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Luminescent platinum complexes containing phosphorus-linked silole ligands†

Janet Braddock-Wilking,* Li-Bin Gao and Nigam P. Rath

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A series of Pt(II) complexes containing silole-based ligands with diphenylphosphino groups terminally bound to a conjugated organic linker unit coordinated to the silole ring in the 2- or 2,5-positions, 1,1-dimethyl-2-(5′-diphenylphosphino-2′-thienyl)-3,4-diphenylsilole (**4**), 1,1-dimethyl-2,5-bis(5′-diphenylphosphino-2′-thienyl)-3,4-diphenylsilole (**5**), and 1,1-dimethyl-2,5-bis(4′-diphenylphosphinophenyl)-3,4-diphenylsilole (**8**), have been prepared from (cod)PtX$_2$ (X = Cl, Me, C$_2$Ph) precursors. Mononuclear, *cis*-P$_2$PtX$_2$ (P = **4**) complexes **6–7** were produced from silole **4** whereas dinuclear macrocyclic, *cis*-*cis*-X$_2$Pt(P–P)$_2$PtX$_2$ (P–P = **5** or **8**) complexes **9–13** were produced from siloles **5** and **8**. The solid state structure of the dinuclear complex **13** obtained from reaction of (cod)Pt(C$_2$Ph)$_2$ with silole **8**, was confirmed by X-ray crystallography. The optical properties of the siloles and the platinum complexes were studied by UV-vis and fluorescence spectroscopy in solution and were found to exhibit long wavelength absorption and emission bands attributed to the π–π* transitions of the silole core.

Introduction

Silole-based π-conjugated systems have received considerable attention in the past two decades due to their distinctive electronic and photophysical properties arising from a low LUMO energy level due to σ*–π* conjugation between the exocyclic bonds at silicon and the π* orbital of the butadiene unit.[1] Siloles have exhibited high electron mobility[2] and affinity,[3] strong photoluminescence especially in the solid state[4] and thus have shown promise in applications in organic light emitting diodes (OLEDs),[5,6,7] organic field-effect transistors (OFETs),[8] chemical sensors,[7,9] and photovoltaic devices.[10] A number of reviews on the preparation, characterization, and reactivity of siloles and related systems are available.[11]

The design of new organic photovoltaics has witnessed tremendous development in the past few years due to the intense interest in energy and environmental concerns and the need to find inexpensive alternatives to traditional silicon-based solar cells. Organic photovoltaics typically contain a donor–acceptor functionality consisting of a polymer such as poly(3-hexylthiophene) and a soluble fullerene derivative, respectively, which facilitate the separation of the photogenerated excitons.[10] Siloles combined with thiophene units, such as in polymers containing dithienosilole and poly(thienylsilole), show great promise for donor–acceptor materials for photovoltaic applications.[10] Our interest in the unique properties and potential applications of silole-thiophene based molecules and materials for potential applications in OLEDs, OFETs, and photovoltaics led us to study the new phosphine-linked silole-thiophene systems described herein.

A common method employed for the preparation of 2,5-disubstituted-3,4-diphenylsiloles has been the reductive cyclization of bis(phenylethynyl)silanes with lithium naphthalenide followed by subsequent reactions to introduce the functional groups at the 2,5-positions of the ring.[12] Studies have shown that the nature of the exocyclic substituents at the silicon center has a primarily inductive effect whereas the choice of groups at the 2,5-positions of the silole ring can dramatically alter the electronic properties of siloles through strong π-interactions.[13] With an interest in further exploring the electronic properties of silole-based compounds with respect to the nature of the groups bound to the silole ring, our research group has been investigating the incorporation of terminal phosphino and phosphine oxide units linked through π-conjugated organic groups bound to the 2,5-positions of the silole ring. The phosphine groups can be used as donor ligands to a range of transition metal centers and allow for development of a variety of conjugated materials with unique interactions and architectures.

We recently reported the preparation and characterization of a series of 1,1-dimethyl-2,5-disubstituted-3,4-diphenylsiloles containing diphenylphosphino or diphenylphosphine oxide groups bound directly to or linked to the terminal positions of a conjugated organic group bound to the 2,5-positions of the silole ring. A luminescent di(gold) complex, 1,1-dimethyl-2,5-bis(4-diphenylphosphino(chlorogold)phenyl)-3,4-diphenylsilole was produced.[14] The coordination chemistry of related phosphine-substituted oligothiophenes with metals such as platinum,[15,16] palladium,[15, 16, 17] and gold,[18] through coordination of the phosphorus centers resulted in the formation of a number of novel phosphino(oligothiophene)metal complexes. Related 2,5-disubstituted siloles containing 7-azaindolylaryl or 2,2′-dipyridylamino groups containing coordinated zinc centers at the open nitrogen sites have also been reported.[19]

Here we report the preparation, spectroscopic characterization, and coordination chemistry of 1,1-dimethyl-2-(5′-diphenylphosphino-2′-thienyl)-3,4-diphenylsilole (**4**) and 1,1-dimethyl-2,5-bis(5′-diphenylphosphino-2′-thienyl)-3,4-diphenylsilole (**5**). The

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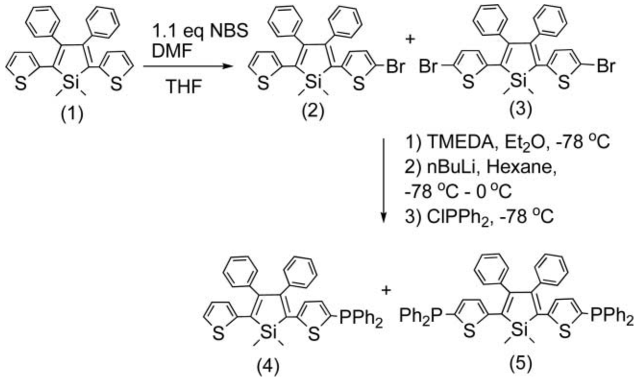
Department of Chemistry and Biochemistry and Center for Nanoscience, University of Missouri-St. Louis, St. Louis, Missouri, 63121, USA. E-mail: wilkingj@umsl.edu

† Electronic supplementary information (ESI) available: Complete listings of geometrical parameters, positional and isotropic displacement coefficients for hydrogen atoms and anisotropic displacement coefficients for the non-hydrogen atoms for complex **13**. CCDC 772326. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0dt00259c

coordination chemistry of these siloles as well as 1,1-dimethyl-2,5-bis(4-diphenylphosphinophenyl)-3,4-diphenylsilole (**8**) with a series of (cod)PtX_2 (X = Cl, Me, C_2Ph) complexes produced either mononuclear, *cis*-P_2PtX_2 (P = **4**) or dinuclear macrocyclic, *cis*-*cis*-$X_2Pt(P–P)_2PtX_2$ (P–P = **5** or **8**) complexes depending upon the silole precursor employed.

Results and discussion

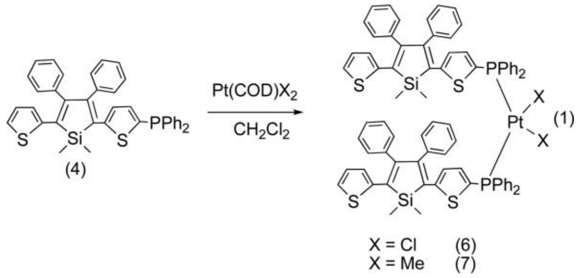
Treatment of 2,5-bis(2′-thienyl)-3,4-diphenylsilole (**1**)[20] with NBS produced a mixture of the mono- and dibromo-substituted thienyl-linked siloles, 1,1-dimethyl-2-(5′-bromo-2′-thienyl)-3,4-diphenylsilole (**2**) and 1,1-dimethyl-2,5-bis(5-bromo-2′-thienyl)-3,4-diphenylsilole (**3**),[21] respectively along with unreacted **1**. Subsequent reaction of the mixture with TMEDA and *n*BuLi followed by diphenylchlorophosphine produced the new silole-thiophene-based phosphine ligands **4** (24% yield) and **5** (17% yield), respectively (Scheme 1). The new complexes described herein were characterized by multinuclear NMR, UV-vis and fluorescence spectroscopy, elemental analysis and X-ray crystallography (**13**).



Scheme 1

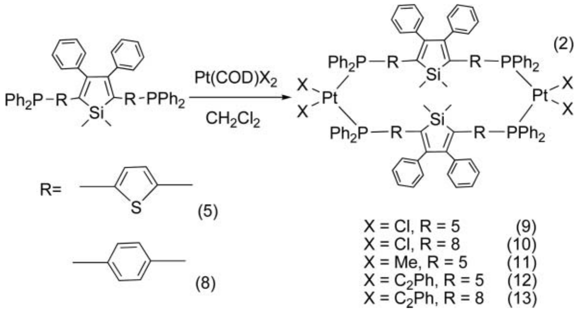
The $^{13}C\{^1H\}$ NMR spectra for **4** and **5** exhibited resonances for the silole and thienyl ring carbon atoms between 133–154 ppm. The $^{29}Si\{^1H\}$ NMR resonances for **4** and **5** were observed at *ca.* 9 ppm and the $^{31}P\{^1H\}$ signals were found upfield of PPh_3[22] at −18 ppm.

The coordination chemistry of **4** and **5** was investigated using the platinum(II) cyclooctadiene complexes, *cis*-(cod)PtX_2 (X = Cl, Me). Reaction of two equivalents of **4** with *cis*-(cod)PtX_2 produced the mononuclear complexes **6** (X = Cl) and **7** (X = Me) as yellow solids in 69 and 73% yields, respectively, as shown in eqn (1).



(1)

Eqn (2) summarizes the reactions of **5** and the related silole **8** (containing a C_6H_4 group linking the silole to the terminal PPh_2 unit), with the corresponding, *cis*-(cod)PtX_2 (X = Cl, Me, C≡CPh) complexes. In all cases, the bimetallic macrocyclic complexes **9–13** were produced as yellow solids in 59–78% yields.



(2)

Complexes **6–7** and **9–13** exhibited $^{31}P\{^1H\}$ NMR resonances with platinum satellites between 4–18 ppm, with the farthest downfield shifts detected for the complexes containing methyl groups bound to the platinum center. Large phosphorus–platinum coupling values were observed for complexes **6**, **9**, and **10** ($^1J_{PtP}$ = 3672–3702 Hz); these values are similar to those observed for the related complexes, *cis*-$(Ph_3P)_2PtCl_2$[23] and *cis*-$Pt(PT_n)_2Cl_2$ (n = 1–3).[15,16] These larger coupling values are generally due to the weak *trans* influence of the chloride ligand *trans* to the phosphorus center. As expected, the stronger *trans* influence ligands, CH_3 and C≡CPh, weaken the phosphorus–platinum coupling in **7** and **11** ($^1J_{PtP}$ = 1858 Hz), as well as **12** and **13** ($^1J_{PtP}$ = 2326–2331 Hz), respectively. The latter coupling values are similar to the values reported for the related complexes, *cis*-$(Ph_3P)_2PtMe_2$[24] and *cis*-$(Ph_3P)_2Pt(C_2Ph)_2$,[25] respectively. The $^{29}Si\{^1H\}$ NMR spectra for the complexes **6–7** and **9–13** exhibit resonances between 8–9 ppm.

UV-vis and emission studies

UV-vis absorption spectra (in CH_2Cl_2 as solutions) for the free ligands (**4**, **5**, and **8**) and the complexes (**6–7**, and **9–13**) are shown in Fig. 1–3. Fig. 1 provides a comparison of the absorption spectra of **4** with the corresponding platinum complexes **6–7**, whereas Fig. 2 shows the absorption spectrum of **5** compared with those of platinum complexes **9**, **11**, and **12**. Fig. 3 provides a comparison of the absorption spectra of **8** with the platinum complexes **10** and **13**.

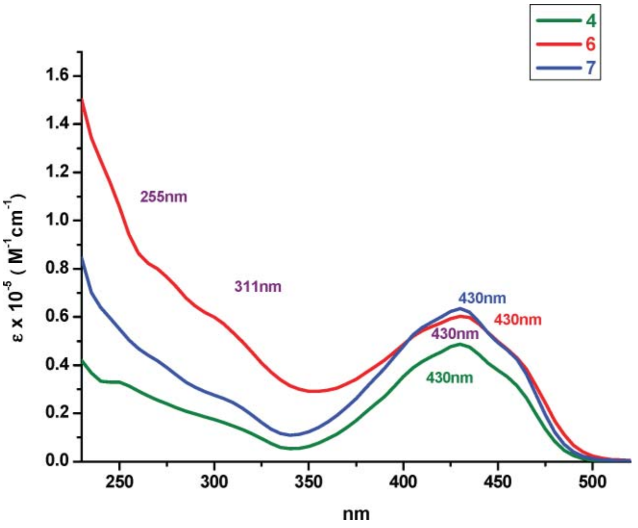


Fig. 1 Electronic absorption spectra of **4**, **6**, and **7** in CH_2Cl_2 at room temperature.

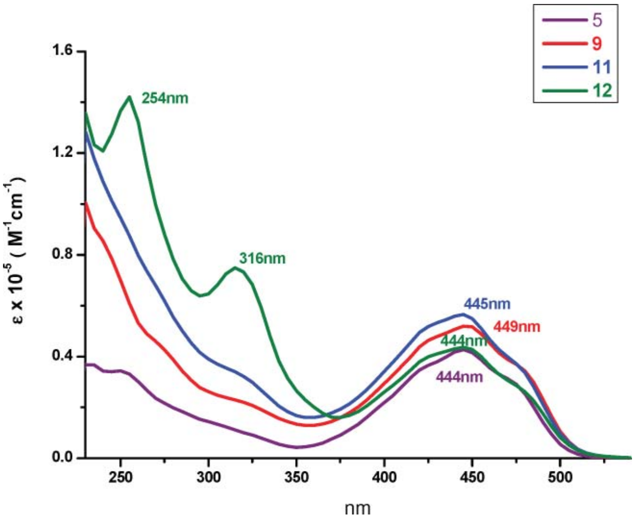


Fig. 2 Electronic absorption spectra of **5**, **9**, **11** and **12** in CH_2Cl_2 at room temperature.

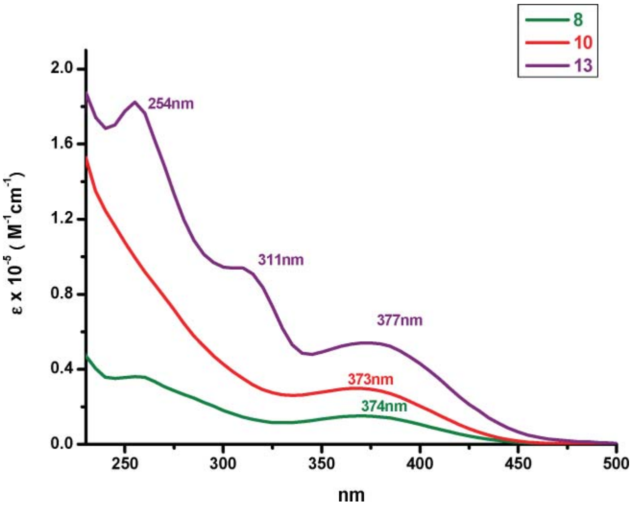


Fig. 3 Electronic absorption spectra of **8**, **10** and **13** in CH_2Cl_2 at room temperature.

All of the spectra in Fig. 1–3 exhibit little change for wavelengths below 350 nm for the free ligands compared to the platinum complexes, except for the bis(phenylethynyl)platinum-containing complexes which show slightly more resolved absorption bands in this region. The prominent long wavelength absorption regions above 350 nm remain essentially unchanged in position but show moderate changes in the intensity of the maxima as displayed in Fig. 1–3. These long wavelength absorption bands near 430, 445, and 375 nm, as observed in Fig. 1, 2, and 3, respectively, are attributed to the π–π* transitions of the silole ring.[26] The shorter wavelength absorption bands observed between 311–316 nm in Fig. 2–3 for complexes **12** and **13** are assigned to the π–π* transitions of the alkyne units.[27] The absorption maximum for *cis*-$Pt(PPh_3)_2(C{\equiv}CPh)_2$ was reported as 314 nm in $CHCl_3$ solution.[28]

A bathochromic shift was observed in the long wavelength absorption bands of the free siloles (**4** and **5**) and the platinum complexes containing one or two thiophene groups (**6–7**, **9**, **11–12**) compared to the silole (**8**) and platinum complexes incorporating the $–(C_6H_4)PPh_2$ units (**10** and **13**) bound to the 2,5-positions of the ring. The unique electronic properties of thiophene-silole based systems have been attributed to the presence of conjugated π-donor thienyl groups in conjunction with electron-accepting silole rings.[29]

Incorporation of thienyl groups in the 2,5-positions of the silole ring in 1,1-dimethyl-3,4-diphenyl-2,5-bis(2-thienyl)silole **A**, resulted in a red-shift of the absorption maximum (418 nm) compared to 1,1-dimethyl-2,3,4,5-tetra(phenyl)silole **B** (359 nm),[20] whereas terthiophene[30] with no silole core exhibits a significant blue-shift in the absorption maximum (353 nm) compared to **A** and **B**. A related bis(diphenylphosphino)dithienosilole, 1,1′-(4,4-diphenyl-4*H*-silolo[3,2-*b*:4,5-*b*′]dithiophene-2,6-diyl)bis[1,1-diphenylphosphine] (**C**) exhibited an absorption maximum at 380 nm and was red-shifted by 35 nm compared to the unsubstituted dithienosilole, further demonstrating the enhanced conjugation effects of the phosphine substituent.[31] Lowering of the LUMO energy levels, as well as red-shifting of the absorption bands in related mono- and diphosphino-substituted thienyl systems relative to the unsubstituted thiophene monomers and oligomers, has also been reported and is due to a bonding interaction between the π-orbitals on the thienyl unit with the phosphorus centers.[32]

The emission spectra recorded for CH_2Cl_2 solutions of compounds **4** and **6–7** are shown in Fig. 4, emission spectra of compounds **5**, **9**, **11**, and **12** in Fig. 5, and emission spectra for compounds **8**, **10**, and **13** in Fig. 6, respectively. The position and intensity of the emission maxima change slightly for the related compounds within each figure, but the most significant difference is in the emission maxima for the different types of silole systems. The shorter wavelength emission maxima are found in Fig. 6 for the siloles containing the $–(C_6H_4)PPh_2$ units bound to the 2,5-positions of the ring and upon replacement of the aryl linker unit with one or two thiophene groups bound to the silole ring, a significant shift to longer wavelength emission is observed. Similar differences were reported for compounds **A** and **B** where the emission maximum for **A** was 515 nm and for **B** the maximum was significantly blue-shifted and observed at 467 nm.[20] The related bis(diphenylphosphino)dithienosilole **C** exhibited a lower energy

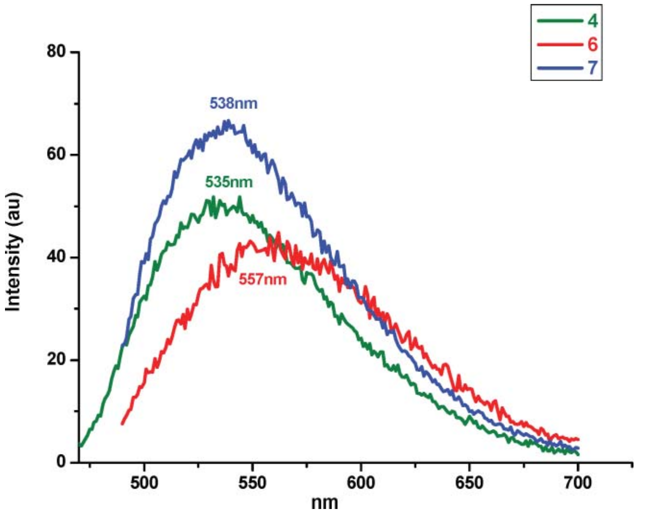


Fig. 4 Emission spectra of **4**, **6**, and **7** in CH_2Cl_2 at room temperature. Excitation wavelengths (nm): **4** (460), **6** (483), **7** (483).

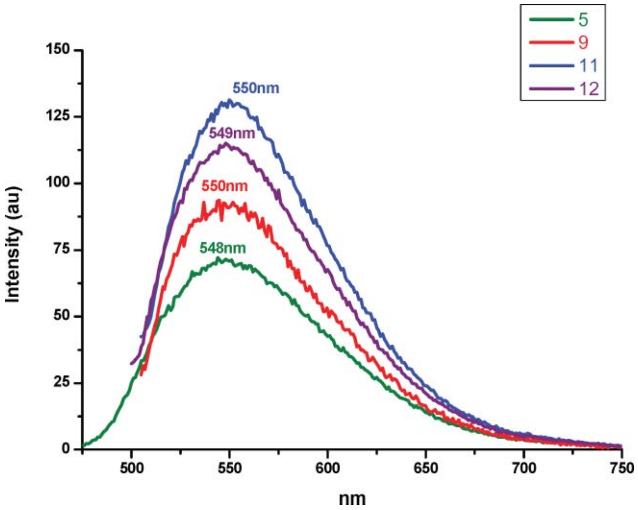


Fig. 5 Emission spectra of **5**, **9**, **11** and **12** in CH_2Cl_2 at room temperature. Excitation wavelengths (nm): **5** (452), **9** (502), **11** (504), **12** (497).

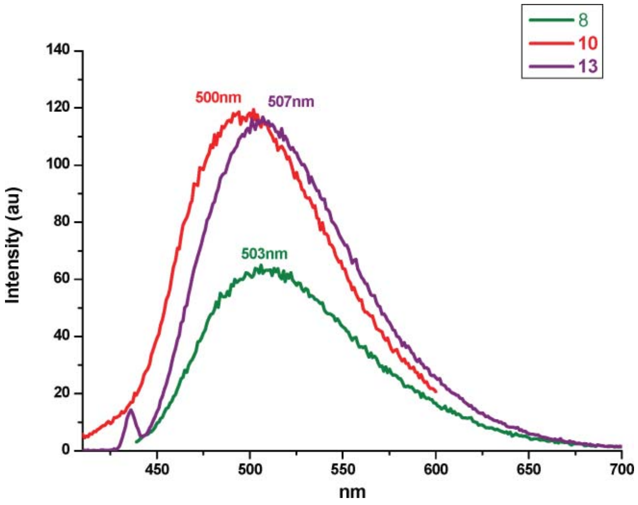


Fig. 6 Emission spectra of **8**, **10** and **13** in CH_2Cl_2 at room temperature. Excitation wavelengths (nm): **8** (429), **10** (427), **13** (435).

emission maximum (465 nm) compared to the unsubstituted dithienosilole (420 nm). Molecular orbital calculations on the model compound **D** containing only hydrogen substituents at both phosphorus and silicon indicated a lower energy LUMO compared to the unsubstituted dithienosilole model complex and the optimized geometry had the phosphine lone pair orbital lying in the same plane as the thiophene unit.[31]

The coordination of the phosphorus centers in **4**, **5**, and **8** to platinum does not significantly change the energy of the absorption and emission maxima as observed in Fig. 1–6. A similar trend was observed for a series of *cis*-$Pt(PT_n)_2Cl_2$ complexes (P = 2-PPh_2, T = thienyl; n = 1–3) where the absorption spectra were dominated by the π–π* transitions for the oligothiophene units and little change in the spectra was observed for the free ligands compared to the platinum complexes, suggesting a minor influence of coordination to the metal center.[15] In contrast, related phosphino(oligothiophene) ligands show an expected bathochromic shift for the π–π* transitions of the thiophene units with chain length, but upon coordination of gold centers to the phosphine units, a hypsochromic shift is observed compared to the free ligand.[33] In addition, these phosphino(oligothiophene) ligands, upon coordination to gold centers, exhibit blue shifts in the emission maxima compared to the free ligand.[32,33] Recently, we prepared a di(gold) complex with the gold centers coordinated to the terminal phosphine sites of ligand **8** and observed a significant blue shift in the emission maximum (416 nm) for the complex compared to the free ligand.[14]

Table 1 Photoluminescent data for compounds **4–13**

Compound	Absorption[a] λ_{abs}/nm	log(ε)	Emission[b] λ_{em}/nm	ϕ_F[c]
4	430	4.68	536	0.41×10^{-2}
5	444	4.63	548	1.42×10^{-2}
6	430	4.78	557	0.30×10^{-2}
7	430	4.80	538	0.61×10^{-2}
8	374	4.18	503	0.69×10^{-2} [d]
9	449	4.71	550	3.35×10^{-2}
10	373	4.46	500	1.28×10^{-2} [d]
11	445	4.75	550	4.54×10^{-2}
12	444	4.63	549	3.77×10^{-2}
13	377	4.73	507	1.24×10^{-2} [d]

[a] Concentration: [M] = 1×10^{-5} M in CH_2Cl_2 at 298 K. [b] Concentration: [M] = 1×10^{-4} M in CH_2Cl_2 at 298 K. [c] Determined with reference to fluorescein. [d] Determined with reference to 9,10-diphenylanthracene.

Table 1 summarizes the photoluminescent data for compounds **4–13**. The moderate photoluminescent quantum efficiencies determined at room temperature in CH_2Cl_2 solution (Table 1) are similar to values reported for other siloles in solution.[20,34] Solid state absorption and emission studies of these and related silole-based ligands and the corresponding platinum complexes described herein are planned.

X-Ray crystallography

The molecular structure of complex **13** was confirmed by X-ray crystallography. Fig. 7 shows the structure of **13** along with selected bond distances and angles. The platinum center adopts a slightly distorted square planar geometry with the two phosphines and the two alkynyl groups in a mutual *cis*-arrangement to each other. The mean plane containing the two phosphorus and two carbon centers bound to platinum exhibits a mean deviation of 0.12 Å from planarity, with the platinum center lying above the plane by 0.048 Å. The P1–Pt–P2 bond angle for the mutually *cis*-phosphines is 99.19(9)°, whereas the angle for the *cis*-phenylethynyl groups, C1–Pt1–C9, is 87.6(4)°. The *cis*-C–Pt–P angles of 84.6(3)–89.2(3)° and the *trans*-P–Pt–C angles of 170.5(3)–171.1(3)° provide further indication of a distorted square planar environment at the metal center. The Pt–C≡C bond angles at the platinum-alkynyl groups are nonlinear at 168.5(8)–170.9(10)°. The Pt–P (2.311(3)–2.318(2) Å) and Pt–C (2.0006(10)–2.013(9) Å) distances of **13** are within the expected range and are similar to the bond distances observed for *cis*-$(Ph_3P)_2Pt(C{\equiv}CPh)_2$[35] and *cis*-$[Pt\{C{\equiv}CC(OH)Me_2\}_2(PPh_3)_2]{\cdot}H_2O$.[28] The bond angles at the platinum centers in the latter two complexes are quite similar, however, some variations are observed for the corresponding angles in **13** but these values are expected based on the constrained geometry of the macrocycle in **13**.[28, 35] The bimetallic platinum centers of **13** exhibit a large Pt···Pt separation of 16.0 Å and a shorter Si···Si separation of 5.2 Å. A related bimetallic

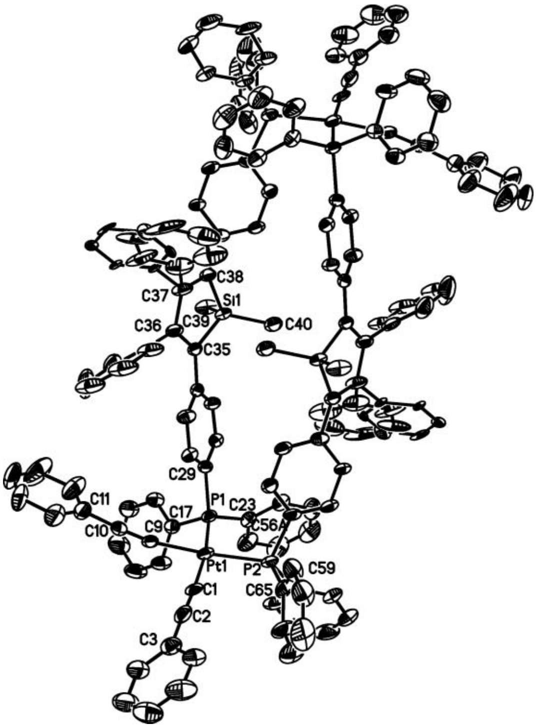


Fig. 7 Molecular structure of complex **13** (with thermal ellipsoids shown at 50% probability level). The H atoms, solvent molecules and disorder atoms are omitted from the figure. Selected bond distances (Å) and angles (°): Pt···Pt = 16.0, Si···Si = 5.2, Pt1–P1 = 2.318(2), Pt1–P2 = 2.311(3), Pt1–C1 = 2.006(10), Pt1–C9 = 2.013(9), P1–C17 = 1.825(10), P1–C23 = 1.832(10), P1–C29 = 1.826(8), P2–C56A = 1.844(9), P2–C59 = 1.820(11), P2–C65 = 1.818(11), Si1–C35 = 1.883(9), Si1–C38 = 1.884(9), Si1–C39 = 1.859(11), Si1–C40 = 1.867(10), C1–C2 = 1.219(14), C2–C3 = 1.441(15), C9–C10 = 1.194(13), C10–C11 = 1.441(14), C35–C36 = 1.353(13), C36–C37 = 1.492(13), C37–C38 = 1.340(14); C1–Pt1–C9 = 87.6(4), P2–Pt1–P1 = 99.19(9), C1–Pt1–P2 = 89.2(3), C9–Pt1–P2 = 170.5(3), C1–Pt1–P1 = 171.1(3), C9–Pt1–P1 = 84.6(3), C17–P1–C29 = 105.2(4), C17–P1–C23 = 101.4(4), C29–P1–C23 = 104.0(4), C17–P1–Pt1 = 111.2(3), C29–P1–Pt1 = 113.3(3), C23–P1–Pt1 = 120.2(3), C65–P2–C59 = 100.4(5), C65–P2–C56A = 103.9(5), C59–P2–C56A = 110.0(5), C65–P2–Pt1 = 116.1(4), C59–P2–Pt1 = 116.2(4), C56A–P2–Pt1 = 109.3(3), C39–Si1–C40 = 110.1(5), C39–Si1–C35 = 113.0(5), C40–Si1–C35 = 113.1(4), C39–Si1–C38 = 111.7(5), C40–Si1–C38 = 116.0(4), C35–Si1–C38 = 92.0(4), C2–C1–Pt1 = 170.9(10), C1–C2–C3 = 177.0(10), C10–C9–Pt1 = 168.5(8), C9–C10–C11 = 176.1(11).

macrocycle containing $PdCl_2$ units linked in a *trans*-arrangement by two 5,5″-bis(diphenylphosphino)-2,2′:5′,2″-terthiophene groups has been recently characterized by X-ray crystallography and was found to exhibit an interplanar separation of approximately 6.3 Å between the nearly parallel terthiophene units.[36] The angles at the palladium center were distorted somewhat from a square planar environment, probably due to ring strain in the macrocycle.

The five-membered silole ring of **13** is essentially planar with a mean deviation of 0.029 Å. The four aryl substituents at the 2, 3, 4, and 5 positions of the silole ring exhibit a non-coplanar propeller type arrangement. The dihedral angles between the aryl groups in the 2,5-substituents and the silole ring in **13** are 21.0 and 32.0°, respectively and are considerably smaller compared to the related complex, 1,1-dimethyl-2,5-bis(4′diphenylphosphinophenyloxide)-3,4-diphenylsilole (**8b**) which exhibited dihedral angles of 41.9–41.6°.[14] The silicon center adopts a distorted tetrahedral geometry with C–Si–C angles of 92.0(4)–116.0(4)°, where the smallest of these angles is found for the endocyclic ring angle, C35–Si–C38. The endo- and exocyclic Si–C distances (1.859(11)–1.883(9) Å) of **13** are similar to those observed for **8b** (1.84–1.87 Å) and other related 1,1-dimethyl-2,3,4,5-tetra(aryl)siloles.[20,37]

Conclusion

The coordination chemistry of 1,1-dimethyl-3,4-diphenylsilole based ligands containing [(5′-diphenylphosphino)-2′-thienyl] units in the 2- or 2,5-positions of the silole ring or (4′-diphenylphosphino) groups in the 2,5-positions of the silole ring has been investigated with $(cod)PtX_2$ (X = Cl, Me, or C_2Ph) precursors to produce either mononuclear *cis*-P_2PtX_2 complexes or macrocyclic dinuclear complexes, *cis*-*cis*-$X_2Pt(P–P)_2PtX_2$. The macrocyclic framework was confirmed for complex **13** by X-ray crystallography. The ligands and the platinum complexes exhibited long wavelength absorption in the region of 350–500 nm and emission maxima near 500–550 nm. The platinum complexes showed little change in the absorption and emission maxima compared to the free ligands, indicating little perturbation in the electronic environment of the ligand with the coordination of the metal center to phosphorus. However, a large difference in the absorption and emission maxima was observed for the [(5′-diphenylphosphino-2′-thienyl)]-based ligands and complexes compared to the (4′-diphenylphosphino)phenyl-based ligands and complexes, where the latter systems were blue shifted by nearly 60 nm and approximately 40 nm, respectively. Future studies involving variations of the choice of the linker groups in the 2,5-positions of the silole ring, the nature of the terminal phosphine units, as well as the metal center and co-ligands should enable us to vary the electronic and structural properties of these unique complexes.

Experimental section

General procedures

Unless otherwise noted, all reactions were carried out under an inert atmosphere of argon or nitrogen using standard Schlenk techniques or a drybox using solvents dried by standard procedures. The following commercially available reagents were purchased from Aldrich and used as received, chlorodiphenylphosphine, n-butyllithium, (2.5 M in hexanes), 2-bromothiophene, TMEDA, and anhydrous $ZnCl_2$. Phenylacetylene, $Pt(cod)Cl_2$ and $Pt(cod)Me_2$ were purchased from Acros Organics. Chloroform-d_1 was purchased from Cambridge Isotopes, Inc., and degassed and dried over activated molecular sieves before use. The following compounds were prepared by literature methods, 1,1-dimethyl-2,5-bis(2′-thienyl)-3,4-diphenylsilole (**1**, TST),[20] dimethylbis(phenylethynyl)silane,[38] 1,1-dimethyl-2,5-bis(5′-bromo-2′-thienyl)-3,4-diphenylsilole (**3**),[39] 1,1-dimethyl-2,5-bis(4′-diphenylphosphinophenyl)-3,4-diphenylsilole (**8**),[14] $Pt(cod)(C{\equiv}C–Ph)_2$.[40] The ^1H, $^{13}C\{^1H\}$, $^{29}Si\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker ARX-500 MHz spectrometer in $CDCl_3$ at room temperature. Proton and carbon NMR chemical shifts (δ) were referenced to the residual peaks of the solvent chloroform-d$_1$. Silicon NMR chemical shifts were referenced to external SiMe$_4$. Phosphorus NMR chemical shifts are referenced relative to external H_3PO_4. Mass spectral data were obtained in EI mode on a JEOL M Station-JMS700. Infrared spectra were recorded on a Thermo-Nicolet Avatar 360 ESP FT-IR spectrometer. UV-vis and fluorescence spectra were recorded on Cary 50 Bio UV-Visible and Cary Eclipse Fluorescence spectrophotometers, respectively. Emission spectra were measured using the λ_{max} value for each compound obtained from the absorption spectra and also by the computer optimized excitation energy resulting in spectra of identical shape and position but with differing intensity. Elemental analysis determinations were obtained from Atlantic Microlabs, Inc., Norcross, GA. X-Ray crystallographic determinations were performed on a Bruker Apex II diffractometer equipped with a CCD area detector.

(1,1-Dimethyl-5-thienyl-2-(5′-bromo-2′-thienyl)-3,4-diphenylsilole (TSTBr, 2) and 1,1-dimethyl-2,5-bis(5′-bromo-2′-thienyl)-3,4-diphenylsilole (BrTSTBr, 3)[39]

To a solution of 1,1-dimethyl-2,5-bis(2′-thienyl)-3,4-diphenylsilole (**1**, 1.6 g, 3.7 mmol) in THF (15 mL) was added dropwise a solution of NBS (0.73 g, 4.1 mmol) in 5 mL of anhydrous DMF. The mixture was stirred at room temperature for 15 min in the dark then poured into 100 mL of water. The organic material was extracted with CH_2Cl_2 (2 × 100 mL), washed with water (3 × 50 mL) and brine (50 mL) then the organic layer was dried over anhydrous $MgSO_4$. After filtration and evaporation of the solvents, the crude product mixture was subjected to silica gel column chromatography (hexane–CH_2Cl_2 = 5 : 1) to give a mixture of **1**, **2** and **3**.

1,1-Dimethyl-5-thienyl-2-(5′-diphenylphosphino-2′-thienyl)-3,4-diphenylsilole (4) and 1,1-dimethyl-2,5-bis(5′-diphenylphosphino-2′-thienyl)-3,4-diphenylsilole (5)

To the solution mixture of **1**, **2** and **3** from above in diethyl ether (100 mL) was added TMEDA (1.2 mL, 7.8 mmol). The mixture was cooled to −78 °C and a solution of n-butyllithium (2.5 M in hexanes, 2.9 mL, 7.4 mmol) was then added dropwise. The mixture was stirred for 90 min and then warmed to 0 °C, stirred for 1 h, then recooled to −78 °C. A diethyl ether (5 mL) solution of chlorodiphenylphosphine (1.6 g, 5.2 mmol) was added dropwise, and stirred at −78 °C for 1 h. The mixture was allowed to warm to rt and stirred overnight. The solvent was removed under vacuum and the residue mixture was subjected to silica gel column chromatography with neat hexane to remove **1**, followed by hexane–dichloromethane (5 : 1) to provide **4** as a yellow powder (0.56 g, 24% based on TST), followed by hexane–dichloromethane (3 : 1) to provide **5** as a yellow powder (0.5 g, 17% based on TST).

Compound **4**. Mp: 190–191 °C; ^{1}H NMR (500 MHz): δ 7.28–7.19 (m, 14H, ArH), 7.16–7.09 (m, 4H, ArH), 7.04–6.99 (m, 4H, ArH), 6.98–6.97 (m, 1H, thienyl H), 6.96–6.92 (m, 3H, thienyl H), 6.88–6.85 (m, 2H, ArH), 6.84–6.82 (m, 2H, ArH), 6.79–6.77 (m, 1H, thienyl H), 0.63 (s, 6H, SiMe). ^{13}C{^{1}H} NMR (125 MHz): δ 154.0, 152.7, 149.5, 142.9, 139.2, 138.8, 138.0 (d, J_{PC} = 8 Hz), 137.6, 137.4, 135.6, 135.5, 133.3 (d, J_{PC} = 19 Hz), 132.3, 131.5, 129.7, 129.4, 128.8, 128.6 (d, J_{PC} = 10 Hz), 128.5 (d, J_{PC} = 7 Hz), 127.7 (d, J_{PC} = 7 Hz), 127.4 (d, J_{PC} = 10 Hz), 127.2, 126.4, 126.1, −1.7. ^{29}Si{^{1}H} NMR (99 MHz, DEPT): δ 9.1. ^{31}P{^{1}H} NMR (202 MHz): δ −18.8. HRMS (EI): *m*/*z* calcd for $C_{38}H_{31}PS_2Si$, 610.1374; found, 610.1381. Anal. Calcd for $C_{38}H_{31}PS_2Si$: C, 74.72; H, 5.12. Found: C, 74.52; H, 5.04.

Compound **5**. Mp: 188–190 °C; ^{1}H NMR (500 MHz): δ 7.37–7.22 (m, 25H, ArH), 7.10–7.04 (m, 7H, ArH), 7.02–6.93 (m, 2H, thienyl H), 6.93–6.88 (m, 4H, ArH), 6.85–6.82 (m, 2H, thienyl H), 0.67 (s, 6H, SiMe). ^{13}C{^{1}H} NMR (125 MHz): δ 153.9, 149.4, 138.8, 137.96 (d, J_{PC} = 9 Hz), 137.89 (d, J_{PC} = 26 Hz), 135.5 (d, J_{PC} = 23 Hz), 133.3 (d, J_{PC} = 19 Hz), 132.1, 129.4, 128.8, 128.6, 128.5 (d, J_{PC} = 7 Hz), 127.9 (d, J_{PC} = 6 Hz), 127.5, −1.7. ^{29}Si{^{1}H} NMR (99 MHz, DEPT): δ 8.9. ^{31}P{^{1}H} NMR (202 MHz): δ −18.8. HRMS (EI): *m*/*z* calcd for $C_{50}H_{40}P_2S_2Si$, 794.1815; found, 794.1831. Anal. Calcd for $C_{50}H_{40}P_2S_2Si$: C, 75.54; H, 5.07. Found: C, 75.07; H, 5.09.

General procedures for the synthesis of complexes (6–7; 9–13).

The appropriate phosphine ligands, dissolved in CH_2Cl_2 (5 mL) were added to a solution of Pt(cod)X_2 in CH_2Cl_2 (5 mL). The reaction mixture was stirred overnight at room temperature and the solvent then removed under vacuum. The resulting solid residue was dissolved in a minimum amount of CH_2Cl_2, and precipitated with 20 mL of hexanes. The precipitate was collected by filtration, washed with hexanes (3 × 15 mL) and dried under vacuum.

Preparation of compound 6. Compound **6** was prepared by the general procedure described above using **4** (100 mg, 0.16 mmol) and Pt(cod)Cl_2 (30.6 mg, 0.08 mmol). After purification, 82.1 mg (0.055 mmol) of **6** obtained in 69% yield as a yellow solid. ^{1}H NMR (500 MHz): δ 7.47–7.42 (m, 2H, thienyl H), 7.18–7.02 (m, 25H, ArH), 6.98–6.90 (m, 19H, ArH), 6.89–6.84 (m, 5H, ArH), 6.81–6.74 (m, 9H, ArH/thienyl H), 6.58 (m, 2H, thienyl H), 0.57 (s, 12H, SiMe). ^{29}Si{^{1}H} NMR (99 MHz, DEPT): δ 9.3. ^{31}P{^{1}H} NMR (202 MHz): δ 4.7 (s, J_{PtP} = 3696 Hz). Anal. Calcd for $C_{76}H_{62}Cl_2P_2PtS_4Si_2$: C, 61.36; H, 4.20. Found: C, 61.36; H, 4.24.

Preparation of compound 7. Compound **7** was prepared by the general procedure described above using **4** (100 mg, 0.16 mmol) and Pt(cod)Me_2 (26.6 mg, 0.08 mmol). After purification, 84.5 mg (0.058 mmol) of **7** was obtained in 73% yield as a yellow solid. ^{1}H NMR (500 MHz): δ 7.37–7.30 (m, 2H, thienyl H), 7.22–7.13 (m, 24H, ArH), 7.11–7.07 (m, 6H, ArH), 7.06–6.89 (m, 17H, thienyl H/ArH), 6.95–6.85 (m, 11H, ArH), 6.65 (m, 2H, thienyl H), 0.69 (s, 12H, SiMe), 0.37 (t, 6H, J_{PtH} = 70 Hz, J_{PH} = 15, PtMe). ^{29}Si{^{1}H} NMR (99 MHz, DEPT): δ 9.0. ^{31}P{^{1}H} NMR (202 MHz): δ 18.1 (s, J_{PtP} = 1858 Hz). Anal. Calcd for $C_{78}H_{68}P_2PtS_4Si_2$: C, 64.75; H, 4.74. Found: C, 64.83; H, 4.89.

Preparation of compound 9. Compound **9** was prepared by the general procedure described above using **5** (100 mg, 0.12 mmol) and Pt(cod)Cl_2 (47.8 mg, 0.12 mmol). After purification, 84.7 mg (0.04 mmol) of **9** was isolated as a yellow solid in 68% yield. ^{1}H NMR (500 MHz): δ 7.65–7.52 (m, 4H, thienyl H), 7.37–7.18 (m, 26H, overlapping with solvent), 7.14–7.00 (m, 36H, ArH), 6.90–6.81 (m, 10H, ArH), 6.73–6.67 (m, 4H, thienyl H), 0.65 (s, 12H, SiMe). ^{29}Si{^{1}H} NMR (99 MHz, DEPT): δ 9.3. ^{31}P{^{1}H} NMR (202 MHz): δ 4.8 (s, J_{PtP} = 3702 Hz). Anal. Calcd for $C_{100}H_{80}Cl_4P_4Pt_2S_4Si_2$: C, 56.60; H, 3.80. Found: C, 56.37; H, 4.39.

Preparation of compound 10. Compound **10** was prepared by the general procedure described above using **8** (100 mg, 0.12 mmol) and Pt(cod)Cl_2 (47.8 mg, 0.12 mmol). After purification, 95.6 mg (0.045 mmol) of **10** was obtained as a yellow solid in 76% yield. ^{1}H NMR (500 MHz): δ 7.40–7.22 (m, 32H, ArH overlapping with solvent), 7.19–6.91 (m, 30H, ArH), 6.84–6.70 (m, 14H, ArH), 0.43 (s, 12H, SiMe). ^{29}Si{^{1}H} NMR (99 MHz, DEPT): δ 8.6. ^{31}P{^{1}H} NMR (202 MHz): δ 13.8 (s, J_{PtP} = 3672 Hz). Anal. Calcd for $C_{108}H_{88}Cl_4P_4Pt_2Si_2$: C, 61.83; H, 4.23. Found: C, 61.65; H, 4.64.

Preparation of compound 11. Compound **11** was prepared by the general procedure described above using **5** (100 mg, 0.12 mmol) and Pt(cod)Me_2 (40.0 mg, 0.12 mmol). After purification, 79.5 mg (0.039 mmol) of **11** was obtained as a yellow solid in 65% yield. ^{1}H NMR (500 MHz): δ 7.59–7.25 (m, 8H, thienyl H/ArH overlapping with solvent), 7.14–6.90 (m, 68H, ArH), 6.72–6.63 (m, 4H, thienyl H), 0.64 (s, 12H, SiMe), 0.36 (s, 12H, J_{PtH} = 70 Hz, PtMe). ^{29}Si{^{1}H} NMR (99 MHz, DEPT): δ 8.6. ^{31}P{^{1}H} NMR (202 MHz): δ 18.1 (s, J_{PtP} = 1858 Hz). Anal. Calcd for $C_{104}H_{92}P_4Pt_2S_4Si_2$: C, 61.22; H, 4.54. Found: C, 61.50; H, 4.67.

Preparation of compound 12. Compound **12** was prepared by the general procedure described above using **5** (100 mg, 0.12 mmol) and Pt(cod)$(C_2Ph)_2$ (60.6 mg, 0.12 mmol). After purification, 84.4 mg (0.035 mmol) of **12** was obtained as a yellow solid in 59% yield. ^{1}H NMR (500 MHz): δ 7.41 (m, 4H, thienyl H), 7.38–7.16 (m, 16H, ArH), 7.12–6.94 (m, 24H, ArH), 6.88–6.76 (m, 18H, ArH), 6.63–6.56 (m, 4H, thienyl H), 0.55 (s, 12H, SiMe). ^{29}Si{^{1}H} NMR (99 MHz, DEPT): δ 8.6. ^{31}P{^{1}H} NMR (202 MHz): δ 7.8 (s, J_{PtP} = 2326 Hz). IR (NaCl, cm^{-1}): 2120 ν(C≡C). Anal. Calcd for $C_{132}H_{100}P_4Pt_2S_4Si_2$: C, 66.48; H, 4.23. Found: C, 66.93; H, 5.03.

Preparation of compound 13. Compound **13** was prepared by the general procedure described above using **8** (100 mg, 0.12 mmol) and Pt(cod)$(C_2Ph)_2$ (60.6 mg, 0.12 mmol). After purification, 110.4 mg (0.046 mmol) of **13** was obtained as a yellow solid in 78% yield. ^{1}H NMR (500 MHz): δ 7.40–7.29 (m, 20H, ArH), 7.25–7.17 (m, 10H, ArH), 7.13–6.90 (m, 36H, ArH), 6.85–6.68 (m, 20H, ArH), 0.38 (s, 12H, SiMe). ^{29}Si{^{1}H} NMR (99 MHz, DEPT): δ 8.3. ^{31}P{^{1}H} NMR (202 MHz): δ 16.0 (s, J_{PtP} = 2331 Hz). IR (NaCl, cm^{-1}): 2121 ν(C≡C). Anal. Calcd for $C_{140}H_{108}P_4Pt_2Si_2$: C, 71.23; H, 4.61. Found: C, 71.00; H, 4.65.

X-Ray experimental for 13. X-Ray diffraction quality crystals of **13** were obtained by slow evaporation from a solution of CH_2Cl_2. A crystal with approximate dimensions of 0.51 × 0.30 × 0.1 mm^3 was mounted on a Mitgen loop in a random orientation. Preliminary examination and data collection were performed using a Bruker Kappa Apex II charge coupled device (CCD) detector system single crystal X-ray diffractometer equipped with an Oxford Cryostream LT device. Data were collected using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) from a fine focus sealed tube X-ray source. Preliminary unit cell constants were determined with a set of 36 narrow frame scans. Typical data sets consist of combinations of ϖ and ϕ scan frames with typical scan width of 0.5° and counting time of 15–30 s/frame at a crystal to detector distance of 4.0 cm. The collected frames were integrated using an orientation matrix determined from the narrow frame scans. Apex II and SAINT software packages were used for data collection and data integration.[41] Analysis of the integrated data did not show any decay. Final cell constants were determined by global refinement of reflections from the complete data set. Collected data were corrected for systematic errors using SADABS[41] based on the Laue symmetry using equivalent reflections.

Table 2 Crystallographic data and structure refinement for **13**

Formula	$C_{146}H_{118}Cl_{18}O_2P_4Pt_2Si_2$
FW	3112.74
Cryst. size/mm	0.51 × 0.30 × 0.11
Cryst. syst.	Monoclinic
Space group	$P2_1/c$
a/Å	22.261(4)
b/Å	14.057(3)
c/Å	22.741(4)
α/°	90
β/°	98.290(7)
γ/°	90
V/Å^3	7042(2)
D_c/g cm^{-3}	1.468
Z	2
μ/mm^{-1}	2.439
θ range/°	2.59 to 27.60
Reflns collected/indep. reflns	157483/16137 [R(int) = 0.1008]
Abs. correct	Numerical
Max. and min. transm.	0.7752 and 0.3704
Final R indices [$I > 2\sigma(I)$]	0.0761
R indices wR_2 (all data)	0.2280
Largest diff. peak and hole/e Å^{-3}	3.332 and −3.139

Crystal data and intensity data collection parameters are listed in Table 2.

Structure solution and refinement were carried out using the SHELXTL-PLUS software package.[42] The structure was solved by direct methods in monoclinic space groups $P2_1/c$ and refined with full matrix least-squares refinement by minimizing $\Sigma w(F_o^2 - F_c^2)^2$. All non-hydrogen atoms were refined anisotropically to convergence. One of the phenyl rings is disordered over two positions. This disorder was resolved with 50% occupancy atoms. Several solvent molecules were found in the lattice. The solvents were modeled as 2.5 $CHCl_3$ and 3.25 H_2O molecules and were resolved with two orientations of 50% occupancy models. All H atoms were added in the calculated position and were refined using appropriate riding models (AFIX m3). The model was refined to convergence to the final residual values of R_1 = 7.1% and wR_2 = 22.2%.

Complete listings of geometrical parameters, positional and isotropic displacement coefficients for hydrogen atoms, and anisotropic displacement coefficients for the non-hydrogen atoms are submitted as ESI (Tables S1–S5†). A table of calculated and observed structure factors is available in electronic format.

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