Structural Chemistry of Methyl- and Allylpalladium(II) Complexes Containing Chiral Thioether Auxiliaries

by **Karin Boog-Wick**, **Paul S. Pregosin***, and **Michael Wörle**

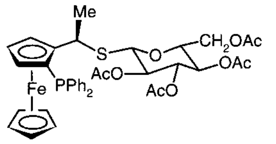
Laboratorium für Anorganische Chemie, ETH-Zentrum, CH-8092 Zürich

and **Alberto Albinati***

Chemical Pharmacy, University of Milan, I-20131 Milan

The molecular structures of three Pd^{II} compounds are reported: *a*) the two [PdCl(Me)] complexes **7a** and **8a** each containing a different chiral N,S-chelate based on {[(dihydrooxazolyl)phenyl]methyl}-thioglucose backbones, *e.g.*, chloro({2-[(4*S*)-4,5-dihydro-4-isopropyloxazol-2-yl-κ*N*]phenyl}methyl 2,3,4,6-tetra-*O*-acetyl-1-(thio-κ*S*)-β-D-glucopyranoside)methylpalladium(II) (**7a**) and *b*) one $[Pd(\eta^3\text{-}C_3H_5)(\overset{\frown}{P\ S})]^+$ cation in which the P,S-chelate stems from a phosphinoferrocene and thioephedrine-derived thioether donor, *i.e.*, [(*S*)-1-(diphenylphosphino-κ*P*)-2-((1*R*)-1-{[(1*R*,2*S*)-1-phenyl-2-(piperidin-1-yl)propyl]thio-κ*S*}ethyl)ferrocene] (η^3-prop-2-enyl)palladium trifluoromethanesulfonate (**11**). In the methylpalladium compounds **7a** and **8a** the thioglucose-κ*S* moiety is pseudo-axial (*Figs. 2* and *3*), whereas in the allyl complex, the thioephedrine-κ*S* moiety is markedly pseudo-equatorial (*Fig. 5*). It is suggested, based on these results, that the shape (chiral pocket) of such coordinated chiral thioethers may not be readily predictable.

Introduction. – Chelating chiral auxiliaries based on tertiary phosphines [1] and/or N-donors [2][3] are both well-known and relatively successful. Only recently it has been recognized that S-donors [4][5] can perform quite well in, *e.g.*, Pd-catalyzed enantioselective allylic alkylation. We have shown [6][7] that the chelating ligands **1**–**3** are good auxiliaries for this reaction, with **2b** achieving a *ca.* 97% ee with a 1,3-diphenylallyl precursor [7].



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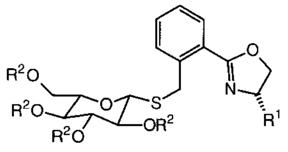
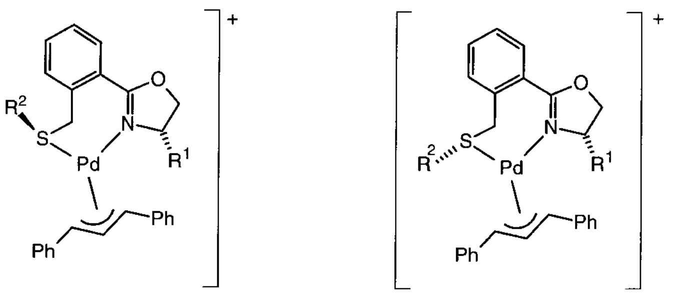


2a R^1 = ^{i}Pr, R^2 = Ac
2b R^1 = ^{i}Pr, R^2 = ^{t}BuCO
3a R^1 = Ph, R^2 = Ac
3b R^1 = Ph, R^2 = ^{t}BuCO

4

Given that these bidentates can be useful, it remains to ask how the chirality is transferred, and, more specifically, what shape (chiral pocket) a ligand such as **2** or **3** would present to a coordinated substrate. There are a number of structural subtleties concerned with a Pd^{II} complex of either **2** or **3**, *e.g.*, the S-atom is a stereogenic center (see **4**). *Gillespie* and coworkers [8] have suggested that lone-pairs on complexed donors occupy a relatively large amount of space. Indeed, in several studies [9] concerned with chelating chiral thioether ligands, it would appear that the substituent on the S-atom (in our case this would be the glycosyl moiety) prefers a pseudo-axial position, thereby remaining relatively remote from both the immediate coordination sphere and the complexed substrate. This would clearly not be advantageous in terms of enantioselectivity. For square planar allyl complexes, there is also the additional complexity arising from structures in which the substituent at the S-atom can be either above or below the coordination plane (see **5** and **6**, resp., in *Fig. 1*).



5 **6**

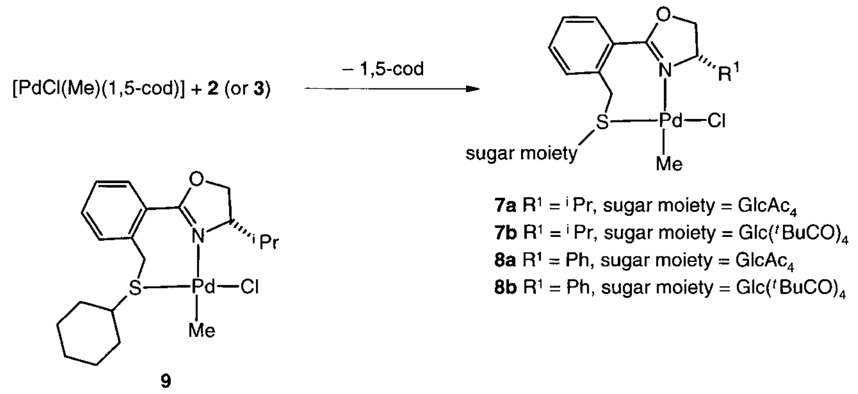
Fig. 1. *Square planar allyl complexes with R^1 and R^2 on the opposite* (see **5**) *or the same side* (see **6**) *of the S–Pd–N plane*

Although we have not been able to obtain suitable crystals of allyl complexes of Pd^{II} containing either **2** or **3**, we have recently prepared several complexes of the type [Pd(Me)Cl(**2**)] (**7**) and [Pd(Me)Cl(**3**)] (**8**). For **7a** and **8a**, (R^2 = Ac) the structure could now be determined by X-ray diffraction methods. In a way this is fortunate since these compounds provide the opportunity to consider the chiral pockets for complexed **2a** and **3a** in a sterically non-demanding environment, *i.e.*, both the ligands Me and Cl are modest in size. Methylpalladium complexes have attracted much interest [10–15].

Results and Discussion. – *Synthesis of Complexes* **7–9** *and X-Ray Diffraction Studies of* **7a** *and* **8a**. The N,S-donating [(glycosylthio)methyl]phenyl-substituted dihydrooxazoles **2** and **3** reacted with [PdCl(Me)(1,5-cod)] (cod = cycloocta-diene) [16] in CH_2Cl_2 to afford the products **7** and **8** (*Scheme 1*). Similarly, we also prepared the [(cyclohexylthio)methyl]phenyl analog with R^1 = i-Pr. The complexes **7–9** all afforded consistent ^{1}H-NMR and mass spectral data, in addition to satisfactory microanalytical results (see *Exper. Part*), and typical ^{13}C-NMR resonances for the coordinated Me group δ(C) −4.0 (**7a**), −2.8 (**7b**), −2.9 (**8a**) −2.8 (**8b**), and −4.4 (**9**). We observed only one geometric isomer in solution (N *trans* to Me), and its structure was assigned based on NOE studies revealing contacts between the Me–Pd and anomeric methine proton of the sugar moiety.

The structures of the complexes **7a** and **8a** were determined by X-ray diffraction methods. *Figs. 2* and *3* show ORTEP plots for these compounds. Both molecules possess essentially square-planar geometry at the metal center with the dihydrooxazole N-atom *trans* to the Me ligand, as expected. The sugar moiety and the substituent R^1 at C(4) of the oxazole ring (i-Pr in **7a**, Ph in **8a**) are on the same side of the coordination plane (*cf. Fig. 1*). This is clearly not the structure one might have expected if steric

Scheme 1



effects between the sugar and oxazole moieties were to be minimized. If one defines the best plane containing the four donor atoms and the metal, and keeping in mind that the S–C bond lengths in **7a** and **8a** are *ca.* 1.8 Å (average of 1.82 Å in **7a** and **8a**), then the observed distances of C(12) (anomeric sugar C-atom) from this plane, *ca.* 1.68 and *ca.* 1.61 Å, suggest that the sugar moieties are pseudo-axial. Clearly, the thioether substituent (R^2 in **6**) is placed away from the coordination plane and the lone-pair of the S-atom prefers a pseudo-equatorial position.

Selected bond lengths and bond angles for **7a** and **8a** are given in *Table 1.* The Pd–C(Me) bonds lengths, 2.086(3) Å and 2.060(4) Å, respectively, are somewhat longer than might have been expected. In methylpalladium complexes with the Pd–C bond *trans* to an N-atom (tmeda [16a], bipy [16b], or P,N-chelate [17]), Pd–C lengths of *ca.* 2.02 Å have been observed. *Alper* and coworkers [18] found *ca.* 2.03 Å for a methylpalladium complex with a bridging formate. In two *cis*-dimethyl(diphosphine) complexes, with the Me group *trans* to the tertiary phosphine ligand, the Pd–C bond

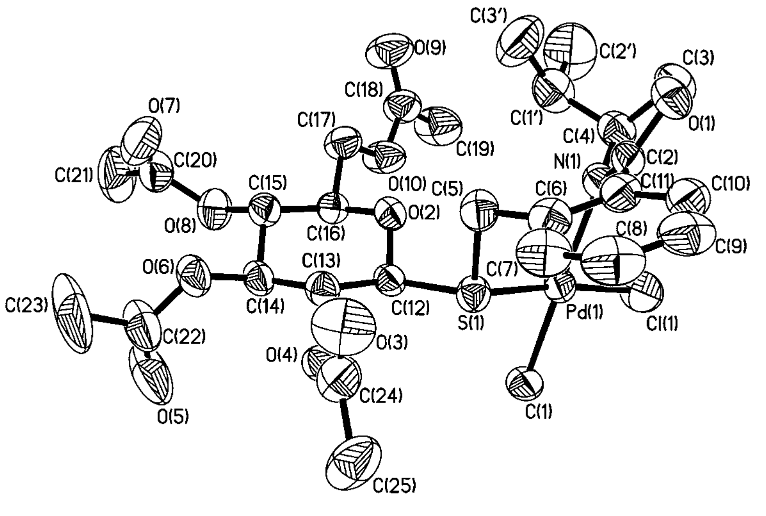


Fig. 2. *ORTEP Plot of* **7a**

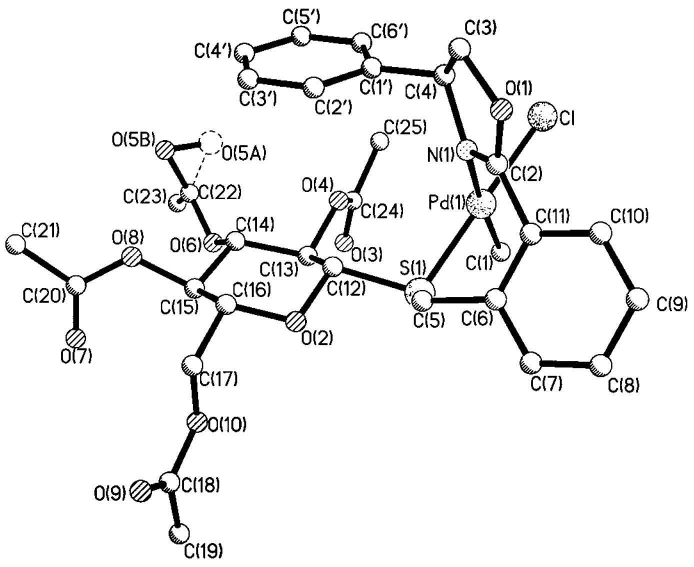


Fig. 3. *ORTEP Plot of* **8a**

length was *ca.* 2.09 Å [16][19]. However, *Dekker et al.* [20] reported 2.068(2) Å for their [PdClMe(PAN)] where PAN is a rigid 1-(dimethylamino)-8-(diphenylphosphino)naphthalene ligand.

Table 1. *Selected Bond Lengths* [Å] *and Bond Angles* [°] *for* **7a** *and* **8a**

	7a	**8a**
Pd(1)–C(1)	2.086(3)	2.060(4)
Pd(1)–Cl	2.3206(10)	2.3293(14)
Pd–S(1)	2.2508(8)	2.2570(13)
Pd(1)–N(1)	2.171(3)	2.144(4)
S(1)–C(12)	1.818(3)	1.821(5)
N(1)–C(2)	1.269(4)	1.258(6)
C(2)–O(1)	1.343(4)	1.353(7)
C(1)–Pd(1)–N(1)	178.8(1)	175.5(2)
C(1)–Pd(1)–S(1)	85.0(1)	88.2(1)
N(1)–Pd(1)–S(1)	96.1(1)	92.9(1)
C(1)–Pd–(1)–Cl(1)	89.2(1)	89.0(1)
N(1)–Pd(1)–Cl(1)	89.7(1)	90.0(1)
Cl(1)–Pd(1)–S(1)	173.5(1)	177.11(5)
Pd(1)–S(1)–C(5)	107.5(1)	107.1(2)
Pd(1)–S(1)–C(12)	107.6(1)	107.0(2)

The Pd–N distances of 2.171(3) and 2.144(4) Å are long but normal for an sp^2 N-donor opposite to a ligand with a relatively large *trans* influence [21][22]. In *trans*-[PdCl$_2$(oxazole)$_2$] [23], the Pd–N bond (2.016(2) Å), is much shorter. The Pd–S distances of *ca.* 2.25–2.26 Å are rather short, the lowest literature values for (thioether)palladium complexes usually being *ca.* 2.28–2.29 Å [24]. The coordination angles are all rather routine.

Fig. 4 gives a superimposed view of the two structures, **7a** and **8a**. Although the immediate coordination sphere seems to be unaffected by the change from ligand **2a** to **3a**, the relative positions of the glucosyl fragments are quite different. It appears that the Ph substituent at the oxazole ring and the glucosyl substituent in **8a** are somewhat closer in space, than the ^{i}Pr group and the sugar fragment in **7a**. Interestingly, the angle subtended by the two thioether C-atoms and the S-atom closes down from 102.5(2)° in **7a** to 93.7(2)° in **8a**, thereby moving the Ph group closer to the sugar moiety.

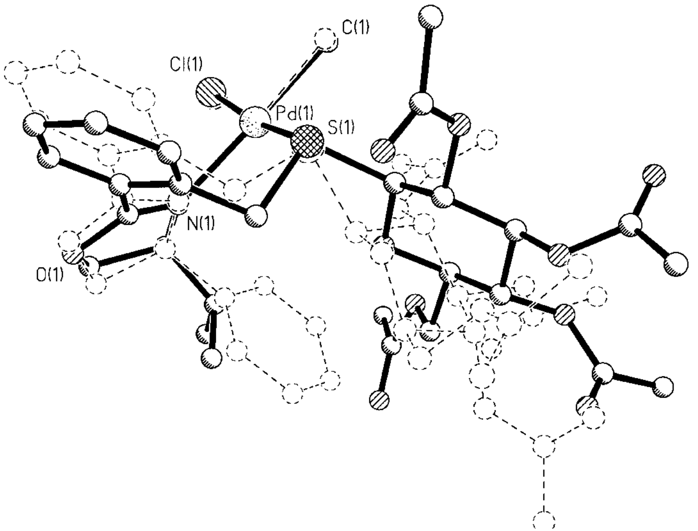


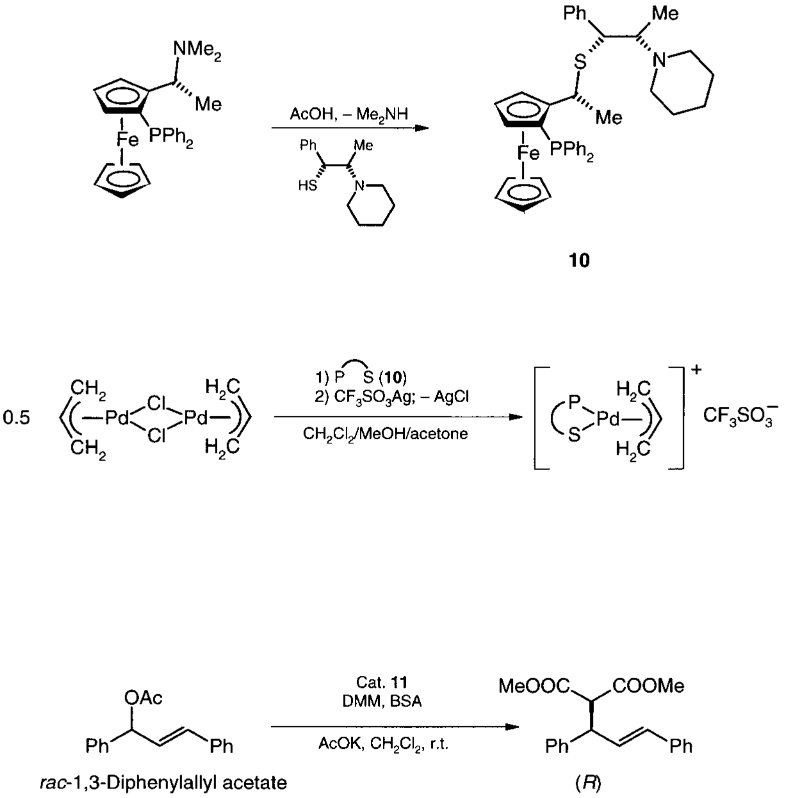
Fig. 4. *Overlay plot of* **7a** (–) *and* **8a** (- - -) *showing the similarity of the coordination sphere and the differences around the glucosyl moiety*

Although we do not suggest that **7a** and **8a** are models for the allyl complexes in our enantioselective-chemistry studies, these diffraction data indicate that both the sugar and dihydrooxazole moieties can be on the same side of the molecule, with the thioether substituent pseudo-axial.

Synthesis and X-Ray Diffraction Studies of Complex **9**. The thioephedrine-like (1*R*,2*S*)-1-phenyl-2-piperidinopropane-1-thiol was prepared according to [25] and treated with the available 1-[1-(dimethylamino)ethyl]-2-(diphenylphosphino)ferrocene to yield the P,S-donating ligand **10** (*Scheme 2*). The corresponding allyl complex **11** was readily available from the chloro-bridged bis(η^3-allyl)di-μ-chlorodipalladium. This P,S-auxiliary **11** was tested in the standard enantioselective allylic alkylation of *rac*-1,3-diphenylallyl acetate (see *Scheme 2*, DMM = dimethyl malonate; BSA = *N*,*O*-bis(trimethylsilyl)acetamide); however, the observed ee, 24.1%, was very modest. A number of other P,S-auxiliaries achieve much higher ee's in this allylic alkylation (see [4][6][9]).

The solid-state structure of **11** was determined by X-ray diffraction methods. *Fig. 5* shows an ORTEP plot for the cation and *Fig. 6* a MacMoMo view of the complex from behind the allyl ligand looking towards ligand **10**. The structure shows no obvious distortions. The relatively large ephedrine-like moiety of ligand **10** is found somewhat remote from the local coordination sphere, presumably for steric reasons. *Table 2* gives

Scheme 2



a list of selected bond lengths and bond angles for **11** which are all of a routine nature [6][9]. As expected, the Pd–C(1) bond, pseudo-*trans* to the P-donor, is somewhat longer.

The most interesting feature in the structure of **11** is the pronounced pseudo-equatorial position of the thioephedrine moiety. The two thioether C-atoms C(4) and C(6) are *ca.* 1.26(1) and 0.73(1) Å from the plane defined by S(1), Pd(1), and P(1) (see *Fig. 5*), with the latter value very definitely what one would expect for a pseudo-equatorial position. In **11**, the angle subtended by the two thioether C-atoms and the S-atom (101.8(6)°) is not very different from that observed in **7a**. Interestingly, the two angles Pd(1)–S(1)–C(4) = 104.1(4)° and Pd(1)–S(1)–C(6) = 114.6(4)° of **11** are quite different, although their average is close to 109°. The four Pd–S–C angles in **7a** and **8a** are all *ca.* 107°. The S(1)–C(6) bond length of **11** is certainly not short (1.90(2) Å); however, the error in this distance is relatively large. Taken together with the large Pd(1)–S(1)–C(6) angle (114.6(4)°), it seems that the cation is distorting slightly to accommodate the 'normally undesirable' equatorial position.

Comment. – These few structures are insufficient for sweeping conclusions; however, it seems fair to note that, even though **7a**, **8a**, and **11** all have large substituents on the thioether donor moiety, the S-atom can accommodate both pseudo-equatorial

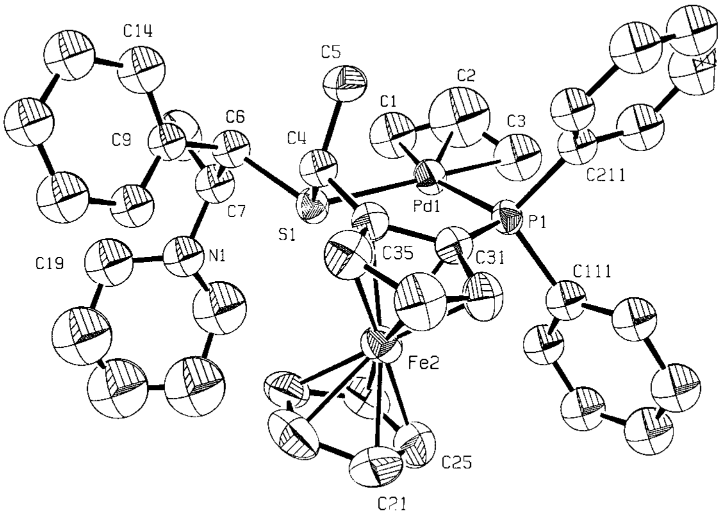


Fig. 5. *ORTEP Plot of* **11**

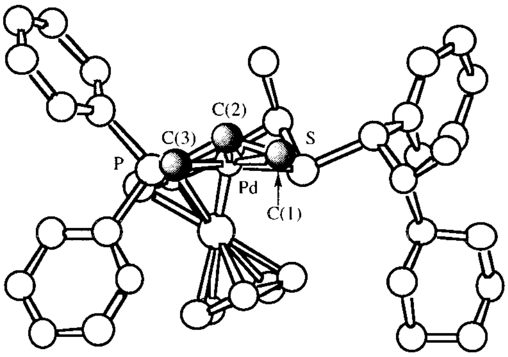


Fig. 6. *MacMoMo view of* **11** *from behind the* (shaded) *allyl ligand.* The thioephedrine moiety is pseudo-equatorial.

Table 2. *Selected Bond Lengths* [Å] *and Bond Angles* [°] *for* **11**

Pd–P	2.308(3)	P–Pd–S	95.7(1)
Pd–S	2.355(3)	S–Pd–C(1)	100.9(5)
Pd–C(1)	2.22(1)	S–Pd–C(3)	166.6(5)
Pd–C(2)	2.15(3)	P–Pd–C(1)	163.4(5)
Pd–C(3)	2.14(2)	P–Pd–C(3)	96.1(6)
C(1)–C(2)	1.30(3)	C(1)–C(2)–C(3)	130(3)
C(2)–C(3)	1.36(4)	C(4)–S(1)–C(6)	101.8(6)
S(1)–C(4)	1.85(1)	C(4)–S(1)–Pd	104.1(4)
S(1)–C(6)	1.90(2)	C(6)–S(1)–Pd	114.6(4)

Angle between the P–Pd–S plane and the allyl plane 123.7°

and pseudo-axial positions without difficulty. Moreover, in the dihydrooxazole complexes **7a** and **8a**, the large organic fragments are relatively close to each another, although a sterically more open alternative is available. We interpret these results to mean that, in solution, there may be only modest barriers to S-inversion¹), and that the shape (chiral pocket) of such thioethers may well be difficult to predict.

Experimental Part

General. The syntheis of the dihydrooxazole ligands **2** and **3** has been described previously [7], and the methylpalladium complexes were all prepared using a modification of the method described by *Vrieze* and coworkers [27]. All reactions were performed under Ar using standard *Schlenk* techniques. Dry and O_2-free solvents were used. IR Spectra: *Perkin-Elmer 882-IR* spectrophotometer; in cm^{-1}. Routine NMR Spectra: *Bruker-DPX-250* and *-300* spectrometers; chemical shifts δ in ppm rel. to $SiMe_4$ (= 0 ppm), coupling constants J in Hz. MS: in m/z (rel. %). Elemental analyses and mass spectroscopic studies were performed at ETHZ.

X-Ray Structure Analyses. Orange crystals of **7a** suitable for X-ray diffraction were obtained by crystallization from CD_2Cl_2/Et_2O while those of **8a** were obtained from CD_2Cl_2/hexane. Air-stable, orange crystals of **11** were obtained from CD_2Cl_2/pentane. The unit-cell constants, space-group determination, and the data collection for both **7a** and **8a** were carried out on a *Siemens-SMART* diffractometer equipped with a *CCD* detector. The space group was unambiguously determined, for both compounds, from the systematic absences. Data were corrected empirically for absorption by using SADABS [28]. The structures were solved by direct methods [29a] and refined by full-matrix least squares on F^2 (the function minimized was $\{[\Sigma w(|1F_o^2| - 1/k|F_c^2|)^2]/[\Sigma w(|F_o^2|^2]\}$ with $w = [\sigma^2(F_o^2) + (\alpha P)^2 + bp]^{-1}$ and $p = [2F_c^2 + \max\ (F_o^2)]/3$. Anisotropic displacement parameters were used for all atoms. The H-atoms were refined using a riding model, while the handedness of the structures were tested by refining *Flack*'s c parameter [30]. For **8a**, atom (05) was refined as a split position with site-occupation factors of 0.433(9) and 0.567(9). Upon convergence, the final *Fourier* difference map showed no significant peaks. All calculations were carried out with the SHELX-96 program [29b].

For **11**, a prismatic crystal was mounted on an *CAD4* diffractometer for the unit-cell and space-group determination and for the data collection. Unit-cell dimensions were obtained by least-squares fit of the 2θ values of 25 reflections ($6.2° \leq \theta \leq 17.2°$). Data were measured with variable scan speed to ensure constant statistical precision on the collected intensities that were corrected for *Lorentz* and polarization factors [31] and empirically for absorption [32] by using the azimuthal (Ψ) scans of three 'high-χ' ($\chi > 84°$) reflections. The structure was solved by *Patterson* and *Fourier* methods and revealed a clathrated solvent molecule (CH_2Cl_2). The refinement was carried out by full-matrix least squares using anisotropic displacement parameters for the heavy atoms (Pd, Fe, P, S), the cyclopentadienyl moieties, and the Cl-atoms of the solvent molecule; all other atoms were treated isotropically.

The contribution of the H-atoms in their idealized positions (C–H 0.95 Å, $B = 1.5 \times B$(C-atom) $Å^2$) was taken into account but not refined. The function minimized was: $[\Sigma w(|F_o| - 1/k|F_c|)^2]$ with $w = [\sigma^2\ (F_o^2) + f^4(F_o^2)]^{-1}$ and $f = 0.03$. Upon convergence, the final *Fourier* difference map showed no significant peaks. The handedness of the structures were tested by refining both enantiomorphs; the coordinates giving the significantly lower R_w [33] factors, were used. All calculations were carried out by using the *Enraf-Nonius* MOLEN package [31]. Final agreement factors and other relevant data for all structures are given in *Table 3*; fractional coordinates and anisotropic displacement parameters for all atoms are deposited in the *Cambridge Crystallographic Data Base* (deposition No. 101583, 101584, and 101585 for **11**, **8a** and **7a**, resp.).

*Chloro({2-[(4*S*)-4,5-dihydro-4-isopropyloxazol-2-yl-κ*N*]phenyl}methyl 2,3,4,6-tetra-*O*-acetyl-1-(thio-κ*S*)-β-*D*-glucopyranoside)methylpalladium(II)* (**7a**). The yellow soln. of {2-[(4*S*]-4,5-dihydro-4-isopropyloxazol-2-yl]phenyl}methyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside (**2a**; 21.0 mg, $3.7 \cdot 10^{-2}$ mmol) and [PdCl(Me)(cod)] (9.8 mg, $3.7 \cdot 10^{-2}$ mmol) in abs. CH_2Cl_2 (1 ml) was stirred for 1 h at r.t. (10-ml *Schlenk* tube). After addition of hexane (2 ml); the solvents were distilled off. The off-white crude solid was treated with a small amount of CH_2Cl_2 and this soln. carefully covered with Et_2O. Storage at −20° gave **7a** (21.3 mg, 80%) as yellow crystals which were suitable for X-ray analysis. M.p. 146° (dec.). $[\alpha]_D = -116.5$ ($c = 1.3$, $CHCl_3$). IR (CsI): 2960*m*, 2935*m*, 1757*s*, 1720*s*, 1636*m*, 1227*s*, 1064s. ¹H-NMR (CD_2Cl_2, 250 MHz): 7.73 (*d*, $J = 8.3$, 1 arom. H); 7.46–7.63 (*m*, 3 arom. H); 5.17–5.49 (*m*, 4 H); 3.96–4.53 (*m*, 9 H); 2.15 (*s*, 3 H); 2.09 (*s*, 3 H);

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¹) It is known that for methyl thioether complexes, the S-inversion barrier is relatively small [26].

Table 3. *Crystallographic Data for Compounds* **7a**, **8a**, *and* **11**

	7a	**8a**	**11** · CH_2Cl_2
Formula	$C_{28}H_{38}ClNO_{10}PdS$	$C_{31}H_{36}ClNO_{10}PdS$	$C_{43}H_{49}Cl_2F_3FeNO_3PPdS_2$
M_r	722.548	756.565	1073.123
Crystal dim. [mm]	0.92 × 0.50 × 0.36	0.40 × 0.40 × 0.01	0.30 × 0.30 × 0.25
Data coll. T [K]	293	293	296
Diffractometer	*Siemens SMART CCD*		*Nonius CAD4*
Crystal system	Orthorhombic	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_1$
a [Å]	13.114(2)	8.180(1)	9.645(2)
b [Å]	13.505(2)	14.939(2)	16.781(10)
c [Å]	18.504(3)	29.204(4)	14.188(7)
β [°]			78.48(3)
V [Å^3]	3277(1)	3569(1)	2250(2)
Z	4	4	2
D_{calc} [g cm^{-3}]	1.464	1.408	1.485
μ [cm^{-1}]	7.64	7.05	9.79
Radiation	MoK_α (graphite monochomated λ 0.7107 Å)		
Measured reflns.	$\pm h, +k, +l$	$\pm h, \pm k, -l$	$\pm h, +k, +l$
θ range [°]	$1.9 < \theta < 28.3$	$1.4 < \theta < 26.5$	$2.5 < \theta < 25.0$
Scan type	ω	ω	$\omega/2\theta$
Time/frame [s]	5	9	
Scan width [°]			1.10 + 0.35 tan θ
Scan width/frame [°]	0.3	0.3	
Max scan speed [°/min]			5.5
Bkgd. time [s]			0.5 × scan-time
No. data coll.	27532	19563	4490
No. of independ. data	8159	7148	4134
No. reflns. in refinement (n_o)	8159	7148	3076 $[F_o\|^2 > 3.0\sigma(\|F\|^2)]$
Transmission coeff.	0.8025 – 0.7036	0.8025 – 0-7036	0.9989 – 0.9596
Decay correction	n.a.	n.a.	1.1658 – 0.9894
No. param. refined (n_v)	379	405	318
Max. param. shift $\Delta p/\sigma$ (at convergence)	< 0.1	< 0.2	< 0.2
R_{av}[a])	0.053	0.061	0.023
R[a])	0.033[b])	0.050[b])	0.063
R_I[a])	0.051[c])	0.104[c])	
R_w[a])	0.073	0.076	0.085

[a]) $R_{av} = \sum_i |F_{o,av} - F_{o,i}| / \sum_i |F_{o,av}|$; $R = \sum(|F_o - (1/k)F_c| / \sum |F_o|$; $R_w = [\sum_w (F_o - (1/k)F_c)^2 / \sum_w F_o|^2]^{1/2}$; $R_I = \sum(F_o^2 - (1/k)F_o^2) / \sum_w |F_o|^2$; [b]) Based on data with $[|F_o|^2 > 2.0\sigma(|F|^2)]$; [c]) All data.

2.05 (2*s*, 6 H); 0.99 (*d*, *J* = 6.8, 6 H); 0.52 (*s*, 3 H). ^{13}C-NMR (CD_2Cl_2, 250 MHz): 170.4 (C=O); 170.1 (C=O); 169.6 (C=O); 169.4 (C=O); 165.6 (C=N); 132.4 (CH); 131.9 (CH); 131.5 (C); 130.2 (CH); 128.8 (CH); 127.3 (C); 83.0 (CH); 77.4 (CH); 72.7 (CH); 70.6 (CH); 69.3 (CH_2O); 67.9 (CH); 67.5 (CH); 61.4 (CH_2); 32.4 (CH_2S); 30.8 (CH); 20.5 (Me); 20.4 (Me); 18.7 (Me); 16.7 (Me); −4.0 (Me). FAB-MS (pos.): 706, 686, 670 (100). Anal. calc. for $C_{28}H_{38}ClNO_{10}PdS$ (722.53): C 46.54, H 5.30, N 1.94; found: C 46.38, H 5.12, N 1.89.

*Chloro({2-[(4*S*)-4,5-dihydro-4-isopropyloxazol-2-yl-κ*N*]phenyl}methyl 2,3,4,6-tetrakis-*O*-(2,2-dimethyl-1-oxopropyl)-1-(thio-κ*S*)-β-*D*-glucopyranoside)methylpalladium(II)* (**7b**). The colorless soln. of {2-[(4*S*)-4,5-dihydro-4-isopropyloxazol-2-yl]phenyl}methyl 2,3,4,6-tetrakis-*O*-(2,2-dimethyl-1-oxopropyl)-1-thio-β-D-glucopyranoside (**2b**; 25.0 mg, $3.4 \cdot 10^{-2}$ mmol) and [PdCl(Me)(cod)] (9.1 mg, $3.4 \cdot 10^{-2}$ mmol) in abs. CH_2Cl_2 (1 ml) was stirred for 1 h at r.t. (10-ml *Schlenk* tube). After addition of hexane (2 ml), the solvents were distilled off. The off-white crude solid was treated with a small amount of CH_2Cl_2 and this soln. carefully covered with hexane. The mixture was then cooled to $-20°$ overnight. The solid which resulted was separated by decanting, washed with hexane, and dried: 21.3 mg (70%) of **7b**. M.p. 130° (dec.). $[\alpha]_D = -92.7$ ($c = 0.9$, $CHCl_3$). IR (CsI): 2966*m*, 2931*m*, 1740*s*, 1633*s*, 1477*m*, 1281*m*, 1168*s*, 1143*s*. ^1H-NMR ($CDCl_3$, 250 MHz): 7.67 (*d*, *J* = 7.6, 1 arom. H); 7.41–7.55 (*m*, 3 arom. H); 4.44–4.50 (*m*, 4 H); 3.92–4.30 (*m*, 6 H); 2.32–2.39 (*m*, 1 H); 1.21 (*s*, 9 H); 1.19 (*s*, 9 H); 1.15 (*s*, 9 H); 1.15 (*s*, 9 H); 1.00 (*d*, *J* = 4.4, 3 H); 0.97 (*d*, *J* = 4.5, 3 H); 0.58 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$, 250 MHz): 177.8 (C=O); 177.7 (C=O); 176.8 (C=O); 176.2 (C=O); 165.6 (C=N); 132.4 (CH); 131.6 (CH); 131.3 (C); 130.4 (CH); 128.9 (CH); 127.3 (C); 83.3 (CH); 77.9 (CH); 72.2 (CH); 70.6 (CH); 69.4 (CH_2O); 67.7 (CH); 66.4 (CH); 61.0 (CH_2); 38.9 (Me_3C); 38.8 (Me_3C); 38.8 (Me_3C); 32.2 (CH_2S); 30.9 (CH); 27.1 (Me_3C); 27.0 (Me_3C); 18.9 (Me); 17.2 (Me); -2.8 (Me). FAB-MS (pos.): 838 (100), 734. Anal. calc. for $C_{40}H_{62}ClNO_{10}PdS$ (890.87): C 53.93, H 7.01, N 1.57; found: C 54.76, H 7.10, N 1.51.

*Chloro({2-[(4*S*)-4,5-dihydro-4-phenyloxazol-2-yl-κ*N*]phenyl}methyl 2,3,4,6-tetra-*O*-acetyl-1-(thio-κ*S*)-β-D-glucopyranoside)methylpalladium(II)* (**8a**). As described for **7b**, from {2-[(4*S*)-4,5-dihydro-4-phenyloxazol-2-yl]phenyl}methyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside (**3a**; 25.0 mg, $4.2 \cdot 10^{-2}$ mmol), [PdClMe(cod)] (11.1 mg, $4.2 \cdot 10^{-2}$ mmol) and abs. CH_2Cl_2 (2 ml): 28.2 mg (90%) of **8a**. Colorless solid. M.p. 153° (dec.). $[\alpha]_D = -41.4$ ($c = 0.9$, $CHCl_3$). IR (CsI): 2928*w*, 1749*s*, 1637*m*, 1372*m*, 1226*s*, 1038*m*. ^1H-NMR ($CDCl_3$, 250 MHz): 7.83 (*d*, *J* = 1.6, 1 arom. H); 7.26–7.80 (*m*, 8 arom. H); 6.41 (*dd*, *J* = 10.2, 5.2, 1 H); 5.00–5.28 (*m*, 3 H); 4.84 (*dd*, *J* = 10.1, 8.9, 1 H); 4.56 (*dd*, *J* = 8.8, 5.2, 1 H); 3.94–4.14 (*m*, 4 H); 3.49–3.54 (*m*, 1 H); 3.32 (*dd*, *J* = 12.7, 2.0, 1 H); 2.14 (*s*, 3 H); 2.10 (*s*, 3 H); 2.03 (*s*, 3 H); 2.00 (*s*, 3 H); 0.54 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$, 250 MHz): 170.3 (C=O); 170.0 (C=O); 169.8 (C=O); 169.4 (C=O); 166.5 (C=N); 141.6 (C); 132.8 (CH); 132.1 (C); 131.9 (CH); 130.9 (CH); 129.0 (CH); 128.3 (CH); 127.3 (CH); 126.5 (C); 83.3 (CH); 77.0 (CH); 75.6 (CH_2O); 73.9 (CH); 68.8 (CH); 68.1 (CH); 67.2 (CH); 60.9 (CH_2S); 33.7 (CH_2); 20.9 (Me_3); 20.8 (Me); 20.5 (Me); 20.5 (Me); -2.9 (Me). FAB-MS (pos.): 704 (100), 600. Anal. calc. for $C_{31}H_{36}ClNO_{10}PdS$ (756.56): C 49.21, H 4.80, N 1.85; found: C 48.63, H 4.70, N 1.71.

*Chloro({2-[(4*S*)-4,5-dihydro-4-phenyloxazol-2-yl-κ*N*]phenyl}methyl 3,4,5,6-tetrakis-*O*-(2,2-dimethyl-1-oxopropyl)-1-(thio-κ*S*)-β-D-glucopyranoside)methylpalladium(II)* (**8b**). As described for **7b**, from {2-[(4*S*)-4,5-dihydro-4-phenyloxazol-2-yl]phenyl}methyl 2,3,4,6-tetrakis-*O*-(2,2-dimethyl-1-oxopropyl)-1-thio-β-D-glucopyranoside (**3b**; 25.6 mg, $3.3 \cdot 10^{-2}$ mmol), [PdClMe(cod)] (8.8 mg, $3.3 \cdot 10^{-2}$ mmol) and abs. CH_2Cl_2 (2 ml): 23.4 mg (76%) of **8b**. Off-white solid. M.p. 105° (dec.). $[\alpha]_D = -24.4$ ($c = 0.4$, $CHCl_3$). IR (CsI): 2869*m*, 2932*m*, 1740*s*, 1621*m*, 1280*m*, 1143*s*. ^1H-NMR ($CDCl_3$, 250 MHz): 7.79 (*d*, *J* = 7.5, 1 arom. H); 7.28–7.59 (*m*, 8 arom. H); 5.89–6.54 (*m*, 1 H); 5.28–5.35 (*m*, 2 H); 5.08–5.15 (*m*, 1 H); 4.84 (*dd*, *J* = 10.1, 8.9, 1 H); 4.52 (*dd*, *J* = 8.6, 5.9, 1 H); 4.31 (*d*, *J* = 9.5, 1 H); 3.94–4.03 (*m*, 2 H); 3.65 (*d*, *J* = 9.9, 1 H); 3.44 (*d*, *J* = 12.7, 1 H); 2.46–2.65 (*m*, 1 H); 1.27 (*s*), 1.15 (*s*), 1.12 (*s*), 0.54 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$, 250 MHz): 177.6 (2 C=O); 176.7 (C=O); 176.1 (C=O); 166.5 (C=N); 141.3 (C); 132.7 (CH); 132.0 (C); 131.9 (CH); 130.8 (CH); 128.9 (CH); 128.8 (CH); 128.3 (CH); 127.2 (CH); 126.6 (C); 123.8 (CH); 100.8 (CH); 82.8 (CH); 77.7 (CH); 75.4 (CH_2); 72.2 (CH); 68.9 (CH); 67.6 (CH); 66.4 (CH); 60.8 (CH_2); 38.9 (Me_3C); 38.8 (Me_3C); 38.7 (Me_3C); 32.5 (Me_3C); 31.0 (CH_2); 27.3 (Me_3C); 27.1 (Me_3C); 27.0 (Me_3C); -2.8 (Me). FAB-MS (pos.): 872 (100), 769. Anal. calc. for $C_{43}H_{60}ClNO_{10}PdS$ (924.87): C 55.84, H 6.54, N 1.51; found: C 54.65, H 6.48, N 1.42.

*Chloro((4*S*)-2-{2-[(cyclohexylthio-κ*S*)methyl]phenyl}-4,5-dihydro-4-isopropyloxazole-κ*N*)methylpalladium(II)* (**9**). As described for **7b**, from (4*S*)-2-{2-[(cyclohexylthio)methyl]phenyl}-4,5-dihydro-4-isopropyloxazole (27.4 mg, $10.3 \cdot 10^{-2}$ mmol), [PdClMe(cod)] (27.4 mg, $10.3 \cdot 10^{-2}$ mmol) and abs. CH_2Cl_2 (3 ml): 28.3 mg (58%) of **9**; after precipitation from CH_2Cl_2/pentane. M.p. > 140° (dec.). $[\alpha]_D = -58.5$ ($c = 1.1$, $CHCl_3$). IR (CsI): 2928*s*, 1627*s*, 1251*m*, 1044*m*, 1026*m*. ^1H-NMR ($CDCl_3$, 250 MHz): 7.70 (*d*, *J* = 7.4, 1.3, 1 arom. H); 7.37–7.57 (*m*, 4 arom. H); 5.21–5.30 (*m*, 1 H); 4.47 (*dd*, *J* = 10.4, 8.8, 1 H); 4.28 (*dd*, *J* = 8.7, 6.8, 1 H); 2.86–2.95 (*m*, 1 H); 3.83 (*s*, 2 H); 2.28–2.50 (*m*, 3 H); 1.55–1.94 (*m*, 5 H); 1.14–1.48 (*m*, 3 H); 1.05 (*d*, *J* = 7.0, 3 H); 0.95 (*d*, *J* = 6.8, 3 H); 0.61 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$, 250 MHz): 165.7 (C=N); 133.0 (CH); 132.0 (C); 131.2 (CH); 130.6 (CH); 128.6 (CH); 127.2 (C); 70.6 (CH); 69.2 (CH_2O); 52.0 (CH); 35.0 (CH_2); 33.4 (CH_2); 33.2 (CH_2); 30.7 (CH); 26.8 (CH_2); 25.2 (CH_2); 19.4 (Me); 16.5 (Me); -4.4 (Me). EI-MS: 317, 234 (100), 203. Anal. calc. for $C_{20}H_{30}ClNOPdS$ (474.40): C 50.64, H 6.37, N 2.95; found: C 49.73, H 6.17, N 2.83.

*(*S*)-1-(Diphenylphosphino)-2-((1*R*)-1-{[(1*R*,2*S*)-1-phenyl-2-(piperidin-1-yl)propyl]thio}ethyl)ferrocene* (**10**). To a soln. of (1*R*,2*S*)-1-phenyl-2-(piperidin-1-yl)propane-1-thiol (48.0 mg, 0.204 mmol, 1.5 equiv.) in Ar-degassed AcOH (1 ml; 10-ml *Schlenk* vessel) (*S*)-1-[(*R*)-1-(dimethylamino)ethyl]-2-(diphenylphosphino)ferrocene (60.0 mg, 0.136 mmol) was added, followed by additional AcOH (2 ml). The resulting soln. was stirred at 253 K for 2 h. After cooling to r.t., the soln. was slowly poured onto sat. Na_2CO_3 soln. the mixture extracted with CH_2Cl_2 (3 ×), the org. phase washed with H_2O, dried ($MgSO_4$), and evaporated, and the residue chromatographed (SiO_2, hexane/AcOEt 9:1, 2% Et_3N; R_f 0.46): 59.0 mg (69%) of **10**. M.p. 50°. $[\alpha]_D = -278.3$ ($c = 0.9$, $CHCl_3$). ^1H-NMR ($CDCl_3$, 500 MHz): 7.06–7.56 (*m*, 15 arom. H); 4.43 (*s*, 1 H(cp)); 4.32

(*s*, 1 H(Cp)); 3.95 (*d*, $J = 6.7$, 1 H); 3.86 (*s*, 5 H(Cp)); 3.66–3.68 (*m*, MeC*H*N); 2.49–2.55 (*m*, 1 H); 2.38 (br., 2 H); 2.26 (br., 2 H); 1.60 (*d*, $J = 6.6$, Me); 1.28 (br., 7 H); 1.23 (*d*, $J = 5.2$, PhC*H*S); 1.10 (*d*, $J = 6.6$, Me). ^{31}P-NMR ($CDCl_3$, 500 MHz): –24.3. ^{13}C-NMR ($CDCl_3$, 500 MHz): 141.8 (C); 140.9 (C); 140.8 (C); 138.6 (C); 138.5 (C); 135.7 (CH); 135.5 (CH); 132.8 (CH); 132.7 (CH); 129.2 (CH); 129.0 (CH); 128.9 (CH); 128.0 (CH); 127.9 (CH); 127.7 (CH); 127.6 (CH); 127.5 (CH); 127.5 (CH); 127.4 (CH); 126.2 (CH); 97.5 (*d*, $J = 26.6$, CH); 74.7 (CH); 71.3 (CH); 69.5 (CH(Cp)); 68.9 (CH); 65.2 (CH); 53.3 (CH); 50.4 (CH_2); 50.5 (CH_2); 36.2 (CH); 26.5 (CH_2); 24.9 (CH_2); 24.8 (CH_2); 21.9 (Me); 12.2 (Me). IR (Csl): 2929*s*, 1448*s*, 1164*s*, 1107*s*. FAB-MS (pos.): 632 ($[M+1]^+$), 429, 397 (100). Anal. calc. for $C_{38}H_{42}FeNPS$ (631.64): C 72.26, H 6.70, N 2.22; found: C 72.04, H 6.83, N 2.39.

[(S)-1-(Diphenylphosphino-κP)-2-((1R)-1-{[(1R,2S)-1-phenyl-2-(piperidin-1-yl)propyl]thio-κS}ethyl)-ferrocene](η^3-prop-2-enyl)palladium Trifluoromethanesulfonate (**11**). To a soln. of **10** (20.1 mg, $3.18 \cdot 10^{-2}$ mmol) in CH_2Cl_2 (2 ml), di-μ-chlorodi(η^3-prop-2-enyl)dipalladium (5.8 mg, $1.59 - 10^{-2}$ mmol, 0.5 equiv.) and additional CH_2Cl_2 (0.5 ml) were added. After dropwise addition of AgOTf (8.2 mg, $3.18 \cdot 10^{-2}$ mmol) in MeOH, the cloudy suspension was stirred in the dark (Al-foil cover) for 1 h. Filtration through *Celite* and evaporation gave 26.3 mg (89%) of **11**, after recrystallization from CH_2Cl_2 and Et_2O. Crystals suitable for diffraction were obtained from CH_2Cl_2/pentane at r.t. M.p. 140° (dec.). $[\alpha]_D = -203.6$ ($c = 1.0$, $CHCl_3$). IR (Csl): 2931*m*, 1479*w*, 1270*s*, 1148*m*, 1029*s*. ^{1}H-NMR (CD_2Cl_2, 250 MHz): 7.33–7.85 (*m*, 15 arom. H); 7.08–7.17 (*m*, 2 H (η^3-C_3H_5)); 5.84 (*ddd*, $J = 10.4$, 1 H (η^3-C_3H_5)); 4.48–4.51 (*m*, 2 H); 4.23 (br., 3 H); 3.95 (*s*, 5 H(Cp)); 3.60–3.87 (*m*, 1 H); 3.51–3.60 (*m*, 1 H); 3.24–3.49 (*m*, 1 H); 3.10–3.16 (*m*, 1 H); 2.39 (br., 3 H); 1.24–1.66 (*m*, 6 H); 1.12 (*d*, $J = 6.9$, 3 H). ^{31}P-NMR (CD_2Cl_2, 250 MHz): 10.6 (br.). ^{13}C-NMR (CD_2Cl_2, 250 MHz): 134.5, 134.2, 133.7, 132.1, 131.0, 130.8, 130.4, 130.1, 129.6, 128.9, 128.7, 128.5, 128.4, 128.0, 122.1, 72.8, 72.6, 71.5, 71.3, 70.8 (CH(Cp)); 70.4, 70.3, 62.7, 61.6, 42.3, 27.2, 26.1 (CH_2); 24.0 (CH_2); 12.7. FAB-MS (pos.): 778 ($[M - CF_3SO_3]^+$). Anal. calc. for $C_{42}H_{49}F_3FeNO_9PPdS_2$ (946.21) (+complex +H_2O): C 53.31, H 5.17, N 1.47; found: C 52.32, H 5.12, N 2.01.

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