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# Coordination chemistry and X-ray studies with novel sterically constrained diphosphonite ligands

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The coordination of two novel, sterically constrained diphosphonite ligands towards different palladium, platinum and rhodium precursors has been studied. Complexes of this hitherto unexplored class of diphosphonites, based on rigid xanthene backbones, have been characterized by X-ray crystallography as well as by NMR and IR spectroscopy. A short and concise overview is given on the scarce literature on phosphonite related chemistry. Structural differences in the complexes obtained due to steric influences of the ligands are discussed. Ligand **1**, bearing 2-*tert*-butylphenolate groups, led to orthometallated complexes *cis*-[MCl{**1**-$\kappa^3$*C*,*P*,*P*}] (M = Pd, Pt) and to *trans*-[RhCl(CO)(**1**)]. These complexes were compared with those formed with ligand **2**, bearing 2,2′-dioxo-3,3′-di-*tert*-butyl-5,5′-dimethoxy-1,1′-biphenyl groups, preventing orthometallation. The complexes *trans*-{$PdCl_2$(**2**)], *cis*-[$PtCl_2$(**2**)] and *trans*-[RhCl(CO)(**2**)] were structurally characterized. Valuable data were collected on chemical shifts, Pt–P coupling constants, as well as CO stretch frequencies of Rh–CO complexes as important tools for structural characterization of such complexes.

## Introduction

Progress and development of homogeneous catalysis is very much related and dependent on the synthesis and availability of ligands. In recent years a number of powerful new ligand classes have emerged, most of which are chelating phosphorus-based compounds[1] such as phosphines[2] or phosphites.[3] Phosphonites however have been widely neglected and only very recently a few examples were reported. Reetz *et al.* used several backbones, amongst others ferrocene, to prepare chelating diphosphonites and used them in asymmetric Rh-catalyzed hydrogenations of the typical benchmark substrates[4] as well as in conjugate addition of aryl boronic acids.[5] Zanotti-Gerosa *et al.* also described diphosphonites but they used the para-cyclophane backbone and performed hydrogenation reactions.[6] Pringle andco-workers used binaphthol-derived mono- and bidentate phosphonites for conjugate additions of diethyl zinc to enones.[7] The same monophosphonites were used by Claver and Pringle in asymmetric hydrogenations.[8] Scharf and co-workers used the monodentate phosphonites based on TADDOL as the chiral auxiliary for the rhodum-catalyzed hydrosilylation of ketones.[9] Börner and co-workers have published on the use of both monodentate and bidentate phosphonite ligands in the hydroformylation of alkenes, with varying results.[10] Finally the Reetz group, in line with their earlier work, prepared phosphite–phosphonite bidentate ligands but no applications in catalysis were reported so far.[11]

During recent years xanthene-based chelating ligands have been introduced and extensively used in transition metal catalyzed C–C bond forming reactions.[12] These backbones provide a unique combination of rigidity and P–P distance in such a way, that specific, large bite-angle coordination modes are supported. Additionally interaction of the central oxygen atom in the backbone with a metal atom coordinated is possible under certain conditions.[13] We have already shown the first catalytic applicability of a chiral diphosphonite derived from such a xanthene backbone, in the asymmetric hydrocyanation of styrene.[14a] We have recently also studied the asymmetric hydroformylation of styrene, with either rhodium[14b] or platinum/tin[14c] as the transition metal system of choice.

We report here on the coordination behavior of a new class of diphosphonite ligands based on such xanthene backbones, combining large bite-angle and π-acceptor properties. Those ligands have recently been developed in our group. Some of those new ligands have turned out to give very active rhodium catalysts for the hydroformylation of both terminal as well as internal alkenes.[15] Focussing on two typical representatives of these new diphosphonites based on 9,9-dimethylxanthene and 2-*tert*-butylphenol (**1**) as well as 2,2′-dihydroxy-3,3′-bis(*tert*-butyl)-5,5′-dimethoxy-1,1′-biphenyl (**2**), respectively (see Fig. 1), we studied the complexation behavior with the platinum group metals.

## Results and discussion

### Synthesis of ligands and determination of the molecular structure of compound 1

The diphosphonite ligands were prepared using a straightforward synthetic route.[14–16] Starting from the commercially available compound 9,9-dimethylxanthene and the appropriate phenols two ligands were prepared (Scheme 1). As an intermediate product the bis-diethylamidophosphonitoxanthene is prepared, *via* a known procedure.[16] By substitution using two equivalents of the appropriate phenol the phosphonite-group is formed under evolution of diethylamine. Tetrazole is used as a catalyst for this reaction, that was carried out in a high-boiling polar, aprotic solvent. Work up to obtain the ligands mainly comprized of removing solvents *in vacuo* and crystallization of the product using layering techniques.

From a crystallization mixture meant to obtain a new metal complex, we obtained single crystals, suitable for X-ray analysis and the molecular structure, displayed in Fig. 2, turned out to

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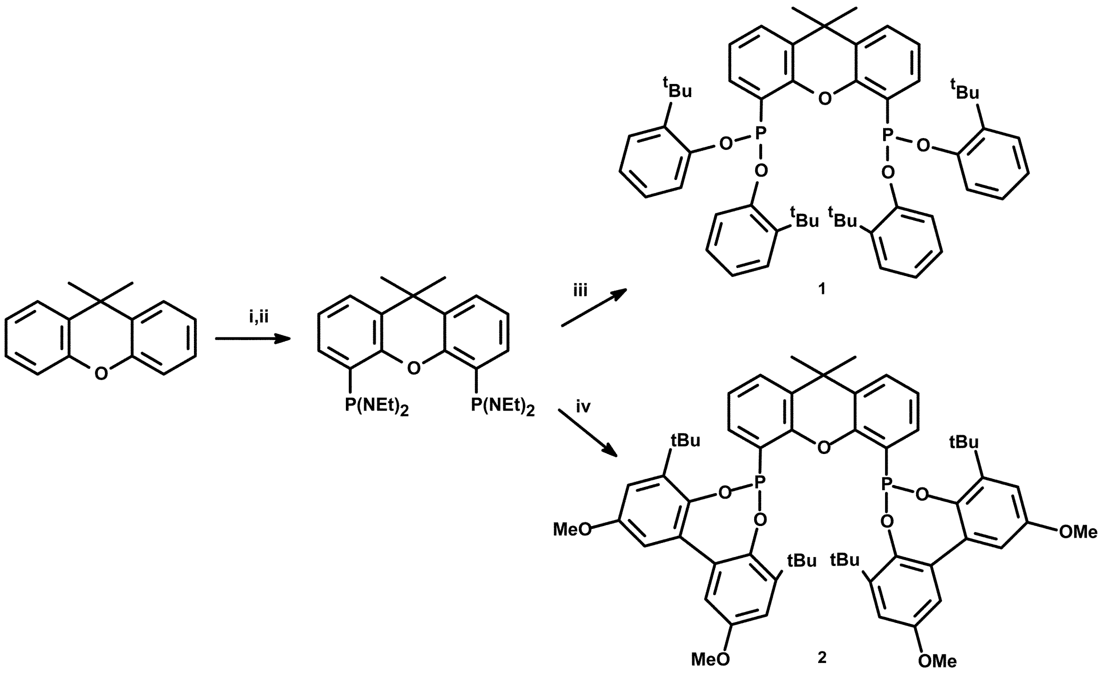


**Scheme 1** Synthetic methodology for ligands **1** and **2**: (i) *n*-BuLi, TMEDA, $Et_2O$, −40 °C, 16 h; (ii) $ClP(NEt_2)_2$, pentane, −60 °C, 16 h; (iii) 2-*tert*-butylphenol (6 mol eq.), diglyme, tetrazole, 4 days reflux; (iv) 2,2′-dihydroxy-3,3′-bis(*tert*-butyl)-5,5′-dimethoxy-1,1′-biphenyl (6 mol eq.), diglyme, tetrazole, 5 days reflux.

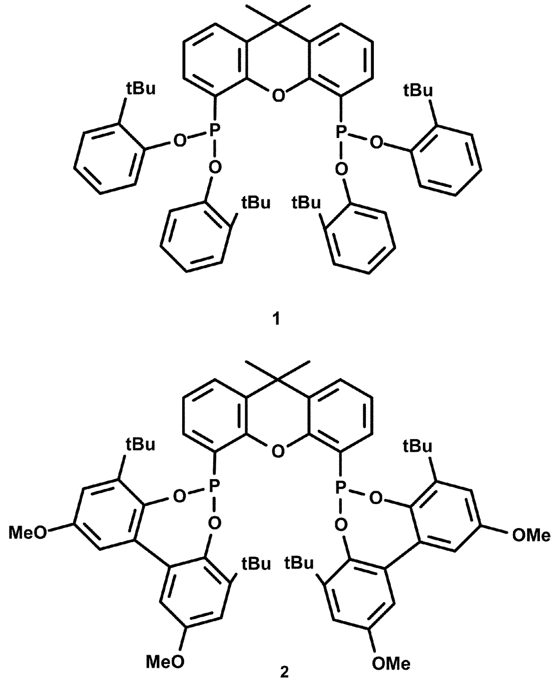


**Fig. 1**

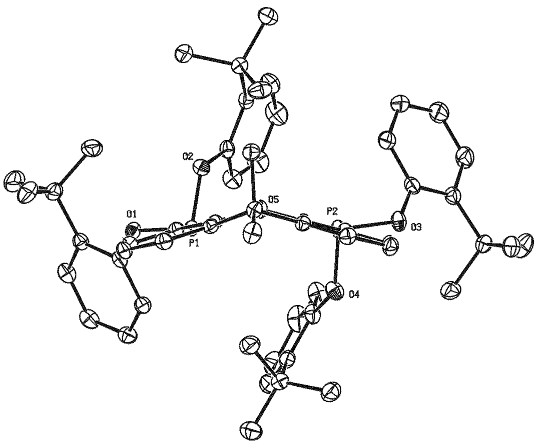


**Fig. 2** Displacement ellipsoid plot of the triclinic polymorph of compound **1**, top view. Displacement ellipsoids are drawn at the 50% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): $P_1$–$O_1$ 1.6531(9), $P_1$–$O_2$ 1.6516(10), $P_2$–$O_3$ 1.6616(9), $P_2$–$O_4$ 1.6454(10), $P_1$–$C_{21}$ 1.8140(12), $P_2$–$C_{34}$ 1.8268(12), $O_5$–$C_{26}$ 1.3818(14), $O_5$–$C_{35}$ 1.3828(14), $P_1$–$P_2$ 3.9261(5); $O_1$–$P_1$–$O_2$ 99.31(5), $O_3$–$P_2$–$O_4$ 100.04(5), $O_1$–$P_1$–$C_{21}$ 95.97(5), $O_2$–$P_1$–$C_{21}$ 97.76(5), $O_3$–$P_2$–$C_{34}$ 97.13(5), $O_4$–$P_2$–$C_{34}$ 93.17(5), $C_{26}$–$O_5$–$C_{35}$ 116.77(9), $C_{25}$–$C_{27}$–$C_{30}$ 107.89(9).

be that of compound **1**. We have also obtained a monoclinic polymorph of the same compound, which will be reported elsewhere.[16] From the structure discussed here, it is evident that due to the steric bulk there is no π-stacking as in the case of the diphenylphosphine derivatives,[12] but that the phenol groups are oriented anti-parallel. Comparing both polymorphs of the same compound there are only minute deviations in most bond angles and lengths. However, in the structure depicted in Fig. 2, the xanthene backbone is bent, so that the dihedral angle between the two aromatic rings is 144°. This leads to an intramolecular $P_1$–$P_2$ distance of 3.9261(5) Å. This behavior is believed to originate solely in the solid state, while in solution the flat backbone is most likely the energetically favored conformation. The phosphorus-oxygen bonds are all around 1.65 Å ($P_1$–$O_1$ 1.6531(9) Å, $P_1$–$O_2$ 1.6516(10) Å, $P_2$–$O_3$ 1.6616(9) Å and $P_2$–$O_4$ 1.6454(10) Å), comparable to bond lengths in known phosphite crystal structures.

To the best of our knowledge, only four papers have appeared on the X-ray structure determination of palladium phosphonite species. Agbossou *et al.*, have characterized a *cis*-dichloro(dioxazaphosphocine)palladium complex as well as a Pd-allyl complex with an aminophosphonite.[17] Braunstein and co-workers synthesized monophosphonite-bis-oxazoline compounds that acted as tridentate ligands in Pd-complexes.[18] The group of Schmutzler reported on the preparation of the diphosphonite 1,8-bis[(dimethoxy)phosphino]naphthalene and its corresponding Pd-complex.[19]

## Coordination of ligands 1 and 2 to palladium

We have performed *in situ* $^{31}P\{^1H\}$ and $^1H$ NMR measurements in order to understand the behavior of ligands **1** and **2** towards palladium using various precursors. It turns out that the difference in steric bulk between these ligands has a big influence on their coordination behavior and on the rate of complexation. With ligand **1** and $PdCl_2$(cod) as a precursor, conversion was only 40% after stirring overnight at room temperature. When the same reaction is carried out at 75 °C, a singlet is observed at $\delta$ 109.7 ppm in the $^{31}P$ NMR spectrum for complex **3**. Attempts to obtain single crystals, suitable for X-ray analysis failed, so in order to be able to determine whether *cis*- or *trans*-coordination was preferred, $[PdCl(CH_3)(cod)]$ was used as the precursor. The complexation was very slow at room temperature, but proceeded readily at 60 °C. For this complex **4** a singlet was found at $\delta$ 123.1 ppm in the $^{31}P$ NMR, while the $^1H$ NMR spectrum showed a clear triplet, at $\delta$ 0.80 ppm, for the methyl-ligand (Fig. 3). Both findings indicate that the desired complex $[PdCl(CH_3)(\mathbf{1})]$ is formed, with a preferred *trans* coordination of the ligand. This might imply that in complex **3** the ligand will also adopt the *trans*-configuration.

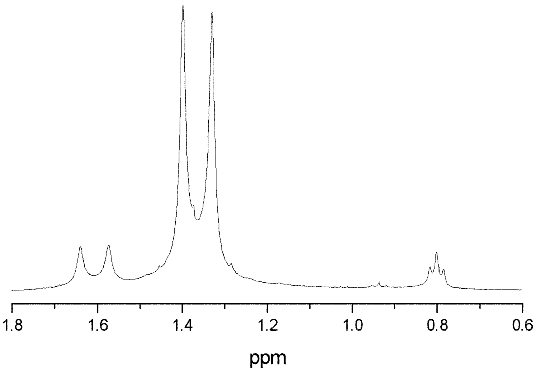
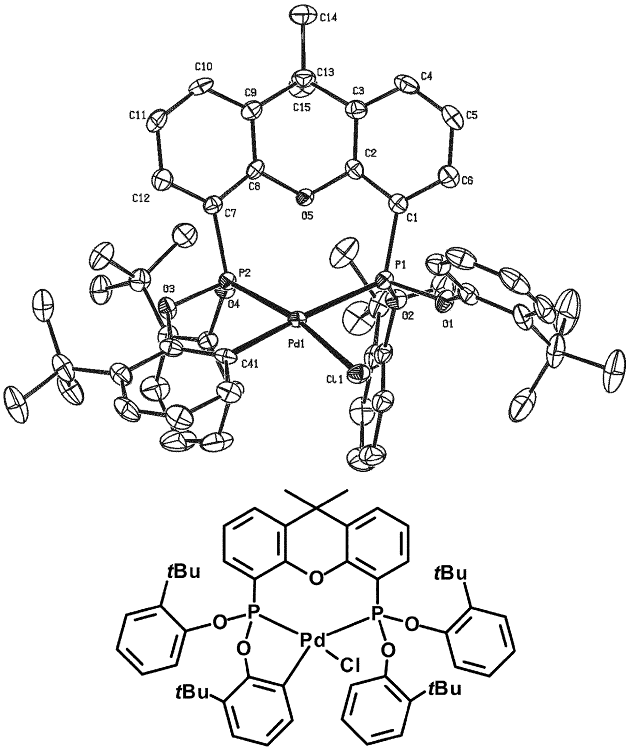


**Fig. 3** $^1H$ NMR spectrum of complex **4**, *trans*-$[PdCl(CH_3)(\mathbf{1})]$, showing both the methyl groups of the xanthene backbone (1), the *tert*-butyl groups of the phosphonite units (2) and the triplet of the methyl ligand (3).

In the $^1H$ NMR spectrum of complex **4** both the methyl-groups in the xanthene backbone as well as the *tert*-butyl groups on the phenol rings of the phosphonite moieties appear as two singlets, since they are chemically inequivalent. This is due to the conformation of the xanthene backbone, which is bent.[16] Single crystals, suitable for X-ray analysis, were obtained, albeit in low yield, by layering with $CH_2Cl_2$–$CH_3CN$. The molecular structure is depicted in Fig. 4.

Much to our surprise the structure corresponds to an ortho-metallated species, with one chlorine atom still bound to the palladium. The methyl group has been replaced by an aryl group, coordinated to the palladium center, leading to [PdCl-{**1**-κ$^3$*C*,*P*,*P*}], complex **4A**. The spectroscopic data of the complex originally formed in solution, however, do not fit with the presence of this complex. Its formation is therefore most likely due to slow activation of the Pd–$CH_3$ bond in the aprotic crystallization solvent $CH_2Cl_2$, leading to the formation of methane. To confirm this, degradation of the initial complex in $CDCl_3$ was followed with time. After one week, two doublets were clearly present in the $^{31}P$ NMR spectrum, thereby confirming the slow conversion of the $[PdCl(CH_3)(\mathbf{1})]$, complex **4**, in the mother-liquor, into complex **4A**, identified by X-ray analysis (Fig. 4)

The geometry around the palladium atom in complex **4A** is distorted square planar, with the two phosphorus atoms coordinating in a *cis*-fashion to the palladium center. The bite angle of the ligand, in this conformation, $P_1$–Pd–$P_2$, is found to be only 103.91(3)°, while the Cl–Pd–$C_{41}$ angle is 91.11(7)°. The Cl–Pd–$P_2$ angle is small at only 169.06(3)° instead of the 180° in case of a true *trans*-configuration. The two Pd–P bond lengths differ quite a lot as Pd–$P_1$ is 2.4416(8) Å while Pd–$P_2$ is only 2.2131(7) Å. This stems from the orthometallation of one of the substituents on the $P_2$ moiety, leading to elongation of the Pd–$P_1$ bond. The carbon–palladium bond length Pd–$C_{41}$ is 2.073(3) Å. This agrees well with other (orthometallated) Pd-aryl complexes.[20,21] Remarkably, the metal atom is positioned relatively far outside of the ligand plane, creating a dihedral angle between the $P_1$–$O_5$–$P_2$ plane and the $Cl_1$–Pd–$C_{41}$ plane of 155°. Alternatively, the dihedral angle between the plane $P_1$–$P_2$–$C_1$ and the plane $Cl_1$–Pd–$C_{41}$ is calculated to be 115.6° (Fig. 5).



**4A**

**Fig. 4** Displacement ellipsoid plot of complex **4A**, [PdCl{**1**-κ$^3$*C*,*P*,*P*}]. The ellipsoids are drawn at the 50% probability level. All hydrogens atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Pd–$P_1$ 2.4416(8), Pd–$P_2$ 2.2131(7), Pd–Cl,2.3416(7), Pd–$C_{41}$ 2.073(3), $P_1$–$O_1$ 1.6208(19), $P_1$–$O_2$ 1.6119(17), $P_1$–$C_1$ 1.826(3), $P_2$–$O_3$ 1.6126(18), $P_2$–$O_4$ 1.6106(17) $P_2$–$C_7$ 1.809(2), $O_5$–$C_2$ 1.387(3), $O_5$–$C_8$ 1.395(3), Pd–$O_1$ 3.5308(16), $P_1$–$P_2$ 3.6685(11); $Cl_1$–Pd–$C_{41}$ 91.11(7); $P_1$–Pd–$P_2$ 103.91(3), Cl–Pd–$P_1$ 85.93(2), $Cl_1$–Pd–$P_2$ 169.06(3), $P_1$–Pd–$C_{41}$ 176.82(7), $P_2$–Pd–$C_{41}$ 78.94(7), $O_1$–$P_1$–$O_2$ 97.54(9), $O_3$–$P_2$–$O_4$ 101.82(9), Pd–$P_1$–$O_1$ 117.08(7), Pd–$P_1$–$O_2$ 114.94(8), Pd–$P_2$–$O_3$,108.79(7), Pd–$P_2$–$O_4$ 121.02(7), Pd–$P_1$–$C_1$ 123.85(8), Pd–$P_2$–$C_7$ 121.84(8), $C_2$–$O_5$–$C_8$ 112.49(17), $C_3$–$C_{13}$–$C_9$ 106.1(2), $O_1$–$P_1$–$C_1$ 100.61(11), $O_2$–$P_1$–$C_1$ 98.22(10), $O_3$–$P_2$–$C_7$ 102.67(10), $O_4$–$P_2$–$C_7$ 97.68(9).

The dihedral angle of the aromatic rings in the backbone was calculated to be 100.34°, meaning a large deformation from the situation in the free ligand in order to accompany this atypical conformation. The constrained *cis*-position of the two phosphorus atoms is also reflected in a decrease of the P–P distance from 3.9261(5) Å in the free ligand, to 3.6685(11) Å in complex **4A**.

With ligand **2**, no unwanted side-reaction to any ortho-palladated complex can occur, since all orthopositions are occupied by *tert*-butyl groups. The reaction of **2** with $PdCl_2$-(cod) proceeded smoothly at room temperature overnight (Scheme 2).

A singlet was found at $\delta$ 136.5 ppm in the $^{31}P$ NMR spectrum. This chemical shift indicates a *trans*-coordination of the diphosphonite ligand, since the chemical shift difference to the free ligand is in the same range as that seen with ligand **1**. We were able to grow single crystals suitable for a crystallographic study from a $CH_2Cl_2$–$CH_3CN$ solution of complex **5**. The molecular structure is depicted in Fig. 6.

Clearly, the *trans* configuration is preserved in solid state as well, with a square-planar geometry around the palladium atom of complex **5**. There is significant distortion, possibly towards a square-pyrimidal configuation. The molecule possesses a plane of symmetry. The $P_1$–Pd–$P_2$ angle is only

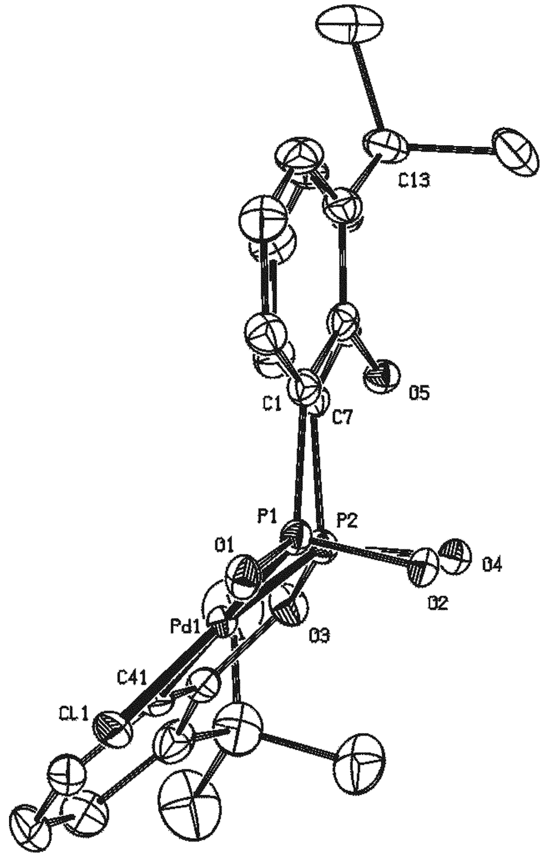
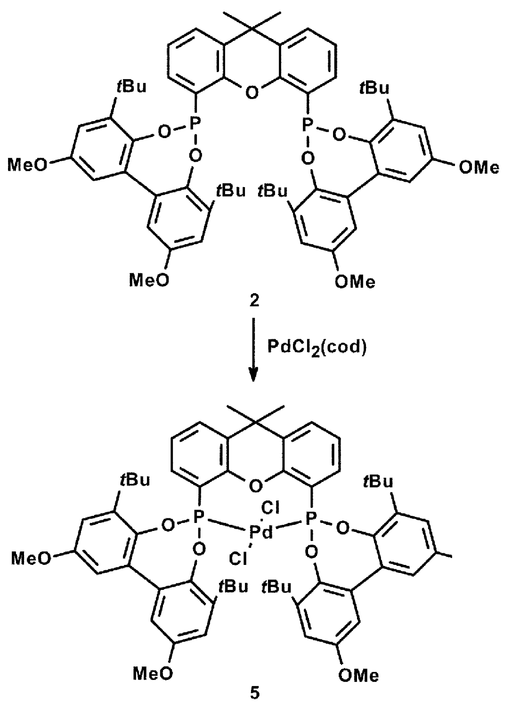


**Fig. 5** Side view on the metallacycle of complex **4A**, showing the non-planarity between the $P_1$–Pd–$P_2$ plane and the $P_1$–$C_1$–$C_5$–$P_2$ ligand plane.



**Scheme 2**

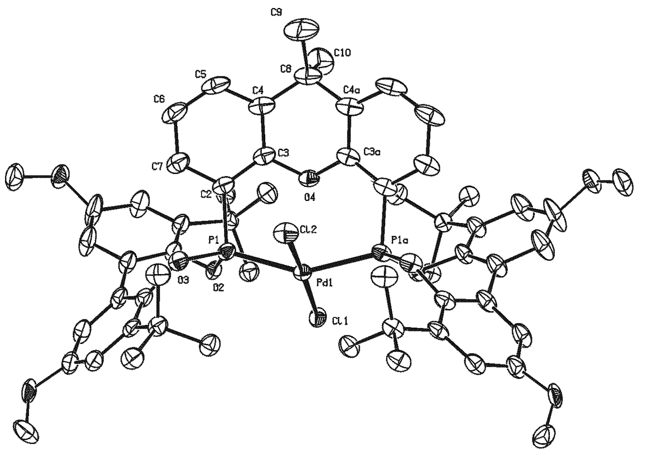


**Fig. 6** Displacement ellipsoid plot of complex **5**, *trans*-[$PdCl_2$(**2**)]. The ellipsoids are drawn at the 50% probability level. All hydrogens atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (°): Pd–$P_1$ 2.2767(6), Pd–$Cl_1$ 2.2823(8), Pd–$Cl_2$ 2.3262(10), $P_1$–$O_2$ 1.6048(18), $P_1$–$O_3$ 1.6114(19), $P_1$–$C_2$ 1.823(2), Pd–$O_4$ 2.694(2), $P_1$–$P_2$ 4.3995(9); $P_1$–Pd–$P_1$a 150.12(3), $Cl_1$–Pd–$Cl_2$ 174.79(4), $Cl_1$–Pd–$P_1$ 93.78(2), $Cl_2$–Pd–$P_1$ 87.53(2) Pd–$P_1$–$O_2$ 113.34(7), Pd–$P_1$–$O_3$ 124.30(7), Pd–$P_1$–$C_2$ 107.21(9), $O_2$–$P_1$–$O_3$ 104.80(9), $O_2$–$P_1$–$C_2$ 108.42(11), $O_3$–$P_1$–$C_2$ 96.86(11), $C_3$–$O_4$–$C_{3a}$ 118.4(2), $C_4$–$C_8$–$C_{4a}$ 109.5(3).

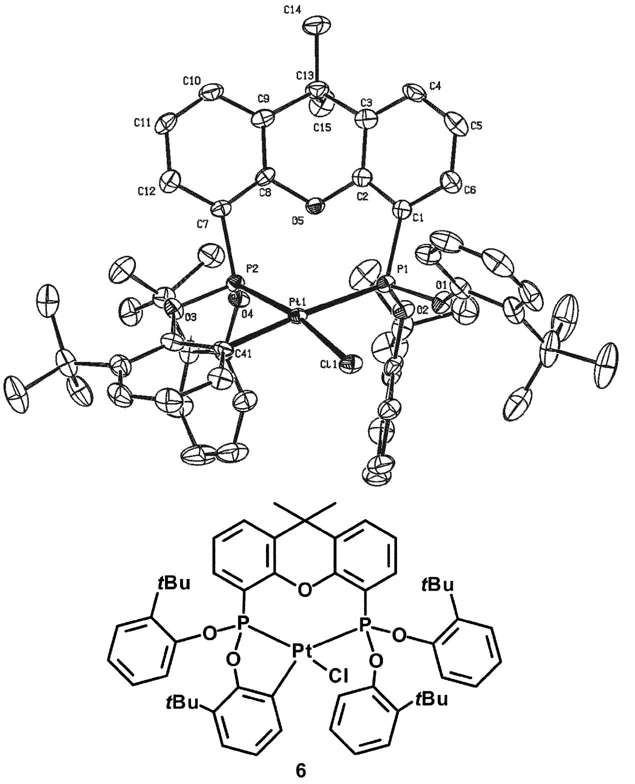
150.12(3)°, while the $Cl_1$–Pd–$Cl_2$ angle is nearly straight at 174.79(4)°. The backbone deformation is only moderate compared to the previous complex, with a dihedral angle between the two aromatic planes of 155.8°. The Pd–P bond length is 2.2767(6) Å, which is in the same range as the distances found in complex **4** and in literature.[17,19] However, due to the *trans*-effect, the Pd–Cl bond is slightly shortened to 2.30 Å on average (Pd–$Cl_1$ is 2.2823(8) Å and Pd–$Cl_2$ is 2.3262(10) Å) compared to complex **4A** and the *cis*-complexes reported in literature, while the Pd–P bond length is slightly longer in comparison with these *cis*-complexes. The palladium–chloride bonds have dimensions close to the values found in (di)phosphite-based structures.[22,23]

The *trans* coordination in square-planar palladium complexes with xanthene-based diphosphine ligands has been reported before by van Leeuwen and co-workers[13] and independently by Yin and Buchwald.[24] In both cases, bite angles of around 150° were found in the solid state structures with Pd–$O_{backbone}$ distances of around 2.6 Å, which might point to a weak bonding interaction, and consequently to a square pyrimidal coordination around the palladium atom. Normal palladium–ether bonds are in the order of 2.04–2.15 Å.[25] In our structure the Pd–$O_5$ intramolecular distance is 2.694(2) Å.

### Coordination of ligands 1 and 2 to platinum

Upon changing to $PtCl_2$(cod) as the metal precursor we found a remarkable difference in reactivity for ligand **1** and **2**. With ligand **1**, a complex spectrum was always obtained. Two broad singlets appeared in a 1 : 1 ratio, one at $\delta$ 118.9 ppm flanked by $^{195}$Pt satellites, and a $^1J_{Pt-P}$ of 5270 Hz, the other at $\delta$ 128.0 ppm with $^{195}$Pt-satellites and a coupling constant $^2J_{Pt-P}$ of only 2517 Hz. To date, only six papers dealing with platinum diphosphonite complexes have appeared. Two reports are based on diphosphonites with 1,2-substituted cyclopentyl backbones, giving typical coupling constants $J_{Pt-P}$ of ~4700 Hz,[26] while the third paper deals with various other alkyl-derived backbones and with one alkyl ligand instead of a chlorine.[27] Due to these differences, those results are not comparible with our present work. A combined effort from the groups of Claver and Pringle has resulted in a study on the use of monophosphonites in asymmetric hydrogenation.[8] Herein, also the X-ray analysis of a $PtCl_2$ complex with a chelating diphosphonite is reported, but without any spectroscopic identification of this complex in solution. Puddephatt and co-workers have reported on a dimeric species, made possible by the use of diethoxyphosphonitomethane as the ligand.[28] The groups of Schmutzler and Börner have prepared a new calix[4]arene-based diphosphonite, starting from 6-chlorodibenzo-1-oxa-$\sigma^3\lambda^3$-phosphorine as the P-building block. They have made notice of the related $PtCl_2$ complex, for which the $^{31}$P NMR spectrum showed two doublets (due to stereogenic P-atoms) and coupling constants $J_{Pt-P}$ of around 5060 Hz.[10b] Puddephatt and co-workers have described a platinum complex containing a monophosphonite, which showed a coupling constant of 4966 Hz.[29] Atherton *et al.* have published several $[PtCl_2(PEt)_3L]$ complexes (L = a monophosphonite), all with coupling constants around 5200 Hz.[30]

We were able to grow single crystals suitable for X-ray structure determination from a $CH_2Cl_2$ solution of complex **5** by layering with $CH_3CN$. The molecular structure obtained for complex **5**, as depicted in Fig. 7, is again the orthometallated species, with one chlorine atom still coordinated to the platinum, making the structure isomorphous to complex **4A**. This also explains the complicated $^{31}P$ NMR spectrum. The broad singlets are due to fluxional behavior of the P-atoms in the ligand while complexed to this orthometallated species. The difference in coupling constants arises from the fact that there is one phosphorus atom *trans* to the chlorine ($^1J_{Pt-P}$ 5240 Hz) and the other phosphorus atom is *trans* to a carbon fragment ($^1J_{Pt-P}$ 2517 Hz). The groups of Pidcock[31] and later Pringle[32] have reported on related $[PtCl(CH_3)(P)_2]$ complexes but unfortunately no P–P coupling constants were reported in either case.

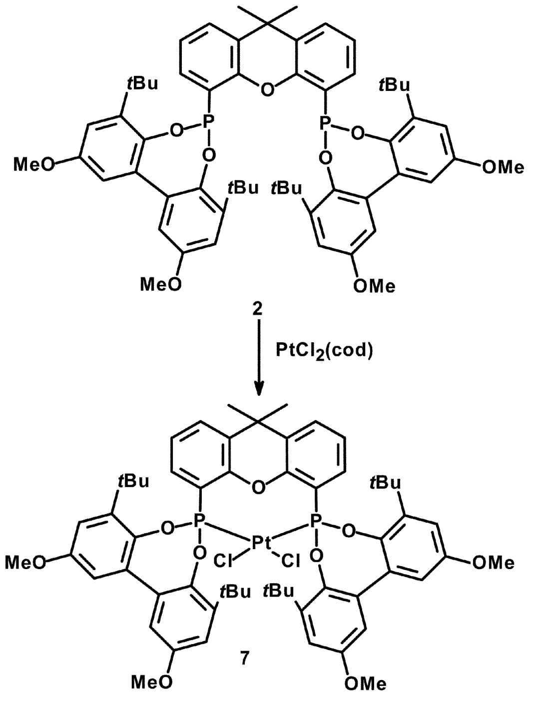


**6**

**Fig. 7** Displacement ellipsoid plot of complex **6**, [PtCl{**1**-κ$^3$*C*,*P*,*P*}]. The ellipsoids are drawn at the 50% probability level. All hydrogens atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Pt–$P_1$ 2.3680(11), Pt–$P_2$ 2.1922(9), Pt–Cl,2.3408(9), Pt–$C_{41}$ 2.073(4), $P_1$–$O_1$ 1.613(3), $P_1$–$O_2$ 1.606(3), $P_1$–$C_1$ 1.826(4), $P_2$–$O_3$ 1.613(3), $P_2$–$O_4$ 1.602(3), $P_2$–$C_7$ 1.803(4), $O_5$–$C_2$ 1.372(4), $O_5$–$C_8$ 1.387(4), Pt–$O_5$ 3.533(2), $P_1$–$P_2$ 3.5828(15); $Cl_1$–Pt–$C_{41}$ 89.87(10), $P_1$–Pt–$P_2$ 103.50(3), Cl–Pt–$P_1$ 86.64(3), Cl–Pt–$P_2$ 168.87(4), $P_1$–Pt–$C_{41}$ 176.12(10), $P_2$–Pt–$C_{41}$ 79.86(10), $O_1$–$P_1$–$O_2$ 97.64(14), $O_3$–$P_2$–$O_4$ 101.68(14), Pt–$P_1$–$O_1$ 116.34(10), Pt–$P_1$–$O_2$ 115.79(10), Pt–$P_2$–$O_3$ 108.04(9), Pt–$P_2$–$O_4$ 121.35(10), Pt–$P_1$–$C_1$ 124.01(13), Pt–$P_2$–$C_7$ 122.19(13), $C_2$–$O_5$–$C_8$ 112.2(3), $C_3$–$C_{13}$–$C_9$ 105.4(3), $O_1$–$P_1$–$C_1$ 100.35(15), $O_2$–$P_1$–$C_1$ 98.13(16), $O_3$–$P_2$–$C_7$ 102.66(16), $O_4$–$P_2$–$C_7$ 97.84(15).

The formation of this complex can be explained by the relatively high temperature applied during the complexation reaction (70 °C). The ligand coordinates in a *cis*-fashion to the platinum center in order to accommodate the phosphonite ring as well. The bite angle, $P_1$–Pt–$P_2$, is found to be only 103.50(3)° while the Cl–Pt–$C_{41}$ angle is 89.87(10)°. The P–Pt bond lengths are found to be 2.3680(11) Å for $P_1$–Pt and 2.1922(9) Å for $P_2$–Pt, the latter being close to the value reported for a phosphonite *trans* to a chlorine.[8,26] The carbon–platinum bond length $C_{41}$–Pt is normal at 2.073(4) Å[33] Comparing the Pt–Cl bond length with the work by Dahlenburg and Mertel we find a similar distance of 2.3408 Å.[26] The Pt–Cl bond length of 2.3408 Å is comparable with the few values reported in literature for other Pt-phosphonite complexes.[8,26] The platinum atom is located outside of the ligand plane, with the angles Pt–$P_1$–$C_1$ of 124.01° and Pt–$P_2$–$C_7$ of 122.19°. Due to the large degree of similarity between complex **4A** and **6**, the dihedral angle between the $Cl_1$–Pd–$C_{41}$ plane and the $P_2$–$P_1$–$C_1$-plane is also 115.6°. This has to be a result of the bulky phosphonite groups and it is in accordance with the same findings in another *cis*-platinum–diphosphonite complex recently obtained in our group.[14c] The xanthene backbone is bent strongly to accompany the *cis*-conformation in the solid state, leading to a dihedral angle of 106.5°, leaving a $P_1$–$P_2$ distance of 3.5828(15) Å, shorter than commonly found for xantphos-derived structures. The distance Pt–$O_5$ is found to 3.533(2) Å, too long to allow for any platinum–oxygen interaction. We are curently investigating the mechanism for the formation of this unique orthoplatinated species, as well as its reactivity. Balakrishna has claimed the formation of an orthometallated platinum complex with the ligand $(PhCH_2O)_2P–N(Ph)–P(OCH_2Ph)_2$ coordinated as a κ$^3$*P*,*P*,*C* chelating ligand, next to the expected *cis*-$PtCl_2$(PP) complex.[34a] This intramolecular rearrangement to the orthometallated species is suggested solely on the basis of the $^{31}P$ NMR spectrum, which showed two doublets with coupling constants $J_{Pt-P}$ of 5381 Hz and 5363 Hz, respectively, for both inequivalent phosphorus atoms, coordinated in a *cis*-fashion. This implies that the *trans*-effect of a chlorine atom is virtually the same as that of a phenyl ligand, which seems highly unlikely and is also clearly contradictory to the spectroscopic and structural data presented in our work. Bennet *et al.* have reported on complexes containing orthoplatinated triphenylphosphine.[34b] Recently, Bedford *et al.* have shown the application of orthoplatinated triaryl phosphite and phosphinite complexes in Suzuki biaryl coupling reactions.[34c]

To prevent the undesired orthometallation and to draw an analogy with the palladium complexes described before, the reaction of $PtCl_2$(cod) with ligand **2** was investigated. The reaction proceeded at room temperature, with 43% conversion after 3 hours but complete disappearance of free ligand after reaction overnight (Scheme 3). The $^{31}P$ NMR spectrum showed a



**Scheme 3**

singlet at $\delta$ 86.8 ppm, flanked by two $^{195}$Pt-satellites and a coupling constant $J_{Pt–P}$ of 5188 Hz. This clearly indicates that with this rigid and sterically constrained ligand the *cis*-coordination is the only occurring mode with ligand **2**.

Yet, since orthometallation is impossible in this case, a true *cis*-coordination for the diphosphonite ligand is anticipated. The $^1$H NMR spectrum contained the same features as for *trans*-[PdCl$_2$(**2**)]. There are two signals for both the *tert*-butyl and the methoxy-groups of the dioxaphosphepin units, showing that there are two chemically inequivalent sets. By layering a dichloromethane solution of complex **7** with acetonitrile, we were able to grow single crystals suitable for an X-ray crystallographic study (Fig. 8).

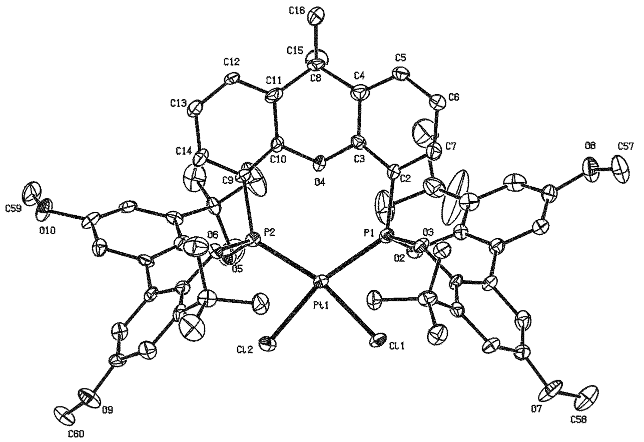


**Fig. 8** Displacement ellipsoid plot of complex **7**, *cis*-[PtCl$_2$(**2**)]. The ellipsoids are drawn at the 50% probability level. All hydrogens atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Pt–P$_1$ 2.2725(16), Pt–P$_2$ 2.2660(16), Pt–Cl$_1$ 2.3216(13), Pt–Cl$_2$ 2.3334(16), P$_1$–O$_2$ 1.612(5), P$_1$–O$_3$ 1.620(4), P$_1$–C$_2$ 1.826(6), Pt–O$_4$ 3.466(4), P$_1$–P$_2$ 3.794(2); P$_1$–Pt–P$_2$ 113.43(6), Cl$_1$–Pt–Cl$_2$ 84.74(5), Cl$_1$–Pt–P$_1$ 80.61(5), Cl$_2$–Pt–P$_1$ 165.32(5), Cl$_1$–Pt–P$_2$ 165.58(5), Cl$_2$–Pt–P$_2$ 81.14(6), Pt–P$_1$–C$_2$ 131.3(2), Pt–P$_1$–O$_2$ 114.24(15), Pt–P$_1$–O$_3$ 104.66(15), O$_2$–P$_1$–O$_3$ 107.1(2), O$_2$–P$_1$–C$_2$ 93.9(2), O$_3$–P$_1$–C$_2$ 103.6(2).

The solid state structure is in good agreement with the spectroscopic data, since the diphosphonite ligand is clearly coordinated in a *cis*-fashion to the platinum atom. The geometry around the platinum atoms is square planar, albeit heavily distorted due to the relatively large bite angle P$_1$–Pt–P$_2$ of 113.43°. This leads to an angle Cl$_1$–Pt–Cl$_2$ of only 84.74(5)°, while the angle P$_1$–Pt–Cl$_1$ is even smaller at 80.61(5)°. The platinum–phosphorus bond lengths of 2.2725(16) and 2.2660(16) Å are longer in comparison with the literature.[8,24,29]

From the side view on the metal core of complex **7** it is clear that the coordination around the platinum atom is square planar (Fig. 9). In contrast to the structure found for complex **6** and in contrast to our other work on Pt-diphosphonite complexes[2c] however, the angle of the P$_1$–Pt–P$_2$ plane with the P$_1$–P$_2$–C$_9$ plane is negligible at 5.1°. Also in complex **7** the xanthene backbone is bent significantly, leading to a dihedral angle between the two aromatic rings of 101.4° (Fig. 9).

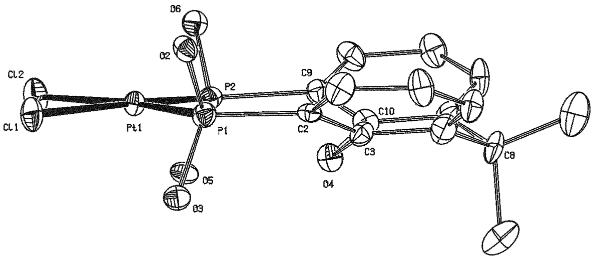
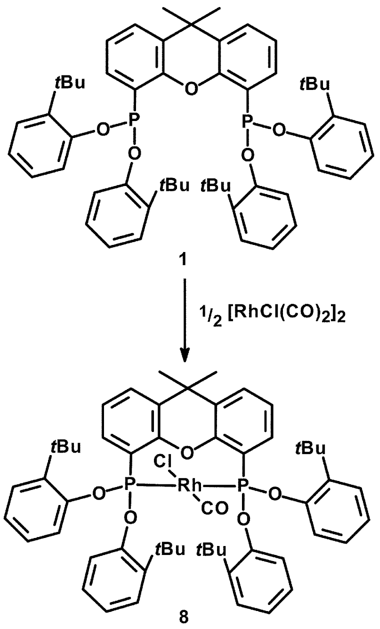


**Fig. 9** Side view on the metallic core of complex **7**, showing the square planarity around the platinum atom and the alignment of the P$_1$–Pt–P$_2$ plane and the P$_1$–P$_2$–C$_2$ plane.

## Coordination of ligands 1 and 2 to rhodium

Starting from the dimeric rhodium precursor [Rh(μ-Cl)(CO)$_2$]$_2$ and either ligand **1** or **2**, a yellow–brown powder was obtained (see example for ligand **1** in Scheme 4). The $^{31}$P NMR spectrum in both cases showed only one doublet, indicating the formation of *trans*-[RhCl(CO)(P–P)] complexes, with a coupling constant $J_{Rh–P}$ of 184 Hz (**1**) and 192 Hz (**2**), respectively.



**Scheme 4**

In the IR spectrum (ATR mode) the CO-stretch vibration is visible at $\nu_{CO}$ = 1996 cm$^{-1}$ (**1**) and 1998 cm$^{-1}$ (**2**) respectively. This indicates that the ligands are virtually the same regarding σ-donor and π-acceptor properties, since the $\nu_{CO}$ for these complexes can be related to the electronic $\chi$-factor as introduced by Tolman for Ni(CO)$_3$L compounds.[35] The $\nu_{CO}$ values found for these Rh-complexes fall between those of typical phosphites (~2015 cm$^{-1}$)[36] and phosphinites (1990 cm$^{-1}$),[37] thereby confirming the findings for the $^{195}$Pt coupling constants, where a similar trend could be observed (*vide supra*). The group of Broussier has made notice of a mixed phosphonite–phosphine ligand with a ferrocenyl backbone. In the corresponding RhCl(CO)-complex, the carbonyl is believed to be positioned *trans* to the phosphonite moiety. This is supported by the observation that the CO stretch vibration appears as high as 2041 cm$^{-1}$.[38] Unfortunately no solid state confirmation of the spectroscopic observations was reported.

For our system, a *trans*-relationship is expected to exist between both P-atoms, since only one doublet without any splitting, that would indicate an inequivalence of both phosphonite moieties, is observed. Both complexes, *trans*-[RhCl(CO)(**1**)] **8** and *trans*-[RhCl(CO)(**2**)] **9** readily crystallized from CH$_2$Cl$_2$–CH$_3$CN as yellow blocks. The complexes turned out to have the anticipated coordination of the chlorine *trans* to the carbonyl ligand and both phosphorus atoms also *trans* to each other, as depicted in Figs. 10 and 11.

For complex **8**, the geometry around the rhodium atom is clearly distorted square planar, possibly towards a square pyrimidal configuration. This is reflected by all angles around the rhodium atom. The P$_1$–Rh–P$_2$ bite angle is 147.19(3)°; the Cl$_1$–Rh–C$_1$ angle is 166.11(8)°. The Rh–O$_4$ distance of only 2.7193(16) Å indicates that there might be a weak interaction. The intramolecular P$_1$–P$_2$ distance is 4.3408(10) Å. The structural differences to complex **9** are mainly found in the orientation of the *tert*-butyl groups, leading to a different steric environment for the phosphorus atoms. Also, the latter complex has crystallographically imposed mirror symmetry. In complex

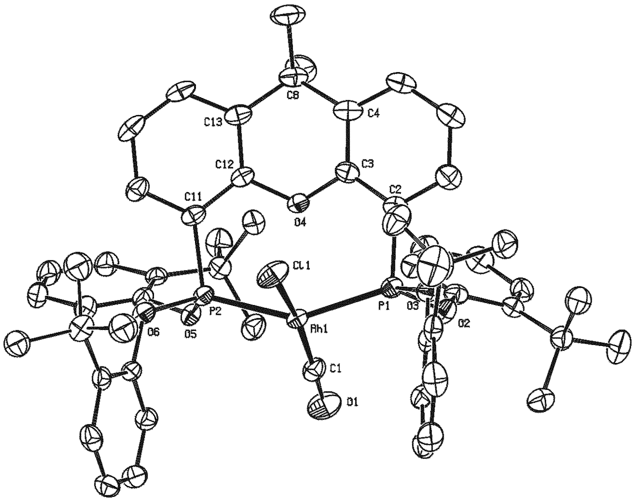


**Fig. 10** Displacement ellipsoid plot of complex **8**, *trans*-[RhCl(CO)(**1**)]. The ellipsoids are drawn at the 50% probability level. All hydrogens atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (°): Rh–$P_1$ 2.2583(7), Rh–$P_2$,2.2668(7), Rh–Cl 2.3504(8), Rh–$C_1$ 1.818(3), $C_1$–$O_1$ 1.149(3), $P_1$–$O_2$ 1.6300(17), $P_1$–$O_3$ 1.6141(17), $P_1$–$C_2$ 1.826(3), Rh–$O_4$ 2.7193(16), $P_1$–$P_2$ 4.3408(10); $P_1$–Rh–$P_2$ 147.19(3), $Cl_1$–Rh–$C_1$ 166.11(8), $P_1$–Rh–$Cl_1$ 88.49(3), $P_1$–Rh–$C_1$ 95.52(8), Rh–$C_1$–$O_1$ 174.1(2), Rh–$P_1$–$O_2$ 120.30(7), Rh–$P_1$–$O_3$ 124.61(7), Rh–$P_1$–$C_2$ 109.74(9), $O_2$–$P_1$–$O_3$ 97.80(9), $O_2$–$P_1$–$C_2$ 103.26(10), $O_3$–$P_1$–$C_2$ 97.13(10).

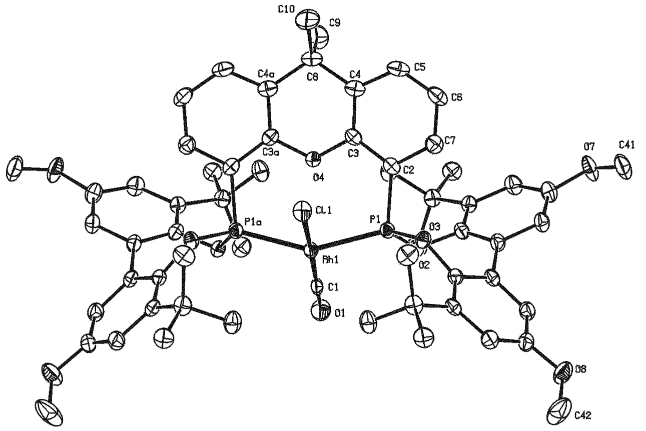


**Fig. 11** Displacement ellipsoid plot of complex **9**, *trans*-[RhCl(CO)(**2**)]. The ellipsoids are drawn at the 50% probability level. All hydrogens atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (°): Rh–$P_1$ 2.2554(9), Rh–$P_2$ 2.2554(9), Rh–Cl 2.3840(3), Rh–$C_1$ 1.818(5), $C_1$–$O_1$ 1.154(6), $P_1$–$O_2$ 1.621(2), $P_1$–$O_3$ 1.626(2), $P_1$–$C_2$ 1.830(3), Rh–$O_4$ 2.664(3), $P_1$–$P_2$ 4.3526(13); $P_1$–Rh–$P_2$ 149.56(3), $Cl_1$–Rh–$C_1$ 172.84(15), $P_1$–Rh–$Cl_1$ 87.89(2), $P_1$–Rh–$C_1$ 93.95(4), Rh–$C_1$–$O_1$ 179.1(4), Rh–$P_1$–$O_2$ 113.26(8), Rh–$P_1$–$O_3$ 125.74(8), Rh–$P_1$–$C_2$ 108.34(11), $O_2$–$P_1$–$O_3$ 103.70(11), $O_2$–$P_1$–$C_2$ 107.25(13), $O_3$–$P_1$–$C_2$ 96.25(13).

**9**, the rhodium atom is also distorted square planar, with the $P_1$–Rh–$P_2$ bite angle at 149.56(3)° and the $Cl_1$–Rh–$C_1$ angle at 172.84(15)°, significantly less deviated from the ideal 180° compared to complex **7**. The intramolecular P–P distance is 4.3526(13) Å and in this case the distance Rh–$O_4$ is 2.664(3) Å.

So far, no examples of X-ray analysis of RhCl(CO)-complexes with diphosphonites exist in literature. That makes it hard to compare bond lengths found for this particular system. The group of Pastor reported a Rh(acac)(diphosphonite) complex,[39] while Nifant'ev *et al.* prepared the [RhCl(CO)(PP)] complex with a ferrocenyl based alkylphosphonite system, however without any mention of crystallographic data.[40] Also their depiction of this structure as an ionic complex seems questionable. Selent and Börner have recently published some interesting (coordination) chemistry of a hydroxyphosphonite, involving transformation to a phosphite.[41] The best alternatives for a good comparison with complexes **8** and **9** are similar structures with (di)phosphite ligands. In such complexes with either mono- or bidentate ligands, normal Rh–P distances are around 2.15 Å and the Rh–Cl distances are on average 2.36–2.37 Å.

Fernandez *et al.* described the first X-ray structure of the type *trans*-[RhCl(CO){P(OR)$_3$}$_2$] with *tert*-butylphenyl groups on the phosphite ligands.[42] Paciello and co-workers published two crystal structures based on ligands known from the patent literature, where the two phosphite groups are clearly co-ordinated in a *cis*-fashion to the rhodium. No spectroscopic or crystallographic data were given for these complexes.[43] Van der Beuken *et al.* also concluded from spectroscopic studies, that a *cis*-[RhCl(CO)(ligand)] complex was present in solution, with the elegant tetraphosphite ligand 1,4-bis{bis[2-(diphenoxyphosphinoxy)-1-naphthyl]methyl}benzene.[44] With a mixed phosphine–phosphite ligand based on a benzene backbone, the group of Pizzano described a *cis*-[RhCl(CO)($P_1$–$P_2$)] complex, the phosphite sitting *trans* to the chlorine ligand.[45] Cobley *et al.* recently reported a chloro-bridged dinuclear rhodium complex with only one, calixarene-based monodentate phosphite coordinated per rhodium atom, leading to a phosphite *trans* of a bridging chlorine atom.[46]

## Conclusions

We have carefully investigated the coordination chemistry of two novel sterically demanding diphosphonite ligands based on the xanthene backbone with palladium, platinum and rhodium. Eight complexes have been characterized by full X-ray crystal analysis, two of which represent interesting orthometallated species. Extensive new $^{31}$P NMR data have been obtained allowing for future comparisons and structure assignments. We believe that the comparably easy synthesis combined with interesting coordination properties give those diphosphonite ligands great potential for applications in catalytic processes such as *e.g.* hydroformylation or hydrocyanation. Research is in progress towards this end.

## Experimental

### General information

All chemicals were purchased from Aldrich, Acros or Merck. Synthesis gas (1 : 1) with a purity of 5.0 was purchased from Hoekloos. All preparations were carried out under an argon atmosphere using standard Schlenk techniques. Solvents were distilled from sodium/benzophenone (diethyl ether, toluene and hexanes) or calcium hydride ($CH_2Cl_2$, $CH_3CN$ and $CDCl_3$) prior to use. All glassware was dried by heating under vacuum. The NMR spectra were recorded on a Varian Mercury 400 MHz spectrometer with both the $^{31}$P and $^{13}$C spectra measured $^1$H decoupled. Chemical shifts are given in ppm referenced to solvent ($^1$H, $^{13}$C{$^1$H}) or a 85% solution of $H_3PO_4$ ($^{31}$P{$^1$H}). $PdCl_2$(cod),[47] PdClMe(cod),[48] and $PtCl_2$(cod)[49] were prepared according to literature procedures. Ligands **1** and **2** were prepared according to a literature procedure.[16]

**[PdCl$_2$(1)] (complex 3).** $PdCl_2$(cod) (28.2 mg, 9.88 µmol) and ligand **1** (87.4 mg, 10.08 µmol) were dissolved in 5 mL of toluene and the solution stirred at 70 °C overnight. The solvent was removed *in vacuo* to leave a yellow solid. Yield 97% (100.1 mg, 9.58 µmol).

$^1$H NMR ($CDCl_3$): $\delta$ 7.75 (d, 4H, $^1J$ = 8.0 Hz), 7.63 (d, 4H, $^1J$ = 8.0 Hz), 7.33 (dd, 4H, $^1J$ = 8.0 Hz, $^2J$ = 1.6 Hz), 7.22 (dt, 4H, $^1J$ = 8.0 Hz, $^2J$ = 1.6 Hz), 7.15 (t, 2H, $^1J$ = 8.0 Hz), 7.09 (dt, $^1J$ = 8.0 Hz, $^2J$ = 1.6 Hz), 1.64 (s, 6H, $CH_3$), 1.36 (s, 36H, C($CH_3$)$_3$).

$^{31}$P{$^1$H} NMR ($CDCl_3$): $\delta$ 109.7 (s).

Anal. Calc. for $C_{55}H_{64}Cl_2O_5P_2Pd$: C, 63.25; H, 6.18. Found: C, 63.18; H, 6.26%.

***trans*-[PdCl($CH_3$)(1)] (complex 4).** PdCl($CH_3$)(cod) (46.6 mg, 175.8 μmol) and ligand **1** (162.1 mg, 187.0 μmol) were dissolved in 5 mL of toluene and the solution stirred at 75 °C overnight. The solvent was removed *in vacuo* to leave **3** as a light-yellowish solid. Yield 95% (171.0 mg, 167.0 μmol). Single crystals, suitable for X-ray analysis, were grown by slow diffusion of $CH_3CN$ into a $CH_2Cl_2$ solution, for complex **4A**, *cis*-[Pd(Cl-{**1**-κ$^3$*P*,*P*,*C*}].

$^1$H NMR ($CDCl_3$): $\delta$ 7.69 (dt, 4H, $^1J = 7.6$ Hz), 7.64 (dq, 2H, $^1J = 4.0$ Hz), 7.57 (dd, 2H, $^1J = 7.6$ Hz, $^2J = 1.2$ Hz), 7.3 (dd, 4H, $^1J = 7.6$ Hz, $^2J = 1.2$ Hz), 7.20 (dt, 4H, $^1J = 7.6$ Hz), 7.10 (t, 2H, $^1J = 7.6$ Hz), 7.07 (m, 2H), 1.63 (s, 3H, $CCH_3$), 1.57 (s, 3H, $CCH_3$), 1.39 (s, 36H, $C(CH_3)_3$), 1.32 (s, 36H, $C(CH_3)_3$), 0.79 (dt, 3H, $PdCH_3$).

$^{13}$C NMR ($CDCl_3$): $\delta$ 153.8, 152.2, 152.0, 140.0, 139.5, 134.0, 129.8, 128.8, 127.6, 127.5, 126.9, 124.0 (d, $^1J_{\text{P–C}} = 20.6$ Hz), 123.5, 120.6, 119.9, 35.6, 34.8, 30.4, 30.3, 29.1, 27.4.

$^{31}$P{$^1$H} NMR ($CDCl_3$): $\delta$ 123.1 (s).

Anal. Calc. for $C_{56}H_{67}ClO_5P_2Pd$: C, 65.69; H, 6.60. Found: C, 65.78; H, 6.67%.

***trans*-[PdCl$_2$(2)] (complex 5).** $PdCl_2$(cod) (16.1 mg, 56.4 μmol) and ligand **2** (56.1 mg, 57.0 μmol) were dissolved in 5 mL of dichloromethane and the solution stirred overnight at r.t. The solvent was then removed *in vacuo* to leave a yellow solid. Yield 92% (65.4 mg, 51.9 μmol). Orange rectangles, suitable for X-ray crystallographic analysis were obtained by layering with $CH_2Cl_2$–$CH_3CN$.

$^1$H NMR ($CDCl_3$): $\delta$ 7.59 (d, $^1$H, $^1J = 7.6$ Hz, $^2J = 1.2$ Hz), 7.22 (m, 2H), 7.10 (dq, 2H, $^1J = 3.6$ Hz, $^1J = 1.2$ Hz), 7.00 (d, 2H, $^1J = 3.6$ Hz), 6.952 (t, 3H, $^1J = 7.6$ Hz), 6.78 (m, 3H), 6.67 (d, 1H, $^1J = 2.8$ Hz), 3.88 (s, 6H, $OCH_3$), 3.81 (s, 6H, $OCH_3$), 1.71 (s, 3H, $CCH_3$), 1.47 (s, 36H, $C(CH_3)_3$), 1.27 (s, 3H, $CCH_3$).

$^{31}$P{$^1$H} NMR ($CDCl_3$): $\delta$ 136.5 (s).

Anal. Calc. for $C_{59}H_{68}ClO_9P_2Pd$: C, 61.07; H, 5.91. Found: C, 61.11; H, 5.84%.

***cis*-[PtCl{1-κ$^3$*P*,*P*,*C*}] (complex 6).** ($PtCl_2$(cod) (155.1 mg, 414.5 μmol) and **1** (366.3 mg, 422.4 μmol) were stirred in 10 mL toluene at 75 °C overnight. During this period a white turbid mixture was formed. After removal of the solvent, a white solid remained. Yield 94% (427.3 mg, 389.6 μmol). Single crystals, suitable for X-ray analysis, were grown from $CH_2Cl_2$–$CH_3CN$.

$^{31}$P{$^1$H} NMR ($CDCl_3$): $\delta$ 118.9 (br s, $J_{\text{Pt–P}} = 5270$ Hz), 128.0 (br s, $J_{\text{Pt–P}} = 2517$ Hz).

Anal. Calc. for $C_{55}H_{63}ClO_5P_2Pt$: C, 60.24; H, 5.79. Found: C, 60.18; H, 5.76%.

***cis*-[PtCl$_2$(2)] (complex 7).** $PtCl_2$(cod) (23.4 mg, 62.5 μmol) and ligand **2** (62.9 mg, 64.0 μmol) were dissolved in 5 mL of dichloromethane and the solution stirred overnight at r.t. The solution was filtered by cannula to remove insolubles and the solvent was then removed *in vacuo* to leave a yellow solid. Yield 88% (68.7 mg, 55.0 μmol). Analytically pure cubic shaped crystals **6** were obtained by layering with $CH_2Cl_2$–$CH_3CN$.

$^1$H NMR ($CDCl_3$): $\delta$ 7.49 (dd, 1H, $^1J = 7.2$ Hz, $^2J = 1.2$ Hz), 7.18 (m, 1H), 6.97 (d, 3H, $^1J = 7.2$ Hz), 6.94 (t, 1H, $^1J = 7.2$ Hz), 6.85 (d, 2H, $^1J = 2.4$ Hz), 6.67 (d, 3H, $^1J = 2.8$ Hz), 6.32 (d, 3H, $^1J = 2.8$ Hz), 3.81 (s, 6H, OMe), 3.78 (s, 6H, OMe), 1.67 (s, 3H, $CCH_3$), 1.43 (s, 18H, $C(CH_3)_3$), 1.38 (s, 18H, $C(CH_3)_3$), 1.21 (s, 3H, $CCH_3$).

$^{31}$P{$^1$H} NMR ($CDCl_3$): $\delta$ 86.8 (s, $J_{\text{Pt–P}} = 5188$ Hz).

Anal. Calc. for $C_{59}H_{68}Cl_2O_9P_2Pt$: C, 56.73; H, 5.49. Found: C, 56.83; H, 5.55%.

***trans*-[RhCl(CO)(1)] (complex 8).** [Rh(μ-Cl)(CO)$_2$]$_2$ (28.2 mg, 103.9 μmol) and ligand **1** (181.0 mg, 208.8 μmol) were dissolved in 5 mL of dichloromethane and the solution stirred overnight at r.t. The solution was filtered by cannula to remove insolubles and the solvent was then removed *in vacuo* to leave a yellow solid. Yield 85% (182.5 mg, 176.6 μmol). An analytically pure sample was obtained by layering with $CH_2Cl_2$–$CH_3CN$.

$^1$H NMR ($CDCl_3$): $\delta$ 8.37 (dd, 2H, $^1J = 8.0$ Hz, $^2J = 1.2$ Hz), 7.81 (ddt, 2H, $^1J = 7.6$ Hz, $^2J = 4.4$ Hz, $^3J$ unresolved), 7.62 (dd, 2H, $^1J = 7.6$ Hz, $^2J = 1.2$ Hz), 7.41 (dd, 2H, $^1J = 7.6$ Hz, $^2J = 1.2$ Hz), 7.35 (dd, 1H, $^1J = 7.6$ Hz, $^2J = 1.6$ Hz), 7.33 (dd, 1H, $^1J = 7.6$ Hz, $^2J = 1.6$ Hz), 7.27 (m, 2H), 7.19 (t, 2H, $^1J = 7.6$ Hz), 7.16 (dt, $^1J = 8.0$ Hz, $^2J = 1.2$ Hz), 7.01 (m, 4H), 1.90 (s, 3H, $CCH_3$), 1.42 (s, 18H, $C(CH_3)_3$), 1.37 (s, 3H, $CCH_3$), 1.25 (s, 18H, $C(CH_3)_3$).

$^{13}$C NMR ($CDCl_3$): $\delta$ 152.2, 140.5, 139.5, 133.5, 129.4, 128.8, 127.5, 127.0 (d, $^1J_{\text{P–C}} = 25.5$ Hz), 124.0 (d, $^1J_{\text{P–C}} = 12.8$ Hz), 123.5, 121.5, 119.2, 35.5, 34.8, 34.6, 34.3, 30.2, 23.7.

$^{31}$P{$^1$H} NMR ($CDCl_3$): $\delta$ 138.4 (s, $J_{\text{Rh–P}} = 184.4$ Hz).

FTIR (ATR mode, solid, cm$^{-1}$): $\nu$ 1996 (Rh(CO)).

Anal. Calc. for $C_{56}H_{64}ClO_6P_2Rh$: C, 65.09; H, 6.24. Found: C, 64.86; H, 6.31%.

***trans*-[RhCl(CO)(2)] (complex 9).** [Rh(μ-Cl)(CO)$_2$]$_2$ (18.3 mg, 47.1 μmol) and ligand **2** (92.7 mg, 94.2 μmol) were dissolved in 5 mL of dichloromethane and the solution stirred for 2 h at r.t.The solvent was then removed *in vacuo* to leave a yellow/red solid. Yield 91% (107.5 mg, 85.7 μmol). Crystals suitable for X-ray analysis were obtained by layering with $CH_2Cl_2$–$CH_3CN$.

$^1$H NMR ($CDCl_3$): $\delta$ 7.54 (dd, 1H, $^1J = 3.6$ Hz, $^2J = 1.2$ Hz), 7.16 (m, 2H), 7.12 (d, 1H, $^1J = 3.2$ Hz), 7.00 (d, 3H, $^1J = 3.2$ Hz), 6.94 (t, 2H, $^1J = 7.6$ Hz), 6.86 (d, 2H, $^1J = 1.2$ Hz), 6.86 (d, 1H, $^1J = 7.6$ Hz), 6.75 (d, 2H, $^1J = 3.2$ Hz), 6.67 (d, 3H, $^1J = 2.8$ Hz), 3.90 (s, 3H, OMe), 3.89 (s, 3H, OMe), 3.81 (s, 6H, OMe), 1.81 (s, 3H, $CCH_3$), 1.62 (s, 18H, $C(CH_3)_3$), 1.47 (s, 36H, $C(CH_3)_3$), 1.30 (s, 3H, $CCH_3$), 1.20 (s, 18H, $C(CH_3)_3$).

$^{31}$P{$^1$H} NMR ($CDCl_3$): $\delta$ 163.6 (s, $J_{\text{Rh–P}} = 191.8$ Hz).

FTIR (ATR mode, solid, cm$^{-1}$): $\nu$ 1998 (Rh(CO)).

Anal. Calc. for $C_{60}H_{68}ClO_{10}P_2Rh$: C, 62.69; H, 5.96. Found: C, 62.78; H, 6.10%.

### Crystal structure determination of 1

The data was collected on a Bruker SMART APEX CCD. Data integration and global cell refinement was performed with the program SAINT. Intensity data were corrected for Lorentz and polarization effects. The structure was solved by Patterson methods and extension of the model was accomplished by direct methods applied to difference structure factors using the program DIRDIF.[50] The positional and anisotropic displacement parameters for the non-hydrogen atoms were refined. The hydrogen atoms were included in the final refinement riding on the C-atom as appropriate with $U_{\text{iso}} = c \times U_{\text{equiv}}$. Final refinement on $F^2$ carried out by full-matrix least-squares techniques converged at $wR(F^2) = 0.1133$ for 12282 reflections and $R(F) = 0.0410$ for 10321 reflections with $F_o \geq 4.0\sigma(F_o)$ and 815 parameters. Crystal data are given in Table 1.

### Crystal structure determinations of 4A–9

Intensity data were collected using graphite-monochromated Mo-Kα radiation, $\lambda = 0.71073$ Å, on a Nonius Kappa CCD diffractometer at 150 K. Corrections for absorption were applied with PLATON/MULABS[51] (complexes **4A** and **6**) or PLATON.DELABS[51] (complex **5**). The structures were solved by direct methods using SHELXS86[52] (complexes **4A**, **7** and **9**) or by Patterson techniques using DIRDIF99[50] (complexes. **5**, **6** and **8**). Refinement on $F^2$ was done by SHELXL97.[52] Hydrogen atoms were introduced at calculated positions and refined riding on their carrier atoms. Structures **4A**, **6** and **9** contain small voids of about 50 Å$^3$. No residual electron density was found in those voids. One molecule of acetonitrile is present in the asymmetric unit cell of complexes **5** and **9**. The unit cell of complex **7** contained four solvent accessible voids filled with disordered solvent, two of 448 Å$^3$, incorporating 47 electrons, and two of 198 Å$^3$, with 34 electrons each. Their contributions

**Table 1** Selected crystallographic data for compound **1** and complexes **4A**–**9**

| | **1** | **4A** | **5** | **6** | **7** | **8** | **9** |
|---|---|---|---|---|---|---|---|
| Formula | $C_{55}H_{64}O_5P_2$ | $C_{55}H_{63}ClO_5P_2Pd$ | $C_{59}H_{68}Cl_2O_9P_2Pd{\cdot}CH_3CN$ | $C_{55}H_{63}ClO_5P_2Pt$ | $C_{59}H_{68}Cl_2O_9P_2Pt$ | $C_{56}H_{64}ClO_6P_2Rh$ | $C_{60}H_{68}ClO_{10}P_2Rh{\cdot}CH_3CN$ |
| Mw/g mol$^{-1}$ | 867.06 | 1007.84 | 1201.43 | 1096.53 | 1249.06 | 1033.37 | 1190.50 |
| Crystal size/mm | 0.52 × 0.49 × 0.37 | 0.03 × 0.12 × 0.36 | 0.18 × 0.24 × 0.45 | 0.03 × 0.06 × 0.33 | 0.10 × 0.15 × 0.25 | 0.06 × 0.09 × 0.28 | 0.05 × 0.10 × 0.20 |
| Crystal system | Triclinic | Monoclinic | Orthorhombic | Monoclinic | Orthorhombic | Orthorhombic | Orthorhombic |
| Space group | $P\bar{1}$ (no. 2) | $P2_1/c$ (no. 14) | *Pnma* (no. 62) | $P2_1/c$ (no. 14) | $P2_12_12_1$ (no. 19) | $Pna2_1$ (no. 33) | *Pnma* (no. 62) |
| *a*/Å | 12.2735(6) | 9.4543(1) | 11.5297(3) | 9.4832(1) | 9.0341(10) | 16.8142(10) | 11.6735(10) |
| *b*/Å | 14.0431(7) | 26.6986(3) | 20.7719(3) | 26.6038(3) | 21.647(2) | 16.2527(11) | 21.125(2) |
| *c*/Å | 15.0026(7) | 21.5052(2) | 24.2993(5) | 21.4405(3) | 32.496(3) | 18.5497(12) | 23.744(3) |
| $\alpha$/° | 79.592(1) | | | | | | |
| $\beta$/° | 73.871(1) | 108.5200(6) | | 108.7890(6) | | | |
| $\gamma$/° | 89.752(1) | | | | | | |
| $V$/Å$^3$ | 2440.3(2) | 5147.15(9) | 5819.5(2) | 5120.96(11) | 6355.0(11) | 5069.2(5) | 5855.3(11) |
| $Z$ | 2 | 4 | 4 | 4 | 4 | 4 | 4 |
| $D_c$/g cm$^{-3}$ | 1.180 | 1.301 | 1.371 | 1.422 | 1.306 | 1.354 | 1.351 |
| $\mu$(Mo-K$\alpha$)/mm$^{-1}$ | 0.136 | 0.520 | 0.522 | 2.900 | 2.391 | 0.502 | 0.450 |
| $T$/K | 100 | 150 | 150 | 150 | 150 | 150 | 150 |
| Total reflections | 23323 | 45983 | 31225 | 43023 | 152479 | 137931 | 126110 |
| Unique reflections ($R_{int}$) | 12282 (0.0171) | 10085 (0.060) | 5882 (0.063) | 9900 (0.058) | 14566 (0.14) | 11597 (0.0816) | 5515 (0.13) |
| $wR_2$ ($F^2$) (all data) | 0.1133 | 0.0774 | 0.0837 | 0.0676 | 0.108 | 0.062 | 0.099 |
| $R_1$ | 0.0410 | 0.0355 | 0.0352 | 0.0315 | 0.047 | 0.033 | 0.042 |
| $F$(000) | 928 | 2104 | 4568 | 2232 | 2544 | 2160 | 2488 |

to the structure factor calculation in the refinement was taken into account using the PLATON/SQUEEZE procedure.[53] Structure validation and molecular graphics preparation were performed with the PLATON package.[53] Crystal data are given in Table 1.

CCDC reference numbers 220609–220615.

See http://www.rsc.org/suppdata/dt/b3/b311328k/ for crystallographic data in CIF or other electronic format.

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