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PAPER

A bisphosphonite calix[5]arene ligand that stabilizes η^6 arene coordination to palladium†

Beatriz E. Rios,[a] Paul Sood,[a] Yaroslav Klichko,[a] Mohan Koutha,[a] Douglas Powell[b] and Michael Lattman*[a]

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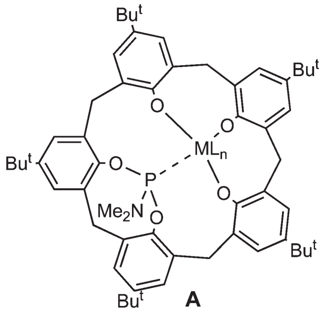
Treatment of a bis(phenylphosphonite)calix[5]arene ligand with either palladium(II) chloride or 1,5-cyclooctadieneplatinum(II) chloride yields square planar metal complexes in which the two phosphorus atoms bind *cis* to the MCl_2 moiety (M = Pd, Pt). Chloride was removed from the palladium complex to open a coordination site at the metal for catalysis. The chloride removal resulted in a rare and unexpected η^6 coordination of an arene to the metal. The reaction is reversible upon addition of tetra-*n*-butyl ammonium chloride.

Introduction

Trivalent phosphines and phosphites are some of the most common ligands in transition metal chemistry, particularly useful for their applications in catalysis. Other trivalent phosphorus ligands have been less studied. Over the past few years, reports on the use of phosphonite [$RP(OR)_2$] ligands suggest that these might be increasingly important in catalytic reactions such as hydroformylations,[1] isomerizations,[2] cross couplings in ionic liquids,[3] phase transfer hydrogenations,[4] and azide alkyne cycloadditions,[5] as well as applications in OLED technologies.[6] Our current work with bisphosphonite calix[5]arene complexes of palladium(II) and platinum(II) broadens the scope of these ligands to include isolation and structural characterization of a stable η^6 arene complex of palladium(II). This is a rare coordination mode for this metal and, to our knowledge, no such complex of palladium(II) has been characterized by X-ray diffraction until now.

Several calix[5]arene ligands containing one and two phosphorus atoms have been reported (Fig. 1).[7,8] The calix[5]arene provides a larger cavity than the common calix[4]arene, while retaining constraint unavailable in larger calixarenes. The series of complexes, illustrated by structure **A**, demonstrate that this unique combination of "constraint and flexibility" leads to a significant variation in ligand–metal interaction. For example, P⋯M (M = W)[8] distances range from 2.74 to 3.15 Å, depending on the choice of ligand L_n. In another study (M = Ti),[9] a conformational change of the calixarene accounts for an even greater variation in P⋯M distance (2.90 to 3.69 Å).


A

Results and discussion

Investigations of metal coordination complexes of the bisphosphonite **3** are being carried out to determine utility of the ligand in catalysis. The X-ray structure of **3** shows it to be in an approximate cone conformation; the phosphorus lone pairs point "inside" the cavity[7] allowing for bidentate coordination of the phosphorus atoms to transition metals.

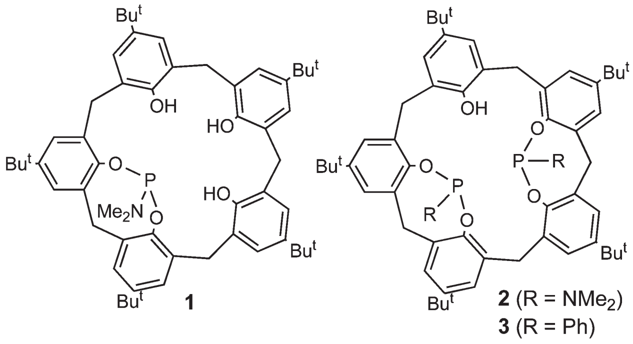

1
2 (R = NMe_2)
3 (R = Ph)

Fig. 1 Phosphorus-based calix[5]arene ligands.

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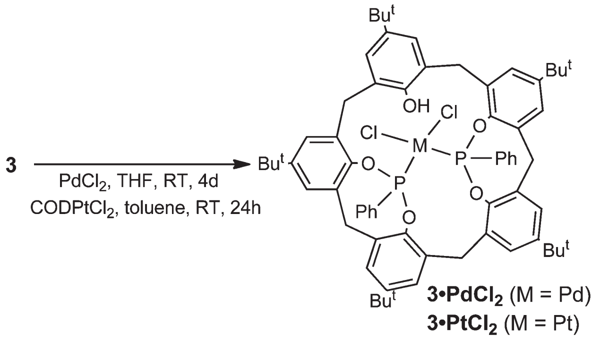
[a] Department of Chemistry, Southern Methodist University, Dallas, Texas 75275, USA. E-mail: mlattman@smu.edu; Fax: +214-768-4089
[b] Department of Chemistry and Biochemistry, University of Oklahoma, Norman, OK 73019, USA

† Electronic supplementary information (ESI) available: NMR spectra of $\mathbf{3 \cdot Pd(O_3SCF_3)_2}$ and details of crystallography (pdf format), and crystallographic data in cif format. CCDC 836670, 836671 and 869888. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt30491k



Scheme 1 Synthesis of bisphosphonite calix[5]arene complexes of square planar palladium and platinum.

Treatment of **3** with palladium(II) chloride (Scheme 1) in THF yields **3·PdCl$_2$** in 78% isolated yield. The ^{1}H NMR spectrum of the product shows that the overall C_s symmetry of the ligand is retained in the complex: three resonances are observed for the *tert*-butyl groups (in a 2 : 2 : 1 ratio) and six doublets (due to geminal $^2J_{HH}$ coupling) are found for the bridging methylene groups (in a 2 : 2 : 2 : 2 : 1 : 1 ratio). The ^{31}P NMR resonance of **3·PdCl$_2$** at δ 116 is shifted upfield by 38 ppm relative to the free ligand. An X-ray crystal structure of the complex was obtained (Fig. 2), and selected distances and angles are shown in Table 1. Both phosphorus atoms are bound to palladium, with the metal in a square planar geometry [sum of the *cis* bond angles around Pd is 359.6(1)°]. The Pd–P and Pd–Cl bond lengths are in usual ranges, and the P–Pd–P bite angle is 102.8°. The calix[5]arene backbone conformation is best described as a "flattened" cone. One distinctive feature of this complex is the close approach of the oxygen of the free phenolic group to the metal (O1⋯Pd distance of 2.80 Å). A similar platinum complex **3·PtCl$_2$** is obtained in an analogous manner (Scheme 1) using 1,5-cyclooctadieneplatinum(II) chloride. The X-ray structure of this complex is shown in Fig. 2. The geometry of the platinum complex is very similar to that of palladium with an almost identical P–Pt–P bite angle. Other bond distances and angles show only slight differences, and the O1⋯M distance is about 0.1 Å longer in the platinum complex. The crystals of **3·PdCl$_2$** and **3·PtCl$_2$** are isomorphous.

The close proximity of the hydroxyl oxygen to the metal in these complexes suggests an opportunity for oxygen (O1) to stabilize an available coordination site suitable for catalysis. Such a site might be obtained by removal of chloride. Treatment of **3·PdCl$_2$** with one equivalent of silver trifluoromethanesulfonate consumes half of the starting material; addition of a second equivalent completely consumes the starting material to give **3·Pd(O$_3$SCF$_3$)$_2$** (Scheme 2). The ^{31}P NMR resonance of the product at δ 122 is shifted slightly downfield compared to **3·PdCl$_2$**. While the ^{1}H NMR spectrum of this product is still consistent with an overall C_s symmetry, two peaks appear at unexpected chemical shifts, and both are due to protons on the free phenolic ring. There is an upfield shift of the resonance of the *t*-butyl protons from δ 1.44 in **3·PdCl$_2$** to −0.07 in **3·Pd(O$_3$SCF$_3$)$_2$**, and an upfield shift from δ 7.28 to 5.90 of the resonance due to the aromatic protons. In addition, this latter resonance is split into a triplet due to phosphorus coupling (J_{PH} = 5 Hz).

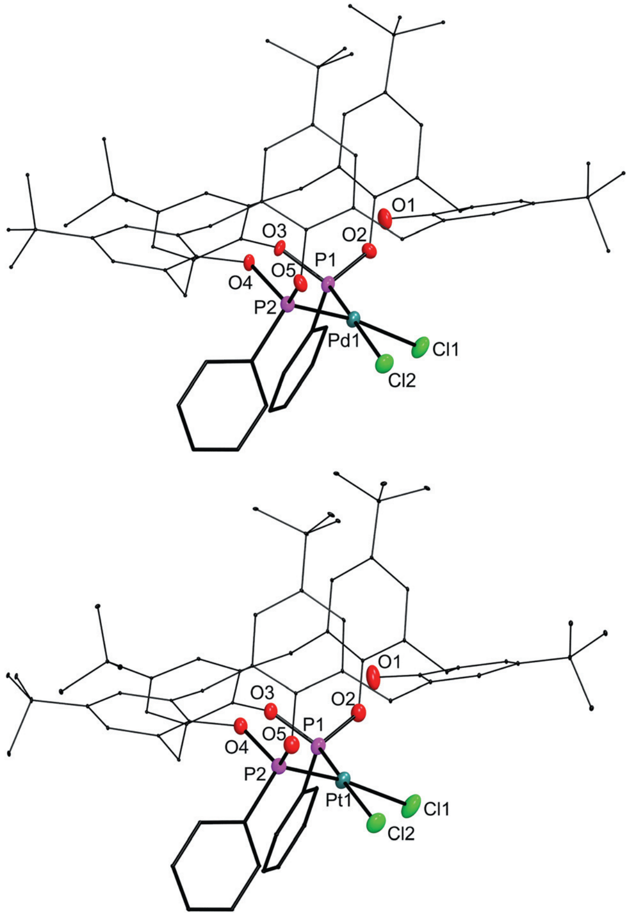
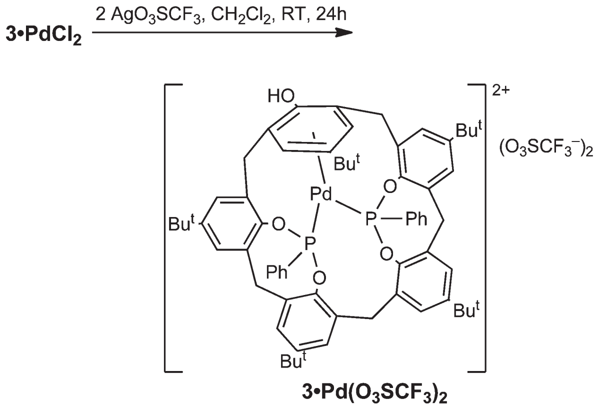


Fig. 2 Molecular structures of the complexes **3·PdCl$_2$** and **3·PtCl$_2$**. Thermal ellipsoids for the labeled atoms are shown at 50% probability. The calixarene ligand backbone is in wireframe. Hydrogen atoms are omitted for clarity.

Table 1 Selected distances (Å) and angles (°) for **3·PdCl$_2$** and **3·PtCl$_2$**

3·PdCl$_2$		**3·PtCl$_2$**	
Pd(1)–P(1)	2.2452(16)	Pt(1)–P(1)	2.2255(10)
Pd(1)–P(2)	2.2384(16)	Pt(1)–P(2)	2.2168(9)
Pd(1)–Cl(1)	2.3342(15)	Pt(1)–Cl(1)	2.3400(9)
Pd(1)–Cl(2)	2.3551(15)	Pt(1)–Cl(2)	2.3600(10)
P(2)–Pd(1)–P(1)	102.82(6)	P(2)–Pt(1)–P(1)	102.61(3)
P(2)–Pd(1)–Cl(1)	171.68(6)	P(2)–Pt(1)–Cl(1)	171.80(3)
P(1)–Pd(1)–Cl(1)	82.18(6)	P(1)–Pt(1)–Cl(1)	83.75(3)
P(2)–Pd(1)–Cl(2)	82.81(6)	P(2)–Pt(1)–Cl(2)	84.42(3)
P(1)–Pd(1)–Cl(2)	173.08(5)	P(1)–Pt(1)–Cl(2)	172.32(3)
Cl(1)–Pd(1)–Cl(2)	91.77(6)	Cl(1)–Pt(1)–Cl(2)	88.97(3)
Pd(1)⋯O(1)	2.803(4)	Pt(1)⋯O(1)	2.919(3)

The X-ray structure of **3·Pd(O$_3$SCF$_3$)$_2$** (Fig. 3) indicates that both chlorides have been removed. Instead of the hydroxyl oxygen binding to the metal, the arene of the free phenolic group π-bonds to palladium in an η^6 coordination mode leading to an 18-electron complex, an unusual count for palladium(II). The upfield shift of the aryl proton resonance is expected as a result of this coordination, and the observed three-bond P–H coupling is reasonable. Because of the arene binding, the *t*-butyl



Scheme 2 Dechlorination of **$3{\cdot}PdCl_2$**.

Table 2 Selected distances (Å) and angles (°) for **$3{\cdot}Pd(O_3SCF_3)_2$**

Pd(1)–P(1)	2.263(6)
Pd(1)–P(2)	2.262(6)
Pd(1)–C(1)	2.433(19)
Pd(1)–C(2)	2.381(18)
Pd(1)–C(3)	2.396(18)
Pd(1)–C(4)	2.43(2)
Pd(1)–C(5)	2.367(18)
Pd(1)–C(6)	2.396(18)
C(1)–C(2)	1.38(2)
C(1)–C(6)	1.37(2)
C(2)–C(3)	1.39(2)
C(3)–C(4)	1.40(2)
C(4)–C(5)	1.41(2)
C(5)–C(6)	1.44(2)
P(2)–Pd(1)–P(1)	97.7(2)

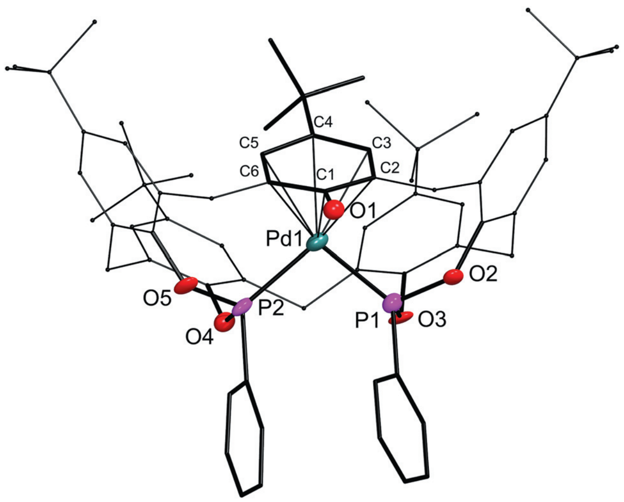


Fig. 3 Molecular structure of the metal dication of **$3{\cdot}Pd(O_3SCF_3)_2$**. Thermal ellipsoids for the labeled atoms are shown at 50% probability. The calixarene ligand backbone is in wireframe. Hydrogen atoms are omitted for clarity. Not shown is a hydrogen bonding interaction between the hydroxyl group (O1) and the oxygen of a trifluoromethanesulfonate group (oxygen⋯oxygen distance of 2.62 Å).

group on that ring is now positioned "inside" the calixarene cavity and shielded by the π systems of the surrounding calixarene aryl groups. This results in the large upfield shift of this resonance in the ^{1}H NMR spectrum.[10] [Not shown in Fig. 3 is a hydrogen bonding interaction between the hydroxyl group (O1) and the oxygen of a trifluoromethanesulfonate group (oxygen⋯oxygen distance of 2.62 Å).]

Several reported X-ray structures of arene π-coordination to palladium(II) demonstrate that η^6 arene coordination is not observed in the solid-state.[11,12] The hapticities observed are best described as two,[13] three,[14] four,[15] five,[16] and sometimes a combination of these values.[17] Some presumed η^6 complexes observed in solution, at low temperatures, decompose at ambient conditions.[18] The palladium atom in **$3{\cdot}Pd(O_3SCF_3)_2$** is centered over the arene ring, with all six Pd–C bond distances in the range 2.37–2.43 Å (Table 2). The Pd–C(1) and Pd–C(4) distances of 2.43 Å are slightly longer than the other four Pd–C distances resulting in a small puckering of the ring. The standard deviations in this structure are larger than in the other two structures due to poorer crystal quality (see Experimental). Nevertheless, these values are within previously reported π-bonded arene Pd–C distances of lower hapticity. For example, an η^3-bound mesitylene shows Pd–C bonding distances of 2.33–2.45 Å;[14] an η^5-bound 2,4,6-trimethylphenoxide shows Pd–C bonding distances of 2.22–2.47 Å.[16] Another significant structural feature is found at the phosphorus atoms. The P–Pd–P bite angle in **$3{\cdot}Pd(O_3SCF_3)_2$** is 98° (5° smaller than in **$3{\cdot}PdCl_2$**), and the phosphonite phenyl rings are almost parallel. An interplanar distance of about 3.3 Å and slightly offset centroids with a distance of 3.55 Å, indicate π–π stacking in the dication.[19] This stacking is not present in **$3{\cdot}PdCl_2$**, since the phenyl rings are too far apart (centroid to centroid distance of 6.26 Å). The π complex is air stable at room temperature in the solid-state and in dichloromethane solution. The complex remains stable in solution after addition of diethyl ether, ethanol and methanol, but it decomposes upon the addition of water.

The conversion of **$3{\cdot}PdCl_2$** to **$3{\cdot}Pd(O_3SCF_3)_2$** is reversible. Addition of tetra-*n*-butylammonium chloride to a solution of **$3{\cdot}Pd(O_3SCF_3)_2$** in dichloromethane forms **$3{\cdot}PdCl_2$** (Fig. 4). Subsequent addition of silver trifluoromethanesulfonate regenerates **$3{\cdot}Pd(O_3SCF_3)_2$**.

The reaction of **$3{\cdot}PtCl_2$** with two equivalents of silver trifluoromethanesulfonate is more complex and, as yet, we have not fully characterized the products. One of the products does appear to be the platinum analog of **$3{\cdot}Pd(O_3SCF_3)_2$**, judging by a large upfield shift of one of the *t*-butyl groups in the ^{1}H NMR spectrum. However, this is not the main product of the reaction.[20]

Conclusion

The constraint and flexibility of the bisphosphonite calixarene ligand **3** plays a major role in the observed geometry changes. This ligand is sufficiently flexible to accommodate a 5° change of the bite angle from the square planar 16-electron complex to the arene π-bonded 18-electron species, while also providing constraint to keep the arene in bonding distance to the metal. It is possible that the π–π stacking of the phosphonite phenyl rings is responsible for driving the stabilization of the η^6 complex. However, this stacking may be due to the decrease in the P–Pd–P bite angle that simply forces the rings into a parallel orientation

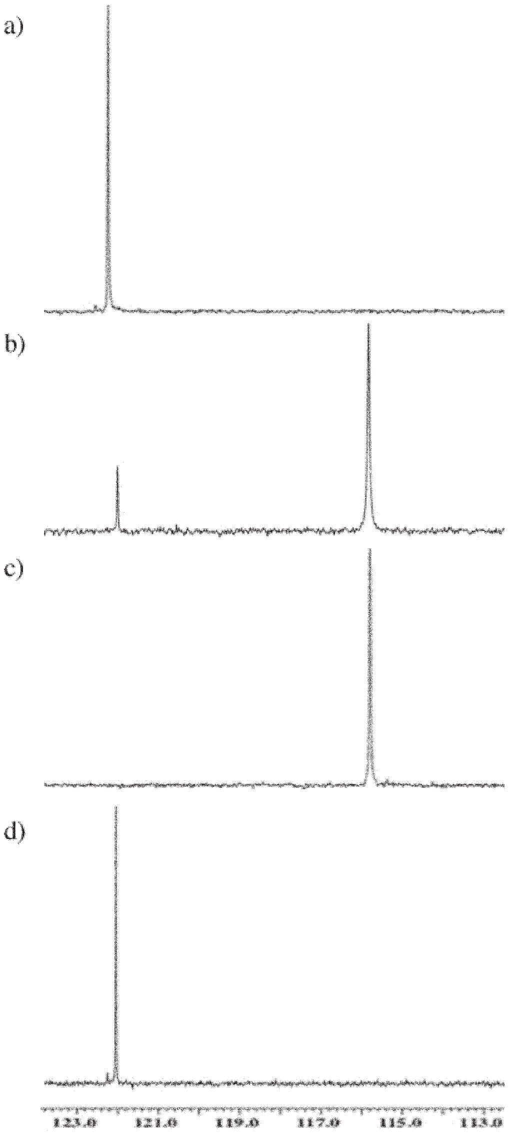


Fig. 4 ^{31}P NMR (ppm) spectra showing the reversible conversion of **3·PdCl$_2$** (δ 116) to **3·Pd(O$_3$SCF$_3$)$_2$** (δ 122). (a) Pure **3·Pd(O$_3$SCF$_3$)$_2$**. (b) Addition of 2 eq of tetra-*n*-butylammonium chloride. (c) Addition of another 2 eq of tetra-*n*-butylammonium chloride. (d) Addition of 4 eq AgO$_3$SCF$_3$.

to avoid steric congestion. Clearly, the metal also plays a role, since platinum does not cleanly form the same complex. Work is currently being conducted to determine the critical factors stabilizing η^6 binding of these ligands.

Experimental

All reactions and manipulations were carried out under an atmosphere of nitrogen in a Vacuum Atmospheres drybox or by using standard Schlenk techniques, unless otherwise indicated. Solvents were dried using standard procedures and distilled under a nitrogen atmosphere and either used immediately or stored in the drybox prior to use. Glassware was oven-dried at 140 °C overnight prior to use. The reagents palladium(II) chloride, 1,5-cyclooctadieneplatinum(II) chloride, and silver trifluoromethanesulfonate were obtained commercially and used without further purification. Ligand **3** was synthesized by the literature procedure.[7] All NMR spectra were recorded on a JEOL ECA-500 multinuclear NMR spectrometer resonating at 500.160 (^{1}H) and 202.468 MHz (^{31}P). ^{1}H NMR resonances were measured relative to residual proton solvent peaks and referenced to tetramethylsilane. ^{31}P NMR resonances were measured relative to external 85% H$_3$PO$_4$. Elemental Analyses were obtained on a Flash EA 1112 Elemental Analyzer.

Synthesis of **3·PdCl$_2$**. Solid palladium(II) chloride (0.250 g, 1.41 mmol) was added to a stirred solution of **3** (1.44 g, 1.41 mmol) in THF (32 mL). The mixture was stirred at room temperature for 4 d. The product came out of solution as a pale yellow solid. The solid was filtered and washed with hexane (3 × 2 mL) and dried under vacuum for 48 hours yielding **3·PdCl$_2$** as an air- and moisture-stable yellow powder (1.32 g, 78%). Anal calcd for $C_{67}H_{76}Cl_2O_5P_2Pd$: C, 67.03; H, 6.38. Found: C, 67.00; H, 6.27. ^{1}H NMR (CD$_2$Cl$_2$, δ): 1.08 (s, 18H, *t*-Bu), 1.20 (s, 18H, *t*-Bu), 1.44 (s, 9H, *t*-Bu), 3.37 (d, 1H, CH$_2$, $^2J_{HH}$ = 12.5 Hz), 3.44 (d, 2H, CH$_2$, $^2J_{HH}$ = 15.7 Hz), 3.51 (d, 2H, CH$_2$, $^2J_{HH}$ = 15.7), 3.95 (s, 1H, OH), 4.09 (d, 1H, CH$_2$, $^2J_{HH}$ = 12.5 Hz), 4.21 (d, 2H, CH$_2$, $^2J_{HH}$ = 15.7 Hz), 5.22 (d, 2H, CH$_2$, $^2J_{HH}$ = 15.7 Hz), 7.025 (d, 2H, CH, $^4J_{HH}$ = 2.5 Hz), 7.026 (d, 2H, CH, $^4J_{HH}$ = 2.5 Hz), 7.12 (d, 2H, CH, $^4J_{HH}$ = 2.5 Hz), 7.26 (d, 2H, CH, $^4J_{HH}$ = 2.5 Hz), 7.28 (s, 2H, CH), 7.55 (m, 6H, CH), 8.27 (m, 4H, CH). ^{31}P NMR (CD$_2$Cl$_2$, δ): 116.

Synthesis of **3·PtCl$_2$**. Solid 1,5-cyclooctadieneplatinum(II) chloride (0.431 g, 1.14 mmol) was added to a stirred solution of **3** (1.161 g, 1.14 mmol) in toluene (65 mL). The mixture was stirred at room temperature for 48 hours (only 24 hours is required for the reaction to reach completion) yielding a white precipitate. The solution was filtered, the white precipitate washed with toluene (10 mL) and dried under vacuum for 20 hours yielding **3·PtCl$_2$** as a white, air-stable, pure solid (1.06 g, 72%). Anal calcd for $C_{67}H_{76}Cl_2O_5P_2Pt$: C, 62.42; H, 5.94. Found: C, 62.20; H, 6.01. ^{1}H NMR (CDCl$_3$, δ): 1.13 (18H, s, *t*-Bu), 1.22 (18H, s, *t*-Bu), 1.41 (9H, s, *t*-Bu), 3.42 (1H, d, $^2J_{HH}$ = 12.6 Hz, CH$_2$), 3.45 (2H, d, $^2J_{HH}$ = 15.5 Hz, CH$_2$), 3.48 (2H, d, $^2J_{HH}$ = 14.9 Hz, CH$_2$), 4.22 (2H, d, $^2J_{HH}$ = 14.9 Hz, CH$_2$), 4.32 (1H, d, $^2J_{HH}$ = 12.6 Hz, CH$_2$), 5.22 (2H, d, $^2J_{HH}$ = 15.5 Hz, CH$_2$), 6.99 (2H, br d, $^4J_{HH}$ = 2.3 Hz, calix[5]arene CH), 7.01 (2H, br d, $^4J_{HH}$ = 2.3 Hz, calix[5]arene CH), 7.13 (2H, br s, CH), 7.17 (2H, br d, $^4J_{HH}$ = 2.3 Hz, calix[5]arene CH), 7.23 (2H, br d, $^4J_{HH}$ = 2.3 Hz, calix[5]arene CH), 7.45 (6H, m, PPh CH), 8.30 (4H, m, PPh CH). ^{31}P NMR (CDCl$_3$, δ): 86.4 ($^1J_{PPt}$ = 5520 Hz).

Synthesis of **3·Pd(O$_3$SCF$_3$)$_2$**. Solid silver trifluoromethanesulfonate (0.043 g, 0.17 mmol) was added to a stirred solution of **3·PdCl$_2$** (0.100 g, 0.0833 mmol) in dichloromethane (20 mL). The flask was sealed with a rubber septum and allowed to stir overnight. The mixture was transferred to a centrifuge tube and centrifuged to separate the solids. The solution was decanted into a clean round bottom flask, and the volatiles were removed under vacuum resulting in a brown solid. The crude material was recrystallized by layering pentane on a solution of dichloromethane yielding **3·Pd(O$_3$SCF$_3$)$_2$** as an air- and moisture-stable brown, crystalline solid (0.089 g, 75%). Attempts at elemental analyses were unsuccessful. Spectra are reproduced in the ESI.†

Table 3 Crystallographic data

	3·PdCl$_2$	**3·PtCl$_2$**	**3·Pd(O$_3$SCF$_3$)$_2$**
Empirical formula	$(C_{67}H_{76}Cl_2O_5P_2Pd)\cdot 3(CH_4O)$	$(C_{67}H_{76}Cl_2O_5P_2Pt)\cdot 3(CH_4O)$	$C_{71}H_{80}Cl_4F_6O_{11}P_2PdS_2$
Formula weight	1296.64	1385.33	1597.61
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a, Å	12.421(2)	12.4596(14)	17.467(5)
b, Å	15.899(3)	15.9029(18)	15.883(4)
c, Å	17.188(4)	17.1665(18)	25.891(7)
α, °	97.341(3)	97.391(2)	90
β, °	98.159(3)	98.535(2)	91.334(14)
γ, °	97.589(4)	97.493(3)	90
Volume, Å^3	3293.2(11)	3296.8(6)	7181(3)
Z, Z'	2, 1	2, 1	4, 1
Density (calculated), Mg m^{-3}	1.308	1.396	1.478
Wavelength, Å	0.71073	0.71073	1.54178
Temperature, K	100(2)	100(2)	100(2)
$F(000)$	1364	1428	3296
Absorption coefficient, mm^{-1}	0.465	2.311	5.048
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.9251 and 0.8468	0.5538 and 0.4162	0.7516 and 0.2949
Theta range for data collection, °	2.35 to 25.50	1.64 to 28.31	5.04 to 32.88
Reflections collected	36340	46574	11891
Independent reflections	12001[R(int) = 0.1090]	16310[R(int) = 0.0389]	2560[R(int) = 0.1040]
Data/restraints/parameters	12001/266/771	16310/254/774	2560/638/945
wR(F^2 all data)	wR_2 = 0.1509	wR_2 = 0.0961	wR_2 = 0.1680
R(F obsd data)	R_1 = 0.0674	R_1 = 0.0387	R_1 = 0.0602
Goodness-of-fit on F^2	0.989	1.000	1.069
Observed data [$I > 2\sigma(I)$]	7189	14365	1865
Largest and mean shift/s.u.	0.005 and 0.000	0.002 and 0.000	0.000 and 0.000
Largest diff. peak and hole, e Å^{-3}	0.755 and −0.811	2.671 and −1.181	0.592 and −0.429

wR_2 = $\{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$, $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

^{1}H NMR (CD$_2$Cl$_2$, δ):−0.07 (s, 9H, *t*-Bu), 1.33 (s, 18H, *t*-Bu), 1.35 (s, 18H, *t*-Bu), 3.63 (d, 2H, CH$_2$, $^2J_{HH}$ = 13.5 Hz), 3.80 (d, 1H, CH$_2$, $^2J_{HH}$ = 15.4 Hz), 3.97 (d of t, 2H CH$_2$, $^2J_{HH}$ = 18.5 Hz, $^4J_{PH}$ = 5 Hz), 4.12 (d, 2H, CH$_2$, $^2J_{HH}$ = 13.5 Hz), 4.38 (d, 1H, CH$_2$, $^2J_{HH}$ = 15.4 Hz), 4.75 (d of t, 2H, CH$_2$, $^2J_{HH}$ = 18.5 Hz, $^4J_{PH}$ = 5 Hz), 5.90 (t, 2H, CH, $^3J_{PH}$ = 2 Hz), 7.2–7.6 (overlapping, 12H, CH), 7.66 (m, 4H, CH), 7.90 (d, 2H, CH, $^4J_{HH}$ = 2.3 Hz). ^{31}P NMR (CD$_2$Cl$_2$, δ): 122.

Single crystals of **3·PdCl$_2$** and **3·PtCl$_2$** were obtained by layering methanol on a solution of the compound in dichloromethane. Single crystals of **3·Pd(O$_3$SCF$_3$)$_2$** were obtained by layering pentane on a solution of the compound in dichloromethane. Crystals were mounted in the cold stream of the diffractometer.

Crystal structure determinations

Crystallographic data are summarized in Table 3.

3·PdCl$_2$. The metal complex contained two *t*-butyl groups that were disordered. The occupancies of C19, C20, and C21 refined to 0.796(12) and 0.204(12) for the unprimed and primed atoms; the occupancies of atoms C41, C42, and C43 refined to 0.565 (10) and 0.435(10) for the unprimed and primed atoms. Restraints on the positional and displacement parameters of the disordered atoms were required. Two methanol solvent sites were severely disordered and were best modeled using the Squeeze program.[21]

3·PtCl$_2$. The asymmetric unit of the cell appeared to contain one molecule of the metal complex and three methanol solvent sites. Two of the methanol sites were severely disordered and were best modeled using the Squeeze program.[21] Two of the *t*-butyl groups were disordered. The occupancies for atoms C19, C20, and C21 refined to 0.799(9) and 0.201(9) for the unprimed and primed atoms. The occupancies for atoms C41, C42, and C43 refined to 0.567(8) and 0.433(8) for the unprimed and primed atoms, respectively. Restraints on the positional and displacement parameters of the disordered *t*-butyl groups were required.

3·Pd(O$_3$SCF$_3$)$_2$. The intensity data were truncated to 1.42 Å resolution because data in higher resolution shells all had R_{int} > 0.25. The two methylene chloride groups were disordered. The occupancies for the S molecule refined to 0.668(6) and 0.332(6) for the unprimed and primed atoms. The occupancies for the T molecule refined to 0.619(10) and 0.381(10) for the unprimed and primed atoms. Restraints on the positional and displacement parameters of the disordered atoms and the displacement parameters of all atoms were required.

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