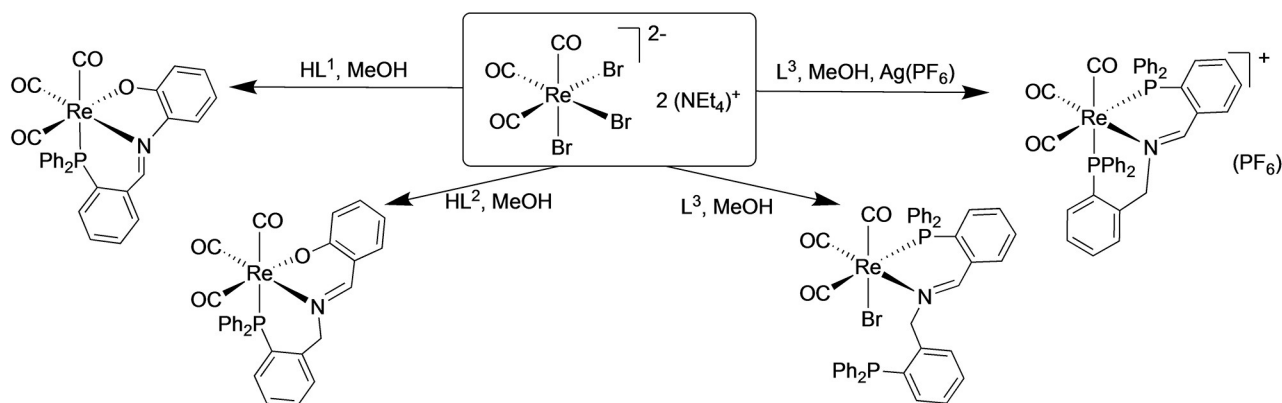
The rhenium coordination spheres in both complexes are distorted octahedra. Main distortions of the bonding angles are due to restrictions caused by the chelating ligands. Thus, the  $\text{N1}-\text{Re1}-\text{P1}$  angles in both compounds are small with values of  $78.1(1)$  and  $79.1(1)^\circ$ , respectively. But also the  $\text{N1}-\text{Re1}-\text{O1}$  angle in  $[\text{Re}(\text{CO})_3(\text{L}^1)]$ , which belongs to a five-membered chelate ring, is remarkably small ( $75.0(2)^\circ$ ). The steric stress caused by the tripodal coordination of  $[\text{L}^1]^-$  is also reflected by a lengthening of the rhenium-nitrogen bond compared to the value in  $[\text{Re}(\text{CO})_3(\text{L}^2)]$ , in which two six-membered chelate rings can be established. The imine bonds in the backbones of both ligands



**Figure 2.** Ellipsoid representations of the molecular structures of a)  $[\text{Re}(\text{CO})_3(\text{L}^1)]$  and b)  $[\text{Re}(\text{CO})_3(\text{L}^2)]$ . Thermal ellipsoids represent 50 per cent probability. Hydrogen atoms have been omitted for clarity.

remain almost located as can be derived from the corresponding  $\text{C}=\text{N}$  bond lengths of  $1.291(7)$  and  $1.262(7)\text{ \AA}$ .

The ready formation of neutral complexes with tripodal coordinated Schiff bases is most probably supported by the deprotonation of the ligands  $\text{HL}^1$  and  $\text{HL}^2$  during their reactions



**Scheme 1.** Reactions performed and composition of the products.

**Table 1.** Selected bond lengths (Å) and angles (°) in  $[\text{Re}(\text{CO})_3(\text{L}^1)]$  and  $[\text{Re}(\text{CO})_3(\text{L}^2)]$ .

	$[\text{Re}(\text{CO})_3(\text{L}^1)]$	$[\text{Re}(\text{CO})_3(\text{L}^2)]$
Re1-C10	1.952(7)	1.950(4)
Re1-C20	1.946(7)	1.958(5)
Re1-C30	1.920(7)	1.901(6)
Re1-O1	2.138(4)	2.119(4)
Re1-N1	2.201(5)	2.168(4)
Re1-P1	2.433(2)	2.456(1)
N1-C27	1.291(7)	1.477(7)
N1-C31/C37	1.431(7)	1.262(7)
O1-Re1-N1	75.0(2)	83.9(2)
O1-Re1-P1	96.6(1)	88.5(1)
N1-Re1-P1	78.1(1)	79.1(1)
C27-N1-C31/C37	122.1(5)	117.5(4)

with  $(\text{NEt}_3)_2[\text{Re}(\text{CO})_3\text{Br}_3]$ , since the corresponding reaction with the ligand  $\text{L}^3$  results in an only incomplete replacement of the bromido ligands and the formation of the neutral complex  $[\text{Re}(\text{CO})_3\text{Br}(\kappa^2\text{P},\text{N}-\text{L}^3)]$ . Expectedly, also the addition of  $\text{NEt}_3$  as a supporting base did not result in the abstraction of the third  $\text{Br}^-$  ligand. The formation of a cationic complex of the composition  $[\text{Re}(\text{CO})_3\text{Br}(\kappa^3-\text{L}^3)](\text{PF}_6)$  finally succeeded by the addition of three equivalents of  $\text{Ag}(\text{PF}_6)$  to  $(\text{NEt}_3)_2[\text{Re}(\text{CO})_3\text{Br}_3]$ , removal of the formed  $\text{AgBr}$  and subsequent addition of  $\text{L}^3$  (Scheme 1).

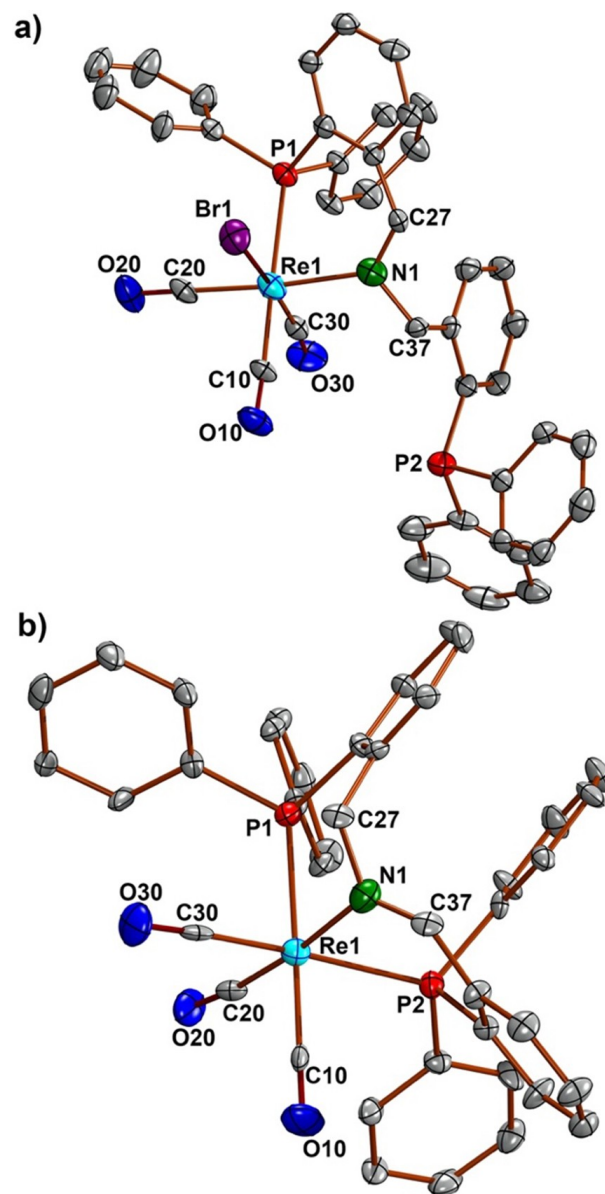
Both complexes with  $\text{L}^3$  are yellow solids, which are readily soluble in organic solvents such as  $\text{CH}_2\text{Cl}_2$  or acetonitrile, but insoluble in diethyl ether or hydrocarbons.

The IR spectra of the two  $\text{L}^3$  complexes show in their carbonyl region the typical facial splitting pattern as has been found for the compounds with  $\{\text{L}^1\}^-$  and  $\{\text{L}^2\}^-$ .  $^{31}\text{P}$  NMR spectroscopy confirms that only one of the phosphorus atoms of  $\text{L}^3$  is coordinated in  $[\text{Re}(\text{CO})_3\text{Br}(\kappa^2\text{P},\text{N}-\text{L}^3)]$ , since only one of the resonances observed for the uncoordinated Schiff base ( $-13.1$ ,  $-15.1$  ppm) is markedly shifted upon coordination to 13.3 ppm. This is different to the spectrum of  $[\text{Re}(\text{CO})_3(\kappa^3-\text{L}^3)]$ , where the coordination of both phosphorus atoms is indicated by signals at 31.6 and 37.3 ppm.

The spectroscopic findings are in accord with the results of single crystal X-ray structural studies on the complexes. Ellipsoid representations of both complex molecules are shown in Figure 3. Selected bond lengths and angles are summarized in Table 2.

An almost ideal octahedral coordination sphere is found for  $[\text{Re}(\text{CO})_3\text{Br}(\kappa^2\text{P},\text{N}-\text{L}^3)]$ , while slightly larger deviations from  $90^\circ$  between neighboring donor atoms are found when  $\text{L}^3$  establishes a tripodal coordination mode. This demonstrates a remarkable flexibility of the neutral, potentially tridentate  $P,N,P$  ligand, particularly keeping in mind that a located  $\text{C}=\text{N}$  double bond is preserved in the backbone of the ligand after coordination.

Although the described complexes with  $\text{L}^3$  are the first  $P,N,P$  Schiff base complexes with a tricarbonylrhenium(I) unit, there are some amine complexes with a similar coordination pattern. They found interest for potential pharmaceutical



**Figure 3.** Ellipsoid representations of the structures of a)  $[\text{Re}(\text{CO})_3\text{Br}(\kappa^2\text{P},\text{N}-\text{L}^3)]$  and b) the complex cation of  $[\text{Re}(\text{CO})_3(\kappa^3-\text{L}^3)](\text{PF}_6)$ . Thermal ellipsoids represent 50 per cent probability. Hydrogen atoms have been omitted for clarity.

applications,<sup>[30–32]</sup> but also because of their catalytic activity for hydrogen transfer and methylation reactions.<sup>[33–36]</sup> Due to their flexibility, such tridentate, pincer-type amine ligands may allow isomerization between the facial and meridional coordination modes and can, thus, activate carbonyl ligands as has been demonstrated for bis[2-diisopropylphosphino]ethyl]amine and related ligands after the addition of a base.<sup>[34,35]</sup> Changes between bidentate and tridentate coordination, as observed for the tricarbonyl complexes of  $\text{L}^3$ , has not been reported for the corresponding amines.

**Table 2.** Selected bond lengths (Å) and angles (°) in [Re(CO)<sub>3</sub>Br(κ<sup>2</sup>P,N–L<sup>3</sup>)] and [Re(CO)<sub>3</sub>(κ<sup>3</sup>–L<sup>3</sup>)](PF<sub>6</sub>).

	[Re(CO) <sub>3</sub> Br(κ <sup>2</sup> P,N–L <sup>3</sup> )]	[[Re(CO) <sub>3</sub> (κ <sup>3</sup> –L <sup>3</sup> )](PF <sub>6</sub> )
Re1–C10	1.942(7)	1.909(9)
Re1–C20	1.893(8)	1.944(9)
Re1–C30	1.917(8)	1.934(9)
Re1–N1	2.194(5)	2.170(7)
Re1–P1	2.456(2)	2.462(2)
Re1–Br1	2.6572(8)	–
Re1–P2	–	2.470(2)
N1–C27	1.294(7)	1.275(9)
N1–C37	1.480(8)	1.477(9)
P1–Re1–N1	82.5(1)	84.8(2)
P1–Re1–Br1/P2	87.90(5)	96.66(8)
N1–Re1–Br1/P2	87.3(3)	82.4(2)
C27–N1–C37	113.8(5)	114.5(7)

## Conclusions

In spite of the preservation of located C=N double bonds of the imines during coordination to {Re(CO)<sub>3</sub>}<sup>+</sup> units, the Schiff bases {L<sup>1</sup>}<sup>–</sup>, {L<sup>2</sup>}<sup>–</sup> and L<sup>3</sup> can act as tripodal ligands. The formation of a bidentate product has only been observed for the neutral P,N,P ligand L<sup>3</sup>. The stability of the products recommends the synthesis of corresponding tricarbonyltechnetium(I) complexes as potential radiopharmaceuticals. Such studies are planned in our laboratory for the future.

## Experimental Section

All chemicals in this study were reagent grade and used without further purification. (NEt<sub>4</sub>)<sub>2</sub>[Re(CO)<sub>3</sub>Br<sub>3</sub>] was prepared from [Re-

(CO)<sub>3</sub>Br] and (NEt<sub>4</sub>)Br in diglyme.<sup>[37,38]</sup> HL<sup>1</sup> was prepared according to a literature procedure.<sup>[39]</sup>

**Analytical Methods.** IR spectra were recorded for KBr pellets on a Shimadzu FTIR spectrometer in the range between 400 and 4000 cm<sup>–1</sup>. ESI<sup>+</sup> mass spectra were recorded on an Agilent 6210 ESI-TOF (Agilent Technologies). EI mass spectra were detected on a MAT 711, Varian MAT, Bremen. The energy of the electrons was 80 eV. NMR spectra were recorded in CDCl<sub>3</sub> on a JEOL-400 MHz spectrometer.

**X-ray Crystallography.** Single crystal X-ray diffraction data were collected on a STOE IPDS II T. Absorption corrections were carried out by integration methods.<sup>[40]</sup> Structure solutions and refinements were done with the SHELX program package.<sup>[41,42]</sup> Hydrogen atoms were placed at calculated positions and refined by the riding model option of SHELXL. More details are given in Table 3. The visualization of the molecular structures was done using the program DIAMOND 4.2.2.<sup>[43]</sup> CCDC 2033898–2033901 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre.

**HL<sup>2</sup>.** 2-((Diphenylphosphino)phenyl)methylamine (1.00 g, 3.55 mmol) and 2-hydroxybenzaldehyde (0.38 ml, 3.55 mmol) were dissolved in 10 mL of EtOH. A yellow solid deposited after heating on reflux for 1.5 h and cooling to room temperature. It was recovered by filtration and recrystallized by slow evaporation of a CH<sub>2</sub>Cl<sub>2</sub>/MeOH solution. Yield: 0.93 g (67%). C<sub>26</sub>H<sub>22</sub>NOP (395.4): calcd. C 79.0, H 5.6, N 3.5%; found C 78.8, H 5.6, N 3.4%. IR (KBr): ν<sub>max</sub> = 3285(m) (OH), 3051(m) (CH), 3011(m) (CH), 1633(s) (C=N), 1429(s) (C=C), 1281(m) (OH) cm<sup>–1</sup>. <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): 9.90 (s, 1H, CH), 7.67–6.80 (m, 18H, phenyl), 5.01 (s, 2H, CH<sub>2</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm): 166.2 (C=N), 136.1–116.8 (phenyl), 61.3 (CH<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, ppm): –14.8 (s). ESI+MS (m/z): 396.1501 (calc. 396.1517) [M+H]<sup>+</sup>.

**L<sup>3</sup>.** 2-((Diphenylphosphino)phenyl)methylamine (1.00 g, 3.55 mmol) and 2-((diphenylphosphino)benzaldehyde (1.00 g, 3.55 mmol) were suspended in 30 mL of EtOH and 3 drops of formic acid were added. A yellow solid deposited after heating on reflux for 2.5 h and cooling to room temperature. It was isolated by filtration and washed carefully with cold EtOH. Yield: 1.64 g (82%). C<sub>38</sub>H<sub>31</sub>NP<sub>2</sub>

**Table 3.** Crystal data and details of the structure determinations.

	[Re(CO) <sub>3</sub> (L <sup>1</sup> )]	[Re(CO) <sub>3</sub> (L <sup>2</sup> )]	[Re(CO) <sub>3</sub> Br(L <sup>3</sup> )]	[Re(CO) <sub>3</sub> (L <sup>3</sup> )](PF <sub>6</sub> ) –0.5 (NEt <sub>4</sub> )(PF <sub>6</sub> )
Formula	C <sub>28</sub> H <sub>19</sub> NO <sub>4</sub> PRe	C <sub>29</sub> H <sub>21</sub> NO <sub>4</sub> PRe	C <sub>41</sub> H <sub>31</sub> NO <sub>3</sub> P <sub>2</sub> Re	C <sub>45</sub> H <sub>41</sub> F <sub>9</sub> N <sub>1.5</sub> O <sub>3</sub> P <sub>3.5</sub> Re
M <sub>w</sub>	650.61	664.64	913.72	1116.39
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic
a/Å	10.088(1)	9.237(1)	10.689(1)	34.724(1)
b/Å	10.412(1)	11.871(1)	14.147(1)	14.724(1)
c/Å	14.777(2)	11.948(1)	15.295(2)	17.827(1)
α/°	109.557(8)	96.88(1)	97.79(1)	90
β/°	106.449(8)	75.28(1)	107.36(1)	98.69(1)
γ/°	112.657(8)	95.23(1)	107.21(1)	90
V/Å <sup>3</sup>	1188.5(2)	1255.5(2)	2044.1(4)	8991(1)
Space group	P $\bar{1}$	P $\bar{1}$	P $\bar{1}$	C2/c
Z	2	2	2	8
D <sub>calc</sub> /g cm <sup>–3</sup>	1.818	1.758	1.484	1.649
μ/mm <sup>–1</sup>	5.25	4.939	4.063	2.907
No. reflect.	12521	9861	17181	34954
No. indep.	6646	4718	7983	8734
No param.	316	326	442	555
R <sub>1</sub> /wR <sub>2</sub>	0.0389/0.0717	0.0453/0.1018	0.0446/0.0840	0.0485/0.0624
GOF	0.862	1.077	0.895	0.652
CCDC	2033898	2033899	2033900	2033901

(563.6): calcd. C 81.0, H 5.5, N 2.5%; found C 79.6, H 5.5, N, 2.3%. IR (KBr):  $\nu_{\max}$  = 3051(m) (CH), 1638(s) (C=N), 1431(s) (C=C)  $\text{cm}^{-1}$ .  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , ppm): 8.91 (s, 1H, CH), 7.37–6.81 (m, 28H, phenyl), 4.90 (s, 2H,  $\text{CH}_2$ ).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , ppm): 161.6 (C=N), 143.9–127.1 (phenyl), 62.8 ( $\text{CH}_2$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , ppm): –15.1 (s), –13.1 (s). EI MS (m/z): 563.2  $[\text{M}]^+$ , 486.4  $[\text{M}-\text{Ph}]^+$ , 378.5  $[\text{M}-\text{PPh}_2]^+$ , 288.3  $[\text{M}-\text{PPh}_2-\text{CH}_2\text{C}_6\text{H}_4]^+$ .

$[\text{Re}(\text{CO})_3(\text{L}^1)]: (\text{NEt}_4)_2[\text{Re}(\text{CO})_3\text{Br}_3]$  (77 mg, 0.1 mmol) was dissolved in 2 mL of MeOH and a solution of  $\text{HL}^1$  (38 mg, 0.1 mmol) in MeOH (3 mL) was added. The mixture was heated under reflux for 30 min and the solvent was removed under vacuum. The residue was recrystallized from MeOH giving orange-red plates. Yield: 42 mg (64%).  $\text{C}_{28}\text{H}_{19}\text{NO}_4\text{PRe}$  (650.6): calcd. C 51.7, H 2.9, N 2.2%; found C 52.0, H 3.1, N 2.2%. IR (KBr):  $\nu_{\max}$  = 2016(vs) (CO), 1937(vs) (CO), 1904(vs) (CO), 1637(s) (C=N)  $\text{cm}^{-1}$ .  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , ppm): 8.38 (s, 1H, CH), 7.85–6.80 (m, 18H, phenyl).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , ppm): 169.9 (C=N), 134.8–114.2 (phenyl).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , ppm): 31.7 (s). ESI+MS (m/z): 624.0808 (calc. 624.0738)  $[\text{M}-\text{CO}+\text{H}]^+$ , 596.0848 (calc. 596.0789)  $[\text{M}-2\text{CO}+\text{H}]^+$ , 568.0901 (calc. 568.0840)  $[\text{M}-3\text{CO}+\text{H}]^+$ .

$[\text{Re}(\text{CO})_3(\text{L}^2)]: (\text{NEt}_4)_2[\text{Re}(\text{CO})_3\text{Br}_3]$  (77 mg, 0.1 mmol) was dissolved in 2 mL of MeOH and  $\text{HL}^2$  (40 mg, 0.1 mmol) was added in 3 mL MeOH. The mixture was heated under reflux for 30 min and the solvent was removed under vacuum. The yellow residue was recrystallized from MeOH. Yield: 51 mg (76%).  $\text{C}_{29}\text{H}_{21}\text{NO}_4\text{PRe}$  (664.7): calcd. C 52.4, H 3.2, N 2.1%; found C 52.5, H 3.1, N 2.0%. IR (KBr):  $\nu_{\max}$  = 2011(vs) (CO), 1924(vs) (CO), 1878(vs) (CO), 1612(s) (C=N)  $\text{cm}^{-1}$ .  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , ppm): 7.85 (s, 1H, CH), 7.65–6.26 (m, 18H, phenyl), 5.02 (s, 2H,  $\text{CH}_2$ ).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , ppm): 166.1 (C=N), 135.7–120.6 (phenyl), 72.5 ( $\text{CH}_2$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , ppm): 37.1 (s). ESI+MS (m/z): 638.0885 (calc. 638.0895)  $[\text{M}-\text{CO}+\text{H}]^+$ .

$[\text{Re}(\text{CO})_3\text{Br}(\kappa^2\text{P},\text{N}-\text{L}^3)]: (\text{NEt}_4)_2[\text{Re}(\text{CO})_3\text{Br}_3]$  (77 mg, 0.1 mmol) was dissolved in 2 mL of MeOH and  $\text{L}^3$  (56 mg, 0.1 mmol) was added in 3 mL MeOH. The mixture was heated under reflux for 30 minutes. A yellow solid precipitated upon cooling. It was recovered by filtration and recrystallized from MeOH/ $\text{CH}_2\text{Cl}_2$ . Yield: 89 mg (97%).  $\text{C}_{41}\text{H}_{31}\text{BrNO}_3\text{P}_2\text{Re}$  (913.8): calcd. C 53.9, H 3.4, N 1.5%; found C 52.9, H 3.3, N 1.9%. IR (KBr):  $\nu_{\max}$  = 2026(vs) (CO), 1930(vs) (CO), 1891(vs) (CO), 1614(s) (C=N)  $\text{cm}^{-1}$ .  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , ppm): 8.13 (s, 1H, CH), 7.76–6.50 (m, 28H, phenyl), 4.90 (s, 2H,  $\text{CH}_2$ ).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , ppm): 176.3 (C=N), 140.2–122.8 (phenyl), 74.2 ( $\text{CH}_2$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , ppm): 13.3 (s), –16.4 (s). ESI+MS (m/z): 834.1349 (calc. 834.1336)  $[\text{M}-\text{Br}]^+$ .

$[\text{Re}(\text{CO})_3(\kappa^3-\text{L}3)(\text{PF}_6)]: (\text{NEt}_4)_2[\text{Re}(\text{CO})_3\text{Br}_3]$  (77 mg, 0.1 mmol) was dissolved in 3 mL of MeOH and  $\text{AgPF}_6$  (75 mg, 0.3 mmol) in 2 mL MeOH was added. The precipitated  $\text{AgBr}$  was filtered off and solid  $\text{L}^3$  (56 mg, 0.1 mmol) was added. The reaction mixture was heated under reflux for 1 h and the solvent was removed under vacuum. The residue was recrystallized from  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  giving yellow needles. Yield: 67 mg (68%). IR (KBr):  $\nu_{\max}$  = 2041(vs) (CO), 1977(vs) (CO), 1919(vs) (CO), 1620(s) (C=N)  $\text{cm}^{-1}$ .  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , ppm): 8.15 (s, 1H, CH), 7.76–6.74 (m, 28H, phenyl), 4.14 (s, 2H,  $\text{CH}_2$ ).  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , ppm): 191.2 (CH), 136.6–128.1 (phenyl), 52.4 ( $\text{CH}_2$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ , ppm): 37.2 (s), 31.6 (s), –143.9. ESI+MS (m/z): 834.1304 (calc. 834.1336)  $[\text{M}]^+$ .

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- [1] R. Hernandez-Molina, A. Mederos, *Acyclic and Macrocyclic Schiff Base Ligands*. in *Comprehensive Coordination Chemistry II* (Eds.: J. A. McCleverty, T. J. Meyer), Elsevier, Amsterdam, **2003**, vol. 1, 411–446.
- [2] P. Guerreiro, S. Tamburini, V. A. Vigato, *Coord. Chem. Rev.* **1995**, *139*, 17–243.
- [3] H. Okawa, H. Furutachi, D. E. Fenton, *Coord. Chem. Rev.* **1998**, *174*, 51–75.
- [4] L. Canali, D. C. Sherrington, *Chem. Soc. Rev.* **1999**, *28*, 85–93.
- [5] D. E. Fenton, P. A. Vigato, *Chem. Soc. Rev.* **1988**, *17*, 69–90.
- [6] P. A. Vigato, S. Tamburini, D. E. Fenton, *Coord. Chem. Rev.* **1990**, *106*, 25–170.
- [7] C. Rossetti, G. Vanoli, G. Paganelli, M. Kwiakowski, F. Zito, F. Colombo, C. Bonino, A. Carpinelli, R. Casati, K. Keutsch, M. Marmion, S. R. Woulfe, F. Lunghi, E. Deutsch, F. Fazio, *J. Nucl. Med.* **1994**, *35*, 1571–1580.
- [8] J. R. Ballinger, T. Muzzammil, M. J. Moore, *J. Nucl. Med.* **1997**, *38*, 1915–1919.
- [9] G. D. Luker, V. V. Rao, C. L. Crankshaw, J. Dahlheimer, D. Piwnica-Worms, *Biochemistry* **1997**, *36*, 14218–14227.
- [10] W. A. Volkert, T. J. Hoffman, *Chem. Rev.* **1999**, *99*, 2269–2292.
- [11] M. J. Heeg, S. S. Jurisson, *Acc. Chem. Res.* **1999**, *32*, 1053–1060.
- [12] F. F. Knapp, *Cancer Biother. Radiopharm.* **1998**, *13*, 337–349.
- [13] J. E. Baumeister, K. M. Reinig, C. L. Barnes, S. P. Kelley, S. S. Jurisson, *Inorg. Chem.* **2018**, *57*, 12920–12933.
- [14] S. M. Soares, S. S. Lemos, M. J. A. Sales, R. A. Burrow, *J. Organomet. Chem.* **2014**, *750*, 80–85.
- [15] D. V. Griffith, Y.-K. Cheong, P. Duncanson, M. Motevalli, *Dalton Trans.* **2011**, *40*, 10215–10228.
- [16] P. D. Benny, G. A. Fugate, T. Ganguly, B. Twanley, D.-K. Bucar, L. R. MacGillivray, *Inorg. Chim. Acta* **2011**, *365*, 356–362.
- [17] C. M. Alvarez, L. A. Garcia-Escudero, R. Garcia-Rodriguez, D. Miguel, *Chem. Commun.* **2012**, *48*, 7209–7211.
- [18] A. J. Osinski, D. L. Morris, R. S. Herrick, C. J. Ziegler, *Inorg. Chem.* **2017**, *56*, 14734–14737.
- [19] V. Yempally, W. Y. Fan, B. A. Arndtsen, A. A. Bengali, *Inorg. Chem.* **2015**, *54*, 11441–11449.
- [20] R. S. Herrick, C. J. Ziegler, A. Gambella, *Eur. J. Inorg. Chem.* **2010**, 3905–3908.
- [21] R. Arevalo, J. Perez, L. Riera, *Chem. Eur. J.* **2015**, *21*, 3546–3549.
- [22] J. W. Faller, G. Mason, J. Parr, *J. Organomet. Chem.* **2001**, *626*, 181–185.
- [23] P. D. Benny, T. Ganguly, L. Raiford, G. A. Fugate, B. Twanley, *Inorg. Chem. Commun.* **2011**, *14*, 392–395.
- [24] A. M. Maroń, A. Szlapa-Kula, M. Matussek, R. Kruszynski, M. Siwy, H. Janeczek, J. Grzelak, S. Maćkowski, E. Schab-Balcerzak, B. Machura, *Dalton Trans.* **2020**, *49*, 4441–4453.
- [25] S. L. Binkley, T. C. Leeper, R. S. Rowlett, R. S. Herrick, C. J. Ziegler, *Metallomics* **2011**, *3*, 909–916.
- [26] D. K. Nayak, R. Baishya, K. K. Halder, T. Sen, B. R. Sarkar, S. Ganguly, M. K. Das, M. C. Debnath, *Metallomics* **2012**, *4*, 1197–1208.
- [27] J. W. Betts, P. Roth, C. A. Pattrick, H. M. Southam, R. M. La Ragione, R. K. Poole, U. Schatzschneider, *Metallomics* **2020**, *12*, 1563–1575.
- [28] R. Alberto, K. Ortner, N. Wheatley, R. Schibli, A. P. Schubiger, *J. Am. Chem. Soc.* **2001**, *123*, 3135–3136.
- [29] R. Schibli, R. Schwarzbach, R. Alberto, K. Ortner, H. Schmalle, C. Dumas, A. Egli, P. A. Schubiger, *Bioconjugate Chem.* **2002**, *13*, 750–756.

- [30] A. T. Radoevich, J. G. Melnick, S. A. Stoian, D. Bacciu, C.-H. Chen, B. M. Foxman, O. V. Ozerov, D. G. Nocera, *Inorg. Chem.* **2009**, *48*, 9214–9221.
- [31] Y.-S. Kim, Z. Hea, R. Schibli, S. Liu, *Inorg. Chim. Acta* **2006**, *359*, 2479–2488.
- [32] G. K. Rao, I. Korobkov, D. Richeson, *Polyhedron* **2018**, *143*, 62–69.
- [33] P. Piehl, M. Pena-Lopez, A. Frey, M. Beller, *Chem. Commun.* **2017**, *53*, 3265–3268.
- [34] D. Wei, T. Roisnel, D. Darcel, E. Clot, J.-B. Sortais, *ChemCatChem* **2017**, *9*, 80–83.
- [35] D. Wei, O. Sadeck, V. Dorcet, T. Roisnel, C. Darcel, E. Gras, E. Clot, J.-B. Sortais, *J. Catalysis* **2018**, *366*, 300–309.
- [36] M. Glatz, J. Pecak, L. Haager, B. Stoeger, K. Kirchner, *Monatsh. Chem.* **2019**, *150*, 111–119.
- [37] L. Kromer, B. Spingler, R. Alberto, *J. Organomet. Chem.* **2007**, *692*, 1372–1376.
- [38] M. Hinrichs, F. R. Hofbauer, P. Klüfers, M. Suhanji, *Inorg. Chem.* **2006**, *45*, 6688–6693.
- [39] A. Barandov, U. Abram, *Polyhedron* **2009**, *28*, 1155–1159.
- [40] P. Coppens, *The Evaluation of Absorption and Extinction in Single-Crystal Structure Analysis*. Crystallographic Computing, Copenhagen, Muksgaard, 1979.
- [41] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2008**, *64*, 112–122.
- [42] G. M. Sheldrick, *Acta Crystallogr. Sect. C* **2015**, *71*, 3–8.
- [43] *Diamond – Crystal and Molecular Structure Visualization Crystal Impact*, Dr. H. Putz & Dr. K. Brandenburg GbR, Bonn, Germany.

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