Inorganica Chimica Acta 423 (2014) 152–162

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Platinum complexes with the SC_6F_4H-4 ligand – Synthesis, structures and spectroscopy

Verena Lingen [a,b], Anna Lüning [a], Christian Strauß [a], Ingo Pantenburg [a], Glen B. Deacon [b,*], Gerd Meyer [a], Axel Klein [a,*]

[a] Universität zu Köln, Department für Chemie, Institut für Anorganische Chemie, Greinstrasse 6, D-50939 Köln, Germany
[b] School of Chemistry, Monash University, PO Box 23, VIC 3800, Australia

ARTICLE INFO

Article history:
Received 11 July 2014
Received in revised form 23 July 2014
Accepted 29 July 2014
Available online 13 August 2014

Keywords:
Platinum
Perfluoro thiophenolate ligands
XRD
^{195}Pt NMR spectroscopy
Electrochemistry

ABSTRACT

The reaction of HSC_6F_4H-4 and base with suitable platinum(II) chlorido precursor complexes leads to mononuclear complexes containing diimine ligands [(N^N)Pt(SC_6F_4H-4)$_2$], or [(N^N)Pt(Me)(SC_6F_4H-4)] (N^N = 2,2′-bipyridine (bpy), dipyrido[3,2-*a*:2′,3′-*c*]phenazine (dppz) or 11-trifluoromethyl-dipyrido[3,2-*a*:2′,3′-*c*]phenazine (CF_3dppz)), cycloocta-1,5-diene (COD) complexes [(COD)Pt(SC_6F_4H-4)$_2$] or [(COD)Pt(R)(SC_6F_4H-4)] (R = Me, Bn (benzyl) or C_6F_5), or phosphine complexes *cis*-[(PPh_3)$_2$Pt(SC_6F_4H-4)$_2$], [(dppe)Pt(SC_6F_4H-4)$_2$] (dppe = 1,2-bis(diphenylphosphino)ethane) and [(dppb)Pt(C_6F_5)(SC_6F_4H-4)] (dppb = 1,4-bis(diphenylphosphino)butane). Reaction of *cis*-[(DMSO)$_2$PtCl$_2$] lead to the labile *cis*- and *trans*-[(DMSO)$_2$Pt(SC_6F_4H-4)$_2$] which rapidly lose DMSO to yield polymeric [Pt(SC_6F_4H-4)$_2$]$_m$. Reaction of HSC_6F_4H-4 and KO*t*Bu with K_2PtCl_4 gave K_2[Pt(SC_6F_4H-4)$_4$]. The new compounds were analysed and characterised by single crystal XRD, ^{1}H, ^{19}F and ^{195}Pt NMR and IR spectroscopy. Both single crystal XRD (in the solid) and NMR (in solution) reveal that the ligand strength of the thiolate ligand $^-SC_6F_4H$-4 strongly depends on the further ligands in the complexes. The crystal structures exhibit various inter- and intra molecular π stacking interactions of the SC_6F_4H-4 coligands. The absorption spectroscopy and electrochemistry of the diimine complexes [(N^N)Pt(SC_6F_4H-4)$_2$] (N^N = bpy, dppz and CF_3dppz) have been investigated and reveal that the Pt complexes are superior to the recently reported Pd derivatives in view of their application in photoactive materials.

1. Introduction

Although perfluoroarylthiolato-(perfluorothiophenolato)-platinum complexes have been described [1–6] from as early as their non-fluorinated counterparts, namely in the 1960s [7–11], the latter have found considerable application in luminescent materials [12–19], some minor interest in catalysis [20,21], as single source precursors in CVD [22] and as DNA intercalators [23,24], whereas almost no applications have been reported for the perfluorinated derivatives. A reasonable explanation for the use of non-fluorinated complexes over perfluorinated derivatives, is that the arylthiolate ligands represent an efficient electron-donor component in the charge-transfer photophysics of such complexes. Thus, in the photo-excited states of the established platinum diimine complexes [(N^N)Pt($SR)_2$] (N^N = diimine, e.g. 2,2′-bipyridine (bpy); R = aryl) [12,14,16,17,19] charge (electron density) has been moved from both the thiolate coligand and Pt d orbitals to the diimine π accepting ligand (mixed $L_{(S)}L'_{(N^N)}CT/M_{(Pt)}L_{(N^N)}CT$ transitions). The same is true for the related and even more important diimine arenedithiolato platinum complexes [(N^N)Pt(S_2R)] (S_2R = arenedithiolates, such as 1,2-benzenedithiolate or 4-toluene-1,2-dithiolate) [12,25]. A closer look reveals that electron-donating substituents on the ^-SR ligand decrease the charge transfer energy, while electron-withdrawing groups lead to higher CT energies [12,13,26,27]. Furthermore, aryldithiolate complexes [(N^N)Pt(S_2-R)] generally exhibit lower CT energies than bis(arylthiolate) complexes [(N^N)Pt($SR)_2$] [12,13]. Even superior in this respect are corresponding ethene-dithiolate or ethane-dithiolate complexes [12,13,25]. For all these reasons, diimine Pt complexes with perfluoroarylthiolate coligands have not been studied widely [27], nor have they been used in luminescent materials. On the other hand, as has been pointed out by Weinstein et al., the higher energy of the excited state goes along with a longer lifetime, in line with the energy gap law [12,27]. For other applications, the differences

* Corresponding authors.
E-mail addresses: glen.deacon@monash.edu (G.B. Deacon), axel.klein@uni-koeln.de (A. Klein).
URLs: http://monash.edu/science/about/schools/chemistry/staff/deacon.html (G.B. Deacon), http://www.klein.uni-koeln.de (A. Klein).

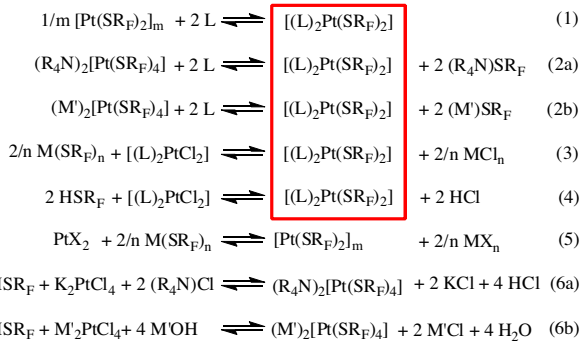
http://dx.doi.org/10.1016/j.ica.2014.07.058
0020-1693/

of perfluorinated complexes compared with non-fluorinated derivatives are less clear. Generally the electron-withdrawing fluorine substituents should stabilise these complexes compared with those of the $^{-}$SPh ligand.

As expected from the soft character of arylthiolate ligands [Pt(SR)] or [Pt(SR)$_2$] moieties are very stable and thus frequently used as building blocks in coordination chemistry [16,18,28]. For perfluoroaryl (SR$_F$) derivatives the combination with good to excellent π-accepting ligands, such as phosphines [1–4,6,29–32], imines [27,33,34], thioethers [35], and COD (COD = cycloocta-1,5-diene) [36,37], is favourable, while complexes of weaker ligands as allyl or amines have not been reported. Interestingly, the complexes [(COD)Pt(SR$_F$)$_2$] (SR$_F$ = SC$_6$F$_5$, SC$_6$F$_4$H-4, SC$_6$F$_4$(CF$_3$)-4, are quite stable [36,37] and thus may be used as precursor complex for further platinum complexes, while no corresponding palladium complex has been reported and allyl-, amine-, or thioether-palladium complexes are also scarce [38].

For the synthesis of mononuclear complexes of both Pd and Pt with arylthiolate ligands of the type [(L)$_2$M(SR)$_2$] (Scheme 1), a frequently encountered problem is the formation of insoluble polymers [M(SR)$_2$]$_m$ [1–3] or oligonuclear complexes [7,31,35,38,39]. This tendency is slightly lower for perfluorinated ligands $^{-}$SR$_F$ compared with non-fluorinated derivatives $^{-}$SR and slightly lower for Pd compared with Pt. As a consequence, the first [Pt(SR)$_2$] complexes carrying non-fluorinated coligands $^{-}$SR were dimeric [7,9] and mononuclear complexes were first prepared from suitable mononuclear precursor complexes (e.g. azido complexes) [8], by oxidative *cis*-addition of corresponding disulfides RS–SR [9], using chelating phosphines [10], or very bulky thiolates [11]. In contrast to this, mononuclear complexes containing perfluorinated arylthiolate ligands SR$_F$ and monodentate phosphine ligands were reported early [3,4], and complexes of chelate ligands can be readily prepared [4,6,26,27,29c,30,31a,31c,32–34,35a,36b,39c].

Several routes to mononuclear Pt perfluoroarylthiolate complexes of the composition [(L)$_2$Pt(SR$_F$)$_2$] have been described. They can be divided into different reaction types (Scheme 1). The oldest reported method (reaction 1 in Scheme 1) is the conceptually simplest [2–4], but disadvantages lie in the use of the still not fully characterised polymeric [Pt(SR$_F$)$_2$]$_m$ starting materials, which have to be prepared from Pt^{II} salts and suitable thiolates M(SR$_F$)$_n$ (M = main group metal) (reaction 5) [1–3,5]. These polymers are almost insoluble, hence their use in synthesis of complexes requires prolonged reaction times or harsh reaction conditions. Furthermore, often product mixtures are obtained. In contrast to this, reaction (2) proceeds very smoothly and the products can be easily separated [3]. However, the method requires the preparation of the corresponding tetraalkylammonium, sodium or potassium salts (A)$_2$[Pt(SR$_F$)$_4$] (A = Bu$_4$N, Et$_4$N, Na or K) (reactions 6a and 6b) [1–3] and results in a loss of two equivalents of $^{-}$SR$_F$. Here, the formation of oligomeric by-products may be a problem. Reaction (3) largely avoids this disadvantage but uses the toxic compounds Tl(SR$_F$) [31,34], Pb(SR$_F$)$_2$ [6,29,33,35–37], and SnPh$_2$(SR$_F$)$_2$ [30], which have to be prepared in separate steps. For all these reasons the direct reaction (4), starting from HSR$_F$ and chlorido precursor complexes is superior but usually requires a stable complex scaffold [(chelate ligand)Pt] to yield monomeric and stereochemically defined products [32]. Another advantage is that the necessary preparation of the precursor complexes [(L)$_2$PtCl$_2$] is usually extremely simple, e.g. the reaction of K$_2$PtCl$_4$ with many chelate ligands such as 2,2′-bipyridine (bpy) [40], 1,2-bis(diphenylphosphino)ethane (dppe) [41], or 1,5-cyclooctadiene (COD) [42] proceeds smoothly with very high yields.



Scheme 1. Preparative routes to perfluorothiolato Pt^{II} complexes (L = one monodentate or half a bidentate ligand; R$_F$ = perfluoroaryl).

We became interested in the preparation of polyfluoroarylthiolate complexes [(N^N)Pt(SC$_6$F$_4$H-4)$_2$] with the S(C$_6$F$_4$H-4) thiolate and α-diimine ligands such as 2,2′-bipyridine (bpy), or dipyrido[3,2-*a*:2′,3′-*c*]phenazine (dppz) (Scheme 2) and explored the reactions 3 and 4, starting from the corresponding dichlorido complexes and KSC$_6$F$_4$H-4 or HSC$_6$F$_4$H-4 (in the presence of base). As alternatives, we sought a "one-pot method" for the preparation of these complexes from suitable simple Pt precursors such as K$_2$PtCl$_4$ or [(DMSO)$_2$PtCl$_2$] and replacement reactions of the previously reported precursor complex [(COD)Pt(SC$_6$F$_4$H-4)$_2$] [36] with N^N ligands. In this contribution we report on the preparation of the diimine complexes [(bpy)Pt(SC$_6$F$_4$H-4)$_2$], [(bpy)Pt(Me)(SC$_6$F$_4$H-4)] and [(dppz)Pt(SC$_6$F$_5$H-4)$_2$] from their chlorido precursor complexes (route 3). In the same way we also prepared the COD complexes, [(COD)PtCl(SC$_6$F$_4$H-4)], [(COD)Pt(Me)(SC$_6$F$_4$H-4)], [(COD)Pt(Bn)(SC$_6$F$_4$H-4)] (Bn = benzyl) and some phosphine Pt complexes. We were able to crystallise many of these compounds suitably for X-ray crystallography. We also report the preparation and crystal structure of K$_2$[Pt(SC$_6$F$_4$H-4)$_4$] prepared from K$_2$PtCl$_4$ and HSC$_6$F$_4$H-4. Furthermore, the absorption spectroscopy and electrochemistry of the diimine complexes [(N^N)Pt(SC$_6$F$_4$H-4)$_2$] (N^N = bpy, dppz or CF$_3$dppz) were investigated and compared with corresponding reported data for the related Pt complexes [(bpy)Pt(SC$_6$F$_5$)$_2$], [(bpy)Pt(SC$_6$F$_4$(CN)-4)$_2$] and [(bpy)Pt(SC$_6$H$_5$)$_2$] [26,27]. The use of dppz (dipyrido[3,2-*a*:2′,3′-*c*]phenazine) and its 11-CF$_3$ derivative (CF$_3$dppz) was motivated by the intriguing properties of dppz, which combines the coordination properties of bpy with the excellent electron-accepting properties of phenazine (phz, Scheme 2) [43–45].

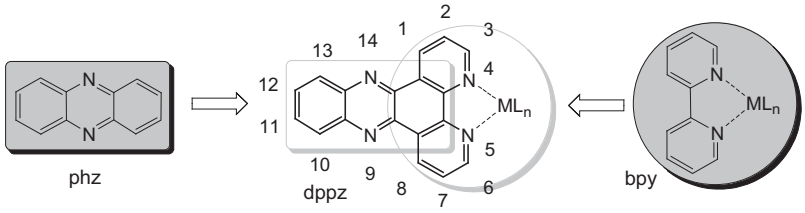
2. Experimental

2.1. General information

Commercially available reagents from Apollo or Alfa Aesar were used without further purification. Acetone was dried over molecular sieves and distilled. All reactions and measurements involving metal complexes were conducted under argon, using standard Schlenk techniques. The solid products were air-stable. The ligands dppz and CF$_3$dppz [43], the potassium thiolate KSC$_6$F$_4$H-4 [46] and the complexes [(COD)PtCl$_2$] [42], [(COD)Pt(Me)Cl] [42], [(bpy)PtCl$_2$] [40], [(dppz)PtCl$_2$] (as for the bpy derivative) [40], [(dppe)PtCl$_2$] [41], [(dppb)PtCl$_2$] [41a], [(dppb)Pt(C$_6$F$_5$)Cl] [47], *cis*-[(PPh$_3$)$_2$PtCl$_2$] [48], and [(DMSO)$_2$PtCl$_2$] [49], were obtained according to literature procedures.

2.2. Instrumentation

The NMR spectra were recorded on a Bruker Avance II 300 MHz (^{1}H: 300.13 MHz, ^{19}F: 282.23 MHz) using a triple resonance ^{1}H, ^{19}F, BB inverse probehead. The broad band coil was tuned to the platinum frequency and the detection coil to the proton frequency, resulting in 90° pulses of 12.5 μs for ^{195}Pt and 12.4 μs for ^{1}H. The unambiguous assignment of the ^{1}H and ^{195}Pt resonances was



Scheme 2. The dppz ligand, showing the component structural features.

obtained from ^{1}H TOCSY, ^{1}H COSY, ^{1}H NOESY, and gradient selected ^{1}H, ^{195}Pt HMBC experiments. All 2D NMR experiments were performed using standard pulse sequences from the Bruker pulse program library. Chemical shifts were relative to TMS for ^{1}H, $CFCl_3$ for ^{19}F and $Na_2[PtCl_6]$ in D_2O for ^{195}Pt. The spectra analyses were performed by the Bruker TopSpin 2 software. Elemental analyses were carried out using a Hekatech CHNS EuroEA 3000 Analyzer. EI-MS spectra were measured with a Finnigan MAT 900 S. Simulations were performed using ISOPRO 3.0. IR spectra were measured in ATR mode using a Perkin Elmer 400 FT-IR spectrometer. UV–Vis absorption spectra were recorded with Varian Cary50 Scan spectrophotometer. Electrochemical experiments were carried out in 0.1 M nBu$_4$NPF$_6$ solutions using a three-electrode configuration (glassy carbon electrode, Pt counter electrode, Ag/AgCl reference) and an Autolab PGSTAT30 potentiostat and function generator. Data were processed using GPES 4.9 (General Electrochemical System Version 4.9). The ferrocene/ferrocenium couple ($FeCp_2/FeCp_2^+$) served as internal reference.

2.3. Single crystal X-ray analysis

The measurements were performed using graphite-monochromated Mo Kα radiation (λ = 7.1073 Å) with an IPDS I or IPDS II (at 293 K) (STOE and Cie.) diffractometer. The structures were solved by direct methods (SHELXS-97) [50] and refined by full-matrix least-squares techniques against F^2 (SHELXL-97) [51]. The non-hydrogen atoms were refined with anisotropic displacement parameters without any constraints. The hydrogen atoms were included by using appropriate riding models.

2.4. Synthesis of the complexes

Synthesis of the platinum complexes from their chlorido precursor complexes, general description: The Pt precursors [(COD)PtCl$_2$], [(COD)Pt(Me)Cl], [(COD)Pt(Bn)Cl], [(bpy)PtCl$_2$], [(dppz)PtCl$_2$], *cis*-[(PPh$_3$)$_2$PtCl$_2$], [(dppe)PtCl$_2$], [(dppb)Pt(C$_6$F$_5$)Cl], and [(DMSO)$_2$PtCl$_2$] (ca. 1 mmol) were dissolved in about 50 mL of acetone and one or two equivalents of HSC$_6$F$_4$H-4 + KO*t*Bu or KSC$_6$F$_4$H-4 were added. After stirring at ambient temperature for the required time, the mixture was filtered over Celite® to remove traces of elemental Pt, precipitated KCl or other undissolved material and the filtrate was evaporated to dryness. The residues were carefully recrystallised from acetone or CH_2Cl_2 to yield the products as microcrystalline material. Four modifications (**A**–**D**) were applied.

(A) Reaction of two equivalents of HSC$_6$F$_4$H-4 with [(COD)PtCl$_2$]: In a first attempt an amount of 200 mg (0.534 mmol) [(COD)PtCl$_2$] and 200 mg (1.1 mmol) HSC$_6$F$_4$H-4 was stirred in 20 mL of acetone at ambient temperature. NMR monitoring showed the intermediate formation of the mono-substituted complex [(COD)Pt(SC$_6$F$_4$H-4)Cl]. After two days >99% conversion to the disubstituted complex was determined. After workup, 300 mg (0.45 mmol = 84%) of faint yellow [(COD)Pt(SC$_6$F$_4$H-4)$_2$] were obtained. Addition of small amounts (~0.2 eq) of KO*t*Bu accelerated the reaction markedly and a reaction time of 1.5 h was sufficient (yield: 95%).

(B) Reaction of one equivalent of HSC$_6$F$_4$H-4 with [(COD)PtCl$_2$], [(COD)Pt(Me)Cl] or [(COD)Pt(Bn)Cl]: In the presence of a small amount of KO*t*Bu the reaction proceeded smoothly and was complete after 2 h. The products containing Me (yield: 82%) or Bn (yield: 85%) coligands were yellow. The faint yellow monosubstituted complex [(COD)Pt(SC$_6$F$_4$H-4)Cl] was obtained in 85% yield.

(C) Reaction of two equivalents of HSC$_6$F$_4$H-4 and KO*t*Bu with [(dppe)PtCl$_2$], *cis*-[(PPh$_3$)$_2$PtCl$_2$], [(bpy)PtCl$_2$], and [(dppz)PtCl$_2$]: These reactions required the presence of two equivalents of KO*t*Bu. Conversion to the red phosphine complexes proceeded smoothly within 5 h with yields, accounting to 83% for dppe, and 90% for PPh$_3$, while the red bpy and dppz complexes formed very slowly and, after 3 days stirring at 298 K and workup we obtained 43% yield for bpy and 38% for dppz.

(D) Reaction of one equivalent of HSC$_6$F$_4$H-4 and KO*t*Bu with [(dppb)Pt(C$_6$F$_5$)Cl]: This reaction also required the addition of one equivalent of KO*t*Bu. Under these conditions the red product was obtained in 78% yield after 3 h reaction time.

One-pot reactions:

(E) Reaction of two equivalents of HSC$_6$F$_4$H-4 and KO*t*Bu with K$_2$PtCl$_4$ and bpy, dppz, and CF$_3$dppz: The reaction were carried out in acetone:MeOH:H_2O 1:1:1 mixture and gave yields of 51% for bpy, 55% for dppz, and 58% for CF$_3$dppz after 3 d reaction time.

(F) Reaction of two equivalent of HSC$_6$F$_4$H-4 and KO*t*Bu with [(DMSO)$_2$PtCl$_2$] and bpy, dppz, and CF$_3$dppz: All three reactions gave excellent yields of 86% for bpy, 85% for dppz, and 90% for CF$_3$-dppz after 2 h reaction time.

Other reactions:

(G) [(bpy)Pt(SC$_6$F$_4$H-4)$_2$] was also prepared from [(COD)Pt(SC$_6$F$_4$H-4)$_2$] by stirring 120 mg (0.18 mmol) of the precursor complex with 35 mg (0.22 mmol) of bpy in 100 mL of toluene at 60 °C for 40 h. After reducing the volume to about 10 mL, the red precipitate was collected by filtration and recrystallised from CH_2Cl_2 to yield 118 mg (0.165 mmol; 92%) of [(bpy)Pt(SC$_6$F$_4$H-4)$_2$].

(H) Reaction of four equivalents of KSC$_6$F$_4$H-4 with K$_2$PtCl$_4$: K_2PtCl_4 (250 mg, 0.60 mmol) and 550 mg (2.5 mmol) of KSC$_6$F$_4$H-4 were suspended in 80 mL of acetone. Upon addition of a few drops of ethanol and water, the red K_2PtCl_4 dissolved and the reaction started. The mixture was stirred for 48 h. After filtration, the volume of the yellow filtrate was reduced to 20 mL and the orange product was collected, recrystallised from ethanol and dried in vacuo yielding 400 mg (0.40 mmol) **K$_2$[Pt(SC$_6$F$_4$H-4)$_4$]:** $C_{24}H_4F_{16}K_2PtS_4$ (997.80): Calc. C, 28.89; H, 0.40; S, 12.85. Found: C, 29.08; H, 0.41; S, 12.60%. ^{1}H NMR ([D$_6$]acetone): δ = 6.72 (m, 4H, H4) ppm. ^{19}F NMR ([D$_6$]acetone): δ = −133.3 (m, 8F, F2,6), −145.2 (m, 8F, F3,5) ppm. Note, that this work-up yielded the material without co-crystallised EtOH (compare crystal structure).

(I) Attempted preparation of [(DMSO)$_2$Pt(SC$_6$F$_4$H-4)$_2$]: 120 mg (0.28 mmol) [(DMSO)$_2$PtCl$_2$], 110 mg (0.60 mmol) HSC$_6$F$_4$H-4 and 68 mg (0.60 mmol) KO*t*Bu were dissolved in 100 mL of acetone and stirred at ambient temperature. After 30 min a small volume

was separated and evaporated to dryness. ^{1}H and ^{19}F NMR spectra in [D$_6$]acetone and $CDCl_3$ revealed the presence of *cis*- and *trans*-[(DMSO)$_2$Pt(SC$_6$F$_4$H-4)$_2$]: ^{1}H NMR ([D$_6$]acetone) *cis*: δ = 7.68 (m, 2H, H4), 3.57 (s, 6H, CH_3, $^{3}J_{Pt-H}$ = 22 Hz); *trans*: δ = 7.68 (m, 2H, H4), 2.61 (s, 6H, CH_3, $^{3}J_{Pt-H}$ = 51 Hz) ppm. ^{1}H NMR ($CDCl_3$) *cis*: δ = 7.12 (m, 2H, H4), 3.56 (s, 6H, $^{3}J_{Pt-H}$ = 22 Hz, CH_3); *trans*: δ = 7.12 (m, 2H, H4), 2.64 (s, 6H, $^{3}J_{Pt-H}$ = 50 Hz, CH_3) ppm. ^{19}F NMR ([D$_6$]acetone) *cis* and *trans*: δ = −135.4 (m, 4F, F2,6), −140.3 (m, 4F, F3,5). After three hours stirring the mixture was filtered over Celite® and the filtrate was evaporated to dryness leaving an orange solid which turned out to be virtually insoluble in most organic solvent. Elemental analysis, MS and IR spectroscopy revealed that this solid was polymeric **[Pt(SC$_6$F$_4$H-4)$_2$]$_m$**. $C_{12}H_2F_8PtS_2$ (557.34): Calc. C, 25.86; H, 0.36; S, 11.51. Found: C, 25.91; H, 0.44; S, 11.41%. IR spectrum (pellet) of the product showed no bands for (DMSO)Pt (e.g., νS=O ≈ 1120–1150 cm^{-1}) but typical signals for the thiolate ligand at $\tilde{\nu}$ = 3069 (vw), 1629 (w), 1490 (vs), 1435 (s), 1367 (s), 1249 (w), 1229 (s), 1175 (s), 1130 (w), 918 (vs), 880 (s), 851 (s) and 712 (s) cm^{-1} which were very similar to those reported recently for the Pd derivative [Pt(SC$_6$F$_4$H-4)$_2$]$_m$ [38]. EI-MS: m/z = 362 [4-HF$_4$C$_6$S–SC$_6$F$_4$H-4]$^+$, 330 [4-HF$_4$C$_6$-S-C$_6$F$_4$H-4]$^+$, 182 [HSC$_6$F$_4$H-4]$^+$. In the filtrate of the reaction mixture, DMSO was found (NMR). The solid can be partially re-dissolved in [D$_6$]DMSO giving ^{1}H and ^{19}F NMR signals corresponding to [(DMSO)$_2$Pt(SC$_6$F$_4$H-4)$_2$]: ^{1}H NMR ([D$_6$]DMSO) *cis*: δ = 7.79 (m, 2H, H4), 3.74 (s, 6H, $^{3}J_{Pt-H}$ = 22 Hz, CH_3); *trans*: δ = 7.79 (m, 2H, H4), 2.73 (s, 6H, $^{3}J_{Pt-H}$ = 51 Hz, CH_3) ppm. ^{19}F NMR ([D$_6$]DMSO) *cis* and *trans*: δ = −133.2 (m, 4F, F2,6), −140.0 (m, 4F, F3,5).

The isolated products from **A**–**G** were:

[(COD)Pt(SC$_6$F$_4$H-4)$_2$]: $C_{20}H_{14}F_8PtS_2$ (665.53): Calc. C, 36.09; H, 2.12; S, 9.64. Found: C, 36.08; H, 2.04; S, 9.60%. ^{1}H NMR ([D$_6$]acetone): δ = 7.32 (m, 2H, H4), 5.08 (m, 4H, COD$_{olef}$, $^{2}J_{Pt,H}$ = 57 Hz), 2.81 (m, 8H, COD$_{aliph}$) ppm. ^{19}F NMR ([D$_6$]acetone): δ = −132.2 (m, 4F, F2,6), −141.7 (m, 4F, F3,5) ppm. ^{195}Pt, ^{1}H HMBC ([D$_6$]acetone): δ = −3614 ppm. IR: $\tilde{\nu}$ = 3081 w, 2971 w, 2745 w, 1630 m, 1485 vs 1430 s, 1374 m, 1249 m, 1224 s, 1167 s, 908 vs 881 s, 841 s, 820 s (sh), 708 vs cm^{-1}. EI-MS: m/z = 665 [M]$^+$, 484 [M−SC$_6$F$_4$H]$^+$.

[(COD)PtCl(SC$_6$F$_4$H-4)]: $C_{14}H_{13}ClF_4PtS$ (519.85): Calc. C, 32.35; H, 2.52; S, 6.17. Found: C, 32.34; H, 2.51; S, 6.20%. ^{1}H NMR ([D$_6$-]acetone): δ = 7.32 (m, 1H, H4), 5.51 (m, 2H, COD$_{olef}$, $^{2}J_{Pt,H}$ = 57 Hz), 5.10 (m, 2H, COD$_{olef}$, $^{2}J_{Pt,H}$ = 60 Hz), 2.81 (m, 8H, COD$_{aliph.}$) ppm. ^{19}F NMR ([D$_6$]acetone): δ = −132.1 (m, 2F, F2,6), −142.2 (m, 2F, F3,5) ppm. ^{195}Pt, ^{1}H HMBC ([D$_6$]acetone): δ = −3599 ppm. EI-MS: m/z = 520 [M]$^+$, 484 [M−Cl]$^+$.

[(COD)Pt(Me)(SC$_6$F$_4$H-4)]: $C_{15}H_{16}F_4PtS$ (499.43): Calc. C, 36.07; H, 3.23; S, 6.42. Found: C, 36.08; H, 3.21; S, 6.50%. ^{1}H NMR ([D$_6$-]acetone): δ = 7.36 (m, 1H, H-4), 4.95 (m, 2H, COD$_{olef}$, $^{2}J_{Pt,H}$ = 37 Hz), 4.64 (m, 2H, COD$_{olef}$, $^{2}J_{Pt,H}$ = 63 Hz), 2.49 (m, 8H, COD$_{aliph.}$), 0.42 (s, 3H, Me, $^{2}J_{Pt,H}$ = 74 Hz) ppm. ^{19}F NMR ([D$_6$]acetone): δ = −133.2 (m, 2F, F2,6), −141.5 (m, 2F, F3,5) ppm. ^{195}Pt, ^{1}H HMBC ([D$_6$]acetone): δ = −3564 ppm. IR: $\tilde{\nu}$ = 3049 w, 2950 w, 2916 w, 2884 w, 2837 w, 2804 w, 1624 m, 1476 vs 1427, s, 1347 m, 1224 m, 1213 s, 1171 vs 909 vs 884 vs 845 s, 818 s, 788 s cm^{-1}. FIR: $\tilde{\nu}$ = 684, 649, 467, 303, 296, 281, 228, 206, 195 cm^{-1}. EI-MS: m/z = 499 [M]$^+$, 483 [M−CH$_4$]$^+$, 302 [M−CH$_4$−SC$_6$F$_4$H]$^+$.

[(COD)Pt(Bn)(SC$_6$F$_4$H-4)]: $C_{21}H_{20}F_4PtS$ (575.52): Calc. C, 43.83; H, 3.50; S, 5.57. Found: C, 43.88; H, 3.51; S, 5.60%. ^{1}H NMR ([D$_6$-]acetone): δ = 7.26 (s, 1H, H-4), 7.13–6.75 (m, 5H, Phenyl), 4.89 (m, 2H, COD$_{olef}$, $^{2}J_{Pt,H}$ = 39 Hz), 4.53 (m, 2H, COD$_{olef.}$, $^{2}J_{Pt,H}$ = 64 Hz), 2.77 (s, 2H, CH$_2$ $_{Bn}$, $^{2}J_{Pt,H}$ = 101 Hz), 2.47–2.25 (m, 8H, COD$_{aliph}$) ppm. ^{19}F NMR ([D$_6$]acetone): δ = −133.3 (m, 2F, F2,6), −145.2 (m, 2F, F3,5) ppm. ^{195}Pt, ^{1}H HMBC ([D$_6$]acetone): δ = −3742 ppm. EI-MS: m/z = 575 [M]$^+$.

***cis*-[(PPh$_3$)$_2$Pt(SC$_6$F$_4$H-4)$_2$]:** $C_{48}H_{32}F_8P_2PtS_2$ (1081.92): Calc. C, 53.29; H, 2.98; S, 5.93. Found: C, 52.98; H, 2.91; S, 5.90%. ^{1}H NMR ([D$_6$]acetone): δ = 7.74 (m, 2H, Ph), 7.62–7.44 (m, 10H, Ph), 7.44–7.35 (m, 8H, Ph), 7.29 (m, 10H, Ph), 6.94 (m, 2H, H4) ppm. ^{19}F NMR ([D$_6$]acetone): δ = −135.2 (m, 4F, F2,6), −143.8 (m, 4F, F3,5) ppm (compare Ref. [30]). ^{31}P NMR ([D$_6$]acetone): δ = 19.2 (s, 2P, $^{1}J_{Pt,P}$ = 3105 Hz). IR: $\tilde{\nu}$ = 3052 w, 2959 w, 2922 m, 2852 w, 1624 w, 1585 w, 1477 vs 1435 s, 1424 s, 1213 w, 1164 s, 1094 s, 998 w, 910 s, 880 s, 825 w, 742 s, 688 vs cm^{-1}. FIR: $\tilde{\nu}$ = 688 , 655, 521, 491, 305, 291, 279 cm^{-1}.

[(dppe)Pt(SC$_6$F$_4$H-4)$_2$]: $C_{38}H_{26}F_8P_2PtS_2$ (955.76): Calc. C, 47.75; H, 2.74; S, 6.71. Found: C, 47.48; H, 2.61; S, 6.65%. ^{1}H NMR ([D$_6$]acetone): δ = 8.06 (m, 10H, Ph), 7.60 (m, 10H, Ph), 6.71 (m, 2H, H4), 2.83 (m, 4H, CH_2) ppm. ^{19}F NMR ([D$_6$]acetone): δ = −133.4 (m, 4F, F2,6), −143.7 (m, 4F, F3,5) ppm (compare Ref. [31a]) ^{31}P NMR ([D$_6$]acetone): δ = 52.2 (s, 2P, $^{1}J_{Pt,P}$ = 3008 Hz). EI-MS: m/z = 955 [M]$^+$, 775 [M−C$_6$F$_4$S]$^+$, 593 [M−2(HSC$_6$F$_4$H-4)]$^+$, 302 [PtPC$_6$H$_4$]$^+$.

[(dppb)Pt(C$_6$F$_5$)(SC$_6$F$_4$H-4)]: $C_{40}H_{29}F_9P_2PtS$ (969.74): Calc. C, 49.54; H, 3.01; S, 3.31. Found: C, 49.38; H, 3.01; S, 3.28%. ^{1}H NMR ([D$_6$]acetone): δ = 7.99 (m, 2H, Ph), 7.56 (m, 6H, Ph), 7.45 (m, 4H, Ph), 7.25 (m, 8H, Ph), 6.90 (m, 1H, H4), 3.03 (m, 2H, CH_2), 2.53 (m, 2H, CH_2), 2.23 (m, 2H, CH_2), 1.71 (m, 2H, CH_2) ppm. ^{19}F NMR ([D$_6$]acetone): δ = −116.9 (m, 2F, F2,6, C$_6$F$_5$) $^{3}J_{Pt,F}$ = 301 Hz, $^{3}J_{F,F}$ = 19 Hz), −131.7 (m, 2F, F2,6), −144.1 (m, 2F, F3,5), −165.4–165.6 (m, 3F, F3,4,5, C$_6$F$_5$) ppm. ^{31}P NMR ([D$_6$]acetone): δ = 12.2 (d, 1P, $^{2}J_{P,P}$ = 21 Hz, $^{1}J_{Pt,P}$ = 2290 Hz, *trans* to C), 20.2 (d, 1P, $^{2}J_{P,P}$ = 21 Hz, $^{1}J_{Pt,P}$ = 2960 Hz, *trans* to S). IR: $\tilde{\nu}$ = 1627 m, 1488 s, 1478 s, 1453 s, 1433 s, 1355 m, 1226 m, 1170 m, 1102 m, 1054 m, 953 vs (νC–F$_{C6F5}$), 909 vs (νC–F$_{C6F4H}$), 886 m, 820 m, 786 m, 746 m, 736 s, 711 m, 690 vs cm^{-1}.

[(bpy)Pt(SC$_6$F$_4$H-4)$_2$]: $C_{22}H_{10}F_8N_2PtS_2$ (713.53): Calc. C, 37.03; H, 1.41; N, 3.93. Found: C, 37.08; H, 1.41; N, 3.90%. ^{1}H NMR ([D$_6$]DMSO): δ = 9.66 (m, 2H, $^{3}J_{Pt,H}$ = 33,6 Hz, bpy6,6′), 8.75 (m, 2H, bpy3,3′), 8.47 (m, 2H, bpy4,4′), 7.92 (m, 2H, bpy5,5′), 7.37 (m, 2H, H4) ppm. ^{19}F NMR ([D$_6$]acetone): δ = −133.4 (m, 4F, F2,6), −141.8 (m, 4F, F3,5) ppm (compare Ref. [33]). IR: $\tilde{\nu}$ = 3102 w, br, 3029 w, 2924 w, 1626 m, 1603 w, 1483 vs 1473 vs 1448 m, 1427 s, 1321 w, 1243 m, 1217 m, 1168 s, 910 vs 886 s, 775 vs 710 s, 696 s cm^{-1}.

[(dppz)Pt(SC$_6$F$_4$H-4)$_2$]: $C_{30}H_{12}F_8N_4PtS_2$ (839.64): Calc. C, 42.91; H, 1.44; N, 6.67. Found: C, 42.88; H, 1.41; N, 6.70%. ^{1}H NMR ([D$_6$]DMSO): δ = 10.02 (m, 2H, $^{3}J_{Pt,H}$ = 33,2 Hz, dppz3,6), 9.89 (m, 2H, dppz1,8), 8.49 (dd, 2H, dppz10,13), 8.20 (m, 2H, dppz11,12), 8.10 (m, 2H dppz2,7), 7.41 (m, 2H, H4) ppm. ^{19}F NMR ([D$_6$]acetone): δ = −133.1 (m, 4F, F2,6), −141.7 (m, 4F, F3,5) ppm. IR: $\tilde{\nu}$ = 3044 w, 1735 w, 1615 m, 1575 w, 1522 w, 1484 vs 1475 s, 1427 m, 1362 m, 1337 w, 1247 m, 1215 m, 1177 m, 1135 m, 1076 w, 1040 w, 1009 w, 906 m, 882 m, 817 s, 766 vs 744 s, 727 vs 709 m, 616 m, 567 w cm^{-1}. EI-MS: m/z = 839 [M]$^+$.

[(CF$_3$dppz)Pt(SC$_6$F$_4$H-4)$_2$]: $C_{31}H_{11}F_{11}N_4PtS_2$ (907.64): Calc. C, 41.02; H, 1.22; N, 6.17. Found: C, 41.08; H, 1.21; N, 6.19%. ^{1}H NMR ([D$_6$]DMSO): δ = 10.0 (m, 2H, $^{3}J_{Pt,H}$ = 32 Hz dppz3,6), 9.92 (m, 2H, dppz1,8), 8.60 (m, 1H, dppz13), 8.42 (m, 1H, dppz10) 8.31 (m, 1H, dppz12), 8.20 (m, 2H dppz2,7), 7.41 (m, 2H, H4) ppm. ^{19}F NMR ([D$_6$]DMSO): δ = −103.8 (m, 3F, CF_3), −133.1 (m, 4F, F2,6), −141.7 (m, 4F, F3,5) ppm. IR: $\tilde{\nu}$ = 3063 vw, 2941 w, 2857 w, 1738 w, 1710 w, 1625 m, 1615 m, 1579 m, 1526 m, 1478 vs 1421 s, 1359 s, 1251 m, 1224 s, 1163 vs 1117 m, 1072 m, 959 m, 908 vs 888 s, 813 vs 721 s, 712 s, 616 m, 563 m, 513 m cm^{-1}. EI-MS: m/z = 907 [M]$^+$.

For comparison, the previously reported complex **[(bpy)Pt(SC$_6$F$_5$)$_2$]** [33] was prepared as described in (**C**) in 88% yield. $C_{22}H_8F_{10}N_2PtS_2$ (749.50): Calc. C, 35.25; H, 1.08; N, 3.74. Found: C, 35.28; H, 1.04; N, 3.75%. ^{1}H NMR ([D$_6$]acetone): δ = 9.87 (m, 2H, $^{3}J_{Pt,H}$ = 32 -Hz, bpy6,6′), 8.67 (m, 2H, bpy3,3′), 8.47 (m, 2H, bpy4,4′), 7.92 (m, 2H, bpy5,5′). ^{19}F NMR ([D$_6$]acetone): δ = −132.7 (m, 4F, F2,6), −157.1 (m, 4F, F3,5), −164.8 (m, 2F, F4) ppm. IR: $\tilde{\nu}$ = 2968 w, 2931 w, 1724 m, 1637 m, 1509 vs 1480 vs 1399 m, 1382 m,

1364 s, 1289 m, 1118 m, 1090 vs 1021 m, 973 vs 856 vs 765 s, 725 m, 634 m, 627 m, 612 w, 548 m, 511 m cm^{-1}. EI-MS: m/z = 749 $[M]^+$.

2.5. Supplementary data

Tables containing complete crystallographic and structural data were provided together with figures showing the crystal and molecular structures of [(COD)Pt(Me)(SC_6F_4H-4)], [(COD)Pt(SC_6F_4-H-4)$_2$], K_2[Pt(SC_6F_4H-4)$_4$], [(dppb)Pt(C_6F_5)(SC_6F_4H-4)], [(dppe)Pt(SC_6F_4H-4)$_2$] and *cis*-[(PPh_3)$_2$Pt(SC_6F_4H-4)$_2$]. Furthermore, cyclic voltammograms and absorption spectra of [(bpy)Pt(SC_6F_4H-4)$_2$], [(dppz)Pt(SC_6F_4H-4)$_2$] and [(CF_3dppz)Pt(SC_6F_4H-4)$_2$] as well as NMR spectra of *cis*- and *trans*-[$(DMSO)_2$Pt(SC_6F_4H-4)$_2$] and IR spectra of [Pt(SC_6F_4H-4)$_2$]$_m$ were provided.

3. Results and Discussion

3.1. Synthesis and analytical characterisation

The reaction of two equivalents of HSC_6F_4H-4 with the Pt precursor complexes [(N^N)$PtCl_2$] (N^N = 2,2′-bipyridine (bpy) or dipyrido[3,2-*a*:2′,3′-*c*]phenazine (dppz)) (type 3 in Scheme 1) and KO*t*Bu as base in acetone at ambient temperature proceeds very slowly due to the low solubility of the precursor complexes in this medium. After about three days and work-up we obtained the red products [(N^N)Pt(SC_6F_4H-4)$_2$] in rather low yields of 43% and 38% (for details see Section 2). The synthesis of the bpy complex, using Pb(SC_6F4H-4)$_2$ was reported to yield 61% [33]. The former reactions carried out with the phosphane complexes *cis*-[$(PPh_3)_2PtCl_2$], [(dppe)$PtCl_2$], and [(dppb)Pt(C_6F_5)Cl] (one equivalent of HSC_6F_4H-4) were finished within 5 h and gave good yields (80–90%). For both diimine and phosphine complexes the use of HSC_6F_4H-4 without base (route 4) results in very slow reaction rates. In contrast to this, the Pt complex [(COD)$PtCl_2$] (COD = 1,5-cyclooctadiene) could be reacted with HSC_6F_4H-4 without the addition of KO*t*Bu, but completion was observed only after 2 days. Upon addition of KO*t*Bu the faint yellow product [(COD)Pt(SC_6F_4H-4)$_2$] was obtained in 1.5 h in 95% yield. Recently, the same complex has been obtained by reacting Pb(SC_6F_4H-4)$_2$ with [(COD)$PtCl_2$] in 96% yield [36]. We also prepared [(COD)PtCl(SC_6F_4H-4)] using one equivalent HSC_6F_4H-4 in a reasonable yield of 85% with almost no by-products [(COD)Pt(SC_6F_4H-4)$_2$] and [(COD)$PtCl_2$], which could be expected from a non-selective (statistical) reaction. Also, [(COD)Pt(Me)(SC_6F_4H-4)], and [(COD)Pt(Bn)(SC_6F_4H-4)] were obtained from their corresponding chlorido precursors (2.4B).

In further attempts, we sought to create a one-pot procedure for the preparation of the diimine complexes by reacting a mixture of K_2PtCl_4 and the diimine ligands bpy, dppz and CF_3dppz with HSC_6F_4H-4 and KO*t*Bu but could not find a suitable solvent to dissolve both the ligands and K_2PtCl_4 (various mixtures of acetone, MeOH and water were tried). Due to the low solubilities, the reactions were very slow and gave the desired products in only moderate yields (50–60%). When starting from the well soluble platinum complex [$(DMSO)_2PtCl_2$], reaction with HSC_6F_4H-4 and KO*t*Bu in acetone were much faster and very high yields were obtained (85–90%). In view of the very simple and efficient preparation of [$(DMSO)_2PtCl_2$] from K_2PtCl_4 (about 5 h, virtually 100% yield) this method appears to be a promising alternative.

Interestingly, reaction of *cis*-[$(DMSO)_2PtCl_2$] with HSC_6F_4H-4 and KO*t*Bu in the absence of any other ligand resulted in a mixture of the *cis*- and *trans* isomer of [$(DMSO)_2$Pt(SC_6F_4H-4)$_2$]. However, only after short reaction times and rapid quenching of the reaction mixture could these species be observed in the NMR spectrum. Longer reaction times and usual workup lead to their complete decomposition yielding the orange polymer [Pt(SC_6F_4H-4)$_2$]$_m$. This polymer can be partially redissolved in DMSO underlining that the labile DMSO ligand can prevent formation of polymeric material only in huge excess, while the labile (chelate) ligand COD stabilises monomeric complexes. Interestingly, the *cis* and *trans* isomers of [$(DMSO)_2$Pt(SC_6F_4H-4)$_2$] were observed in an almost 1:1 ratio (for a Figure see Supplementary Data), while for the chlorido derivative [$(DMSO)_2PtCl_2$] the *trans* isomer has not been reported yet. Reaction of K_2PtCl_4 with HSC_6F_4H-4 in an acetone:water mixture (10:1) allowed us to isolate the compound K_2[Pt(SC_6F_4H-4)$_4$], which contains the homoleptic complex dianion [Pt(SC_6F_4H-4)$_4$]$^{2-}$ [36b]. Finally, [(COD)Pt(SC_6F_4H-4)$_2$] was successfully converted to [(bpy)Pt(SC_6F_4H-4)$_2$] to demonstrate the suitability of the COD complexes as precursors.

3.2. NMR spectroscopy

^{19}F [52] and ^{195}Pt [53] NMR spectroscopy was a very useful method to monitor the identity of the corresponding complexes and their occurrence in reaction mixtures. Table 1 lists some data (the full data is available in Section 2).

From earlier studies it is well known that the $^2J_{Pt,H(=CH,COD)}$ coupling constants reflect very well the general Pt–ligand bond

Table 1
Selected chemical shifts and coupling constants of the platinum complexes.[a]

	δ (^{19}F) (F2,6)	δ (^{19}F) (F3,5)	δ (^{1}H) (H4)	δ (^{195}Pt)	$^nJ_{Pt,E}$
[(COD)Pt(SC_6F_4H-4)$_2$]	−132.1	−142.2	7.02	−3614	57[b]
[(COD)Pt(Me)(SC_6F_4H-4)]	−133.2	−141.5	7.36	−3564	63, 37[b]
[(COD)Pt(Bn)(SC_6F_4H-4)]	−133.3	−145.2	7.26	−3742	64, 39[b]
[(COD)PtCl(SC_6F_4H-4)]	−132.2	−141.7	7.32	−3599	57, 60[b]
K_2[Pt(SC_6F_4H-4)$_4$]	−133.3	−145.2	6.72	–	–
cis-[(PPh_3)$_2$Pt(SC_6F_4H-4)$_2$]	−135.2	−143.8	6.94	–	3105[c]
[(dppe)Pt(SC_6F_4H-4)$_2$]	−133.4	−143.7	6.71	–	3008[c]
[(dppb)Pt(C_6F_5)(SC_6F_4H-4)]	−131.7	−144.1	6.97	–	2960, 2290[c]
[(bpy)Pt(SC_6F_4H-4)$_2$]	−134.2	−144.8	7.01	–	36.0[d]
[(dppz)Pt(SC_6F_4H-4)$_2$]	−133.1	−141.7	7.04	–	33.2[d]
[(CF_3dppz)Pt(SC_6F_4H-4)$_2$]	−133.9	−143.4	7.05	–	32.0[d]
cis-[$(DMSO)_2$Pt(SC_6F_4H-4)$_2$]	−135.4	−140.3	7.68	–	22[e,f]
trans-[$(DMSO)_2$Pt(SC_6F_4H-4)$_2$]	−135.4	−140.3	7.68	–	51[e,f]
[(bpy)Pt(SC_6F_5)$_2$]	−132.7	−157.1	–	–	36.7[d]

[a] Measured in [D_6]acetone; chemical shifts δ in ppm, coupling constants J in Hz.
[b] $^2J_{Pt,H(=CH,COD)}$, for unsymmetrical complexes the first number refers to the =CH group *trans* to SC_6F_4H-4, the second to the =CH group *trans* to R′ or Cl.
[c] $^1J_{Pt,P}$.
[d] $^3J_{PtNCH}$.
[e] $^3J_{Pt,CH3}$.
[f] For *cis*-[$(DMSO)_2PtCl_2$] a 22.7 Hz $^3J_{Pt,CH3}$ coupling is observed at 3.54 ppm in [D_6]acetone.

strength of a ligand *trans* to the corresponding olefin proton in CODPt complexes [54]. Table 1 shows a $^{2}J_{Pt,H(=CH,COD)}$ coupling constant of 57 Hz for the symmetric complex [(COD)Pt(SC_6F_4H-4)$_2$] putting the SC_6F_4H-4 coligand with relatively weak coligands alongside alkynyls (~50 Hz) or halides (~70 Hz). For comparison, [(COD)Pt(Me)$_2$] has a coupling constant of 41 Hz (for the strong Me ligand), while [(COD)PtCl$_2$] gives 69 Hz for the weak Cl ligand [54], In the "unsymmetric" complexes [(COD)Pt(R′)(SC_6F_4H-4)] (R′ = Me, Bn) the situation is slightly modified. The thiolate coligands seem to lose some of their binding strength (increased *trans* $^{2}J_{Pt,H}$), while the methyl and benzyl coligands reveal their very high ligand strength (decreased *trans* $^{2}J_{Pt,H}$). The same phenomenon has been observed for [(COD)Pt(Me)Cl], where the corresponding values are 74 and 32 Hz [54]. Maybe the increased electron-donation by the alkyl ligand requires efficient π back-donation, which stands in stark contrast with the rather poor π donating ability of the thiolate ligand in the symmetrical complexes. An interesting situation is found in [(COD)PtCl(SC_6F_4H-4)], here Cl and SC_6F_4H-4 exert seemingly similar bond strength, SC_6F_4H-4 being only slightly stronger. In corresponding dithiolate complexes [(COD)Pt(S_2R)] smaller *trans* $^{2}J_{Pt,H}$ values were found (S_2R = SCH_2-CH_2S (dt): 53 Hz; or SCH = CHS (edt): 53 Hz; SC(CN)=C(CN)S (mnt): 54 Hz), indicative of much higher ligand strength [55].

Also other $^{n}J_{Pt,X}$ coupling constant have been very successfully correlated with the strength of *trans* Pt–ligand bonds [55–60]. In our study, the *cis*-configuration of *cis*-[(PPh_3)$_2$Pt(SC_6F_4H-4)$_2$] is clearly reflected in the large $^{1}J_{Pt,P}$ coupling constant, which lies in the same range as found for the other two and related *cis*-configured bis-phosphine Pt complexes [55–57,60]. For the corresponding dithiolate complexes [(PPh_3)2Pt(S_2R)] only slightly smaller $^{1}J_{Pt,P}$ coupling constants of ~2900 Hz were found [55], which indicates an only slightly increased *trans* influence (ligand strength) for the dithiolates (S_2R) compared with SC_6F_4H-4. For the mixed complex [(dppb)Pt(C_6F_5)(SC_6F_4H-4)] the same phenomenon as discussed for the COD complexes was found. While $^{1}J_{Pt,P}$ for the P atom *trans* to the C_6F_5 coligand is markedly smaller (thus the Pt–P bond longer = weaker), $^{1}J_{Pt,P}$ for the P atom trans to the SC_6F_4H-4 coligand is slightly increased compared with the symmetric derivatives. The same situation is found in [(dppe)Pt(C_6F_5)(SC_6F_5)], which exhibits $^{1}J_{Pt,P}$ of 2936 (*trans* to SC_6F_5) and 2320 Hz (*trans* to C_6F_5) [34], or [(dppb)Pt(C_6F_5)Cl], with $^{1}J_{Pt,P}$ values of 3776 (*trans* to Cl) and 2149 Hz (*trans* to C_6F_5) [59], Finally, in [(dppb)Pt(C_6F_5)(H_2O)]$^{+}$, containing the very weak H_2O ligand, the $^{1}J_{Pt,P}$ values are 4530 and 2140 Hz [59]. Thus, while in the COD complexes the SC_6F_4H-4 coligand shows a *trans* influence (and thus ligand strength) only slightly superior to Cl, in phosphine complexes SC_6F_4H-4 is markedly stronger than Cl and reaches almost the strength of C_6F_5.

A remarkable difference for the $^{3}J_{Pt\text{-}CH3}$ coupling was observed for the *cis* (22 Hz) vs. *trans* (51 Hz) isomers of [(DMSO)$_2$Pt(SC_6F_4-H-4)$_2$]. As for the COD complexes, the S ligand exerts almost the same ligands strength as the chlorido ligand in [(DMSO)$_2$PtCl$_2$] (Table 1). The value for the *trans* isomer exceeds by far those of related organoplatinum complexes *trans*-[(DMSO)$_2$Pt(R)$_2$] (R = alkyl or aryl) which are around 30 Hz [57b]. The latter study showed that the *trans* configuration is observed for bulky coligands in bis-DMSO complexes, while the *cis* configuration is more stable for electronic reasons. Since SC_6F_4H-4 and Cl exhibit approximately the same ligand strength, the bulkiness of the thiolate coligand must thus be responsible for the observation of the *trans* isomer.

Another important NMR parameter is the ^{195}Pt NMR shift, which lies in the typical range of Pt^{II} complexes for the investigated complexes [53]. Although no correlation can be drawn between the (electronic) structure of the complexes and the chemical shift values, the exceedingly broad scale of the ^{195}Pt shift usually allows the unequivocal detection of such complexes even in complex mixtures [58,61].

3.3. Crystal and molecular structures

From acetone solutions of the compounds [(COD)Pt(SC_6F_4H-4)$_2$], [(COD)Pt(Me)(SC_6F_4H-4)], [(dppe)Pt(SC_6F_4H-4)$_2$] [(dppb)Pt(C_6F_5)(SC_6F_4H-4)] and *cis*-[(PPh_3)$_2$Pt(SC_6F_4H-4)$_2$]·3acetone single crystals were obtained, while [K_2(EtOH)$_2${Pt(SC_6F_4H-4)$_4$}] crystallised from EtOH solution. Suitable single crystals were submitted to X-ray diffraction and crystal and molecular structures were determined. Figs. 1–3 show all structures, Tables 2–4 list the corresponding data (further Figures are in the Supplementary Data).

The crystal structures of the two crystallographically isostructural COD Pt complexes (monoclinic $P2_1/c$) do not exhibit *pronounced* intramolecular interactions. Only for the symmetric complex [(COD)Pt(SC_6F_4H-4)$_2$] weak intermolecular $SR_F \cdots SR_F$ π stacking interactions were found (Table 4; Figures in the Supplementary Data). A closer look reveals centroid distances of about 3.72 Å, which, together with the observed offset of the aromatic rings, points to only very weak attractive interactions [62]. Corresponding intramolecular π stacking interactions are far weaker. The same has been concluded for the related complexes [(COD)Pt($SC_6F_4(CF_3)$-4)$_2$] (monoclinic $C2/c$) [36a], and [(COD)Pt(Me)(SC_6H_5)] [63]. The molecular structures of the two complexes (Fig. 1) exhibit perfect planar stereochemistry of the Pt atoms (sum of angles ~360°), and X–Pt–X angles of ~86° (X represents the C=C centroids), very similar to related COD Pt complexes [36a,54,55,63,64]. Also, the Pt–S [36a,55,63] and Pt–X bond lengths are in the range of comparable compounds. A closer look reveals that in the mixed complex [(COD)Pt(Me)(SC_6F_4H-4)], two markedly different Pt–X bond lengths were found (~2.02 Å for the Pt–X bond *trans* to the thiolate coligand and ~2.20 Å *trans* to the Me coligand), values which, in line with the NMR data, reflect

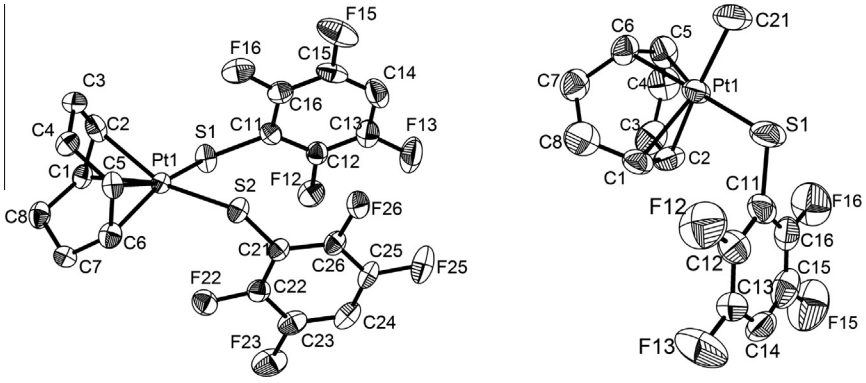


Fig. 1. Molecular structures of [(COD)Pt(SC_6F_4H-4)$_2$] (left) and [(COD)Pt(Me)(SC_6F_4H-4)] (right) at 50% probability level (with numbering); protons were omitted for clarity.

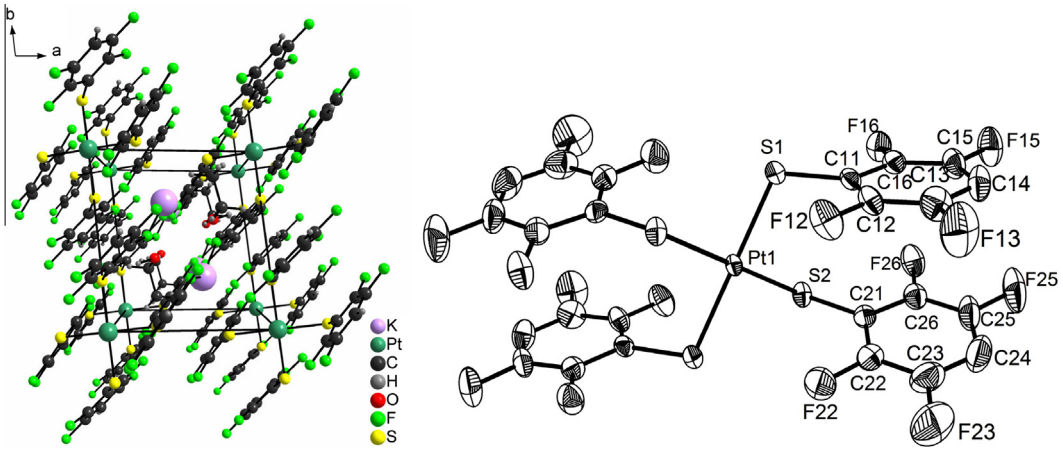


Fig. 2. Crystal structure (left) of $[K_2(EtOH)_2\{Pt(SC_6F_4H\text{-}4)_4\}]$ and a view of the dianionic complex $[Pt(SC_6F_4H\text{-}4)_4]^{2-}$ at 50% probability level (with numbering); protons were omitted for clarity (right).

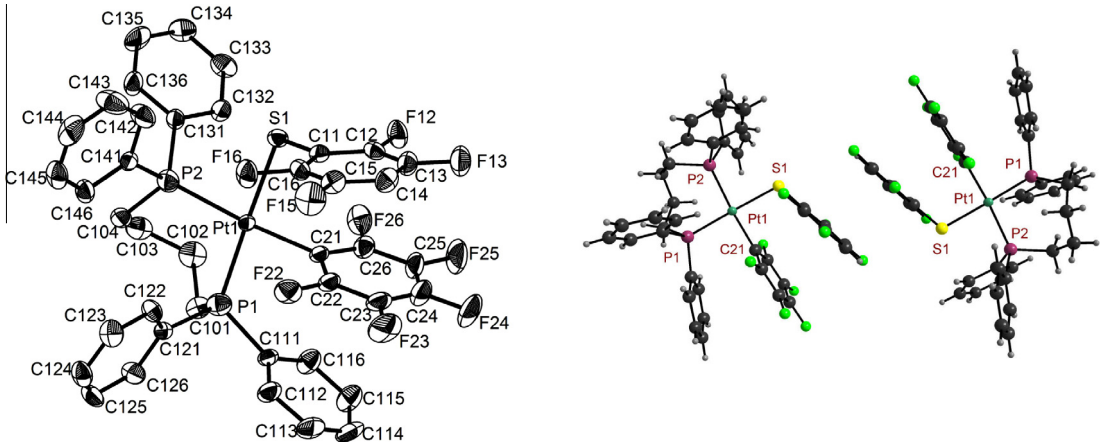


Fig. 3. Molecular structure of $[(dppb)Pt(C_6F_5)(SC_6F_4H\text{-}4)]$ at 50% probability level (with numbering); protons were omitted for clarity (left) and view of two molecules in the crystal showing multiple π-stacking interactions (compare Table 4) (right).

the different ligand strength of the coligands. The same has been observed e.g. for [(COD)Pt(Me)Cl] [54,64a].

In the crystal structure of $[K_2(EtOH)_2\{Pt(SC_6F_4H\text{-}4)_4\}]$ (Fig. 2) weak intramolecular π stacks were found, the potassium ions exhibit contacts with EtOH O atoms (2.76 and 2.80 Å), F atoms (2.81, 2.84, 3.05 Å) and S atoms (3.25, 3.30, 3.32 Å) making a coordination number of eight in a very distorted square prismatic arrangement. The molecular structure of the dianion $[Pt(SC_6F_4H\text{-}4)_2]^{2-}$ in $[K_2(EtOH)_2\{Pt(SC_6F_4H\text{-}4)_4\}]$ reveals an almost perfect square planar stereochemistry of the Pt atom (Fig. 2). For this crystal structure, there is, to our knowledge, no precedent. However, the crystal structure of the binuclear $[Bu_4N]_2[(4\text{-}HF_4C_6S)_2Pt(\mu\text{-}SC_6F_4H\text{-}4)_2Pt(SC_6F_4H\text{-}4)_2]$ ($P2_1/n$) (together with the corresponding SC_6F_5 and $SC_6F_4(CF_3)$-4 derivatives) [37] and the hetero trinuclear compound $[Cl(Cp^*)Ir(\mu\text{-}SC_6F_4H\text{-}4)_2Pt(\mu\text{-}SC_6F_4H\text{-}4)_2Ir(Cp^*)Cl]$ (Cp^* = pentamethyl-cyclopentadienide) formally containing the coordinated $[Pt(SC_6F_4H\text{-}4)_4]^{2-}$ dianion [65] were reported with quite similar bonding parameters. Also, in the hetero tetranuclear complex $[(C_6F_5)Pd\{(\mu\text{-}C_6F_5)_2Pt\}Pd(C_6F_5)_2]^{2-}$ [31b] and interestingly, also in the non-fluorinated derivatives $[Et_4N]_2[Pt(SC_6H_5)_4]$ [66] and $[Pt_3(\mu\text{-}SC_6H_4(CH_3)\text{-}4)_4(dppm)_2](CF_3SO_3)_2$ [67] the bonding parameters around Pt are essentially the same.

In the crystal structures of the three phosphine complexes weak intra- and inter molecular π stacking interaction were found (Fig. 3, Table 4), but very probably they have no impact on the molecular structures. The complex *cis*-$[(PPh_3)_2Pt(SC_6F_4H\text{-}4)_2]$ has been structurally characterised before in the solvate *cis*-$[(PPh_3)_2Pt(SC_6F_4H\text{-}4)_2]\cdot CH_2Cl_2$ (monoclinic $P2_1/n$) [30] with essentially the same bonding parameters. In addition, *cis*-$[(PPh_3)_2Pt(SC_6F_5)_2]\cdot$MeOH (monoclinic $C2/c$) [30] has been reported with very similar parameters.

The crystal structure of $[(dppe)Pt(SC_6F_4H\text{-}4)_2]$ has not been reported before, however, the Ni (triclinic $P\bar{1}$) [31a] and Pd (monoclinic $C2/c$) [29c] analogues have been reported, the latter together with the very similar complexes $[(dppe)Pt(SC_6F_5)_2]$ ($C2/c$) and $[(dppe)Pt(SC_6H_4(CF_3)\text{-}4)_2]$ ($P\bar{1}$) [29c]. A comparison of the Ni, Pd and Pt analogues $[(dppe)M(SC_6F_4H\text{-}4)_2]$ reveals that the M–P and M–S distances increase along the series Ni ≪ Pt < Pd, which is in line with the generally assumed smaller size of Pt(II) compared with Pd(II) [68].

In the complex $[(dppb)Pt(C_6F_5)(SC_6F_4H\text{-}4)]$ (Fig. 3) the Pt–S distance is virtually identical with the values in the other phosphine complexes. Interestingly, also in complexes of electron-rich arylthiolates as in $[(dppb)Pt(SC_6H_3(CH_3)_2\text{-}2,6)_2]$ (orthorhombic *Pbca*), this distance is non-variant around 2.36 Å [56]. As expected from the two different coligands, the Pt–P distances in $[(dppb)Pt(C_6F_5)(SC_6F_4H\text{-}4)]$, 2.299(1) Å for the Pt–P bond *trans* to the C_6F_5 coligand and 2.267(1) Å for the bond *trans* to SC_6F_4H-4, are very different.

Table 2
Parameters of crystal structure measurements, refinement and selected structural data of COD Pt complexes and $K_2[Pt(SC_6F_4H\text{-}4)_4]\cdot 2EtOH$.[a]

	[(COD)Pt(SC_6F_4H-4)$_2$]	[(COD)Pt(Me)(SC_6F_4H-4)]	[K_2(EtOH)$_2${Pt(SC_6F_4H-4)$_4$}]
Formula	$C_{20}H_{14}F_8Pt_1S_2$	$C_{15}H_{16}F_4Pt_1S_1$	$C_{28}H_{14}F_{16}Pt_1K_2O_2S_4$
Weight (g mol^{-1})	665.52	499.43	1089.94
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a (Å)	12.184(2)	11.7018(19)	7.9915(11)
b (Å)	7.0615(8)	8.5594(8)	8.6162(12)
c (Å)	23.563(4)	15.453(2)	13.0032(19)
α (°)	90	90	98.254(17)
β (°)	90.816(15)	94.347(18)	99.219(17)
γ (°)	90	90	95.491(16)
V (Å)^3/Z	2027.1(5) / 4	1543.3(4) / 4	868.2(2) / 4
ρ_{calc} (g cm^{-3})	2.181	2.149	2.085
μ (mm^{-1})	7.205	9.258	4.636
Limiting indices	$-15 < h < 15$, $-8 < k < 9$, $-30 < l < 30$	$-15 < h < 15$, $-10 < k < 10$, $-20 < l < 20$	$-10 < h < 10$, $-11 < k < 11$, $-17 < l < 17$
Reflections collected/unique	20779/4499	14220/3529	10450/3873
R_{int}	0.0919	0.0900	0.0607
Data/restraints/parameters	4499/0/281	3529/0/191	3873/0/241
Goodness-of-fit on F^2	0.755	0.935	0.886
Final R_1, wR_2 ($I > 2\sigma(I)$)	0.0321, 0.0381	0.0457, 0.0956	0.0327, 0.0514
R_1, wR_2 (all data)	0.1074, 0.0468	0.0816, 0.1048	0.0480, 0.0551
$\Delta\rho_{min/max}$ (10^{-6} e/pm^3)	−2.286/1.265	−1.178/1.473	−1.246/1.221
Distances (Å)			
Pt–S	2.318(2), 2.324(2)	2.288(3)	2.334(1), 2.341(1)
Pt–C_{Me}	–	2.050(11)	–
Pt–X[b]	2.075(2), 2.103(3)	2.017(3), 2.170(3)	–
Angles (°)			
S–Pt–S	96.45(8)	–	90.45(4), 89.55(4)
S–Pt–C_{Me}	–	82.90(40)	–
X–Pt–X[b]	85.59(38)	84.79(50)	–
X–Pt–C_{Me}	–	91.46(42)	–
X–Pt–S[b]	89.79(59), 88.83(54)	100.82(38)	–
Sum of angles Pt	360.66(45)	359.97(32)	360.00(4)
C–S–Pt	110.00(30), 108.40(20)	111.10(30)	106.94(15), 109.93(15)

[a] Radiation wavelength λ = 0.71073 Å; T = 293(2) K; refinement method: full-matrix least-squares on F^2.
[b] X: Centroids of the C=C double bond.

The same was observed in [(dppb)Pt(C_6F_5)(H_2O)](SO_3CF_3)·H_2O [69] with 2.312(3) Å for the Pt–P bond *trans* to the C_6F_5 coligand and 2.212(3) Å for the bond *trans* to the very weak H_2O ligand.

When comparing all Pt–S distances, the phosphine complexes have the longest (about 2.36–2.38 Å), followed by the homoleptic complex $[Pt(SC_6F_4H\text{-}4)_4]^{2-}$ (~2.33 Å) and the symmetric COD complex (2.32 Å). The shortest Pt–S bond lengths were observed in the unsymmetrical COD complex (2.29 Å) and the bpy complex [(bpy)Pt(SC_6F_4H-4)$_2$] (~2.29 Å) [33]. Most surprising in this series is that the Pt–S bond length for the unsymmetric COD complex is shorter than the values for the symmetric complex. This stands in contrast to our conclusions from NMR spectroscopy, where the unsymmetric complex shows an increased *trans* $^2J_{Pt,H}$ coupling constant compared with the symmetric dithiolate derivative, indicative of decreased bond strength of the SC_6F_4H-4 coligand. From the NMR data we have also concluded that in phosphine complexes the SC_6F_4H-4 coligand exhibits markedly higher ligand strengths than in the COD complexes, which conclusion stands also in contrast with the above series of decreasing Pt–S distances (from phosphines to COD). However, structural data represents bond distances in the restrained surrounding of a crystal and includes the effects of crystal packing or intermolecular interaction such as π stacking, while NMR coupling constants of molecules in solution can be far better correlated with bond (or ligand) strength [54,57].

3.4. Electrochemistry and UV–Vis absorption spectroscopy of [(N^N)Pt(SC_6F_4H-4)$_2$] complexes

Since the electrochemical and photophysical properties of the related Pt complexes [(bpy)Pt($SR)_2$] with R = C_6F_5, C_6F_4(CN)-4, $C_6H_4(NO_2)$-4, C_6H_4(OMe)-4, $C_6H_4(NMe_2)$-4 and C_6H_5 [26,27], and the corresponding Pd complex [(bpy)Pd(SC_6F_4H-4)$_2$] [38] have been studied in detail, we embarked on a brief study of the new diimine Pt complexes.

The cyclic voltammetry of the three new Pt complexes revealed two one-electron reduction waves and one oxidation wave in MeCN solution (data in Table 5, figures in the Supplementary Data), which has also been observed for related Pt complexes (Table 5) [26,27]. Within the series of the three complexes with the SC_6F_4H-4 ligand increasing π-accepting ability of the N^N ligand bpy < dppz < CF_3dppz [43] facilitates the reduction (increasing potentials), while the energy of the long-wavelength MLCT absorption decreases. At the same time the decreasing oxidation potentials along the same series reflects the decreasing donor capacity of these N^N ligands. Interestingly, the dppz and bpy complex exhibit rather identical first reduction potentials, while the oxidation potentials are different. Even more striking is the difference in the second reduction potential. A closer view reveals that for dppz the difference between first and second reduction lies markedly below the typical 0.63 V for the first and second reduction of diimines, such as bpy [43]. This nicely reflects that dppz features two very close low-lying unoccupied MO, one of bpy-character, one of phenazine character. The more or less identical first reduction potential points to the fact, that in [(dppz)Pt(SC_6F_4-H-4)$_2$] the reduction occurs at the bpy-centred LUMO, while for the second reduction the phenazine type LUMO seems to be the target. For the CF_3 derivative both reductions seem to occur at the bpy-centred LUMO (lowered presumably by the electron-withdrawing effect of the substituent. As a consequence of the more electron-demanding C_6F_5 group compared with the C_6F_4H-4, the complex

Table 3
Parameters of crystal structure measurements, refinement and selected structural data of SC_6F_4H-4 platinum complexes with phosphane ligands.[a]

	cis-[$(PPh_3)_2Pt(SC_6F_4H\text{-}4)_2$]·3acetone	[(dppe)$Pt(SC_6F_4H\text{-}4)_2$]	[(dppb)$Pt(C_6F_5)(SC_6F_4H\text{-}4)$]
Formula	$C_{57}H_{50}F_8Pt_1P_2S_2O_3$	$C_{38}H_{26}F_8Pt_1S_2$	$C_{40}H_{29}F_9P_2Pt_1S_1$
Weight (g mol^{-1})	1256.12	955.74	969.72
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$C2/c$	$P2_1/c$
a (Å)	9.5868(9)	18.805(2)	12.5390(11)
b (Å)	20.9851(17)	12.7754(10)	16.8347(16)
c (Å)	26.889(3)	15.8250(17)	20.704(2)
α (°)	90	90	90
β (°)	97.003(8)	107.634(9)	122.207(7)
γ (°)	90	90	90
V (Å)$^3/Z$	5369.1(8)/6	3623.3(7)/4	3695.6(7)/4
ρ_{calc} (g cm^{-3})	1.554	1.752	1.742
μ (mm^{-1})	2.822	4.145	4.012
Limiting indices	$-11 < h < 11$, $-25 < k < 24$, $-31 < l < 31$	$-24 < h < 24$, $-16 < k < 16$, $-18 < l < 18$	$-16 < h < 16$, $-22 < k < 22$, $-27 < l < 27$
Reflections collected/unique	36915/9313	20965/3988	34026/8793
R_{int}	0.0734	0.0540	0.1368
Data/restraints/parameters	9313/0/646	3988/0/232	8793/0/507
Goodness-of-fit on F^2	0.956	1.047	0.901
Final R_1, wR_2 ($I > 2\sigma(I)$)	0.0416, 0.0902	0.0239, 0.0572	0.0377, 0.0621
R_1, wR_2 (all data)	0.0869, 0.1274	0.0275, 0.0588	0.0762, 0.0694
$\Delta\rho_{min/max}$ (10^{-6} e/pm^3)	−3.948/3.313	−0.674/0.949	−0.807/0.971
Distances (Å)			
Pt–S	2.366(2), 2.380(2)	2.361(1), 2.361(1)	2.367(2)
Pt–P	2.295(2), 2.304(2)	2.254(1), 2.254(1)	2.267(1), 2.299(1)
Pt–C	–	–	2.046(7)
Angles (°)			
S–Pt–S	93.78(7)	98.80(4)	–
S–Pt–P	86.40(8), 84.25(8)	87.76(3), 87.76(3)	86.84(5)
P–Pt–P	95.97(8)	85.74(4)	94.54(5)
P–Pt–C	–	–	90.06(18)
S–Pt–C	–	–	88.54(18)
Sum of angles Pt	360.40(8)	360.06(4)	359.98(12)
C–S–Pt	109.10(30), 108.80(30)	110.74(11)	103.30(20)

[a] Radiation wavelength λ = 0.71073 Å; T = 293(2) K; refinement method: full-matrix least-squares on F^2.

Table 4
Distances (Å) and angles (°) of π contacts.

	Type	Angle	Centroid distance	Offset	Inter-planar distance
[(COD)Pt(Me)(SC_6F_4H-4)]	None	–	–	–	–
[(COD)Pt($SC_6F_4H\text{-}4)_2$]	Intra SR_F	2.94(29)	4.239(3)	1.932(3)	3.874(3)
	Inter SR_F	2.94(26)	3.725(3)	1.545(3)	3.390(3)
[$K_2(EtOH)_2${Pt($SC_6F_4H\text{-}4)_4$}]	Intra SR_F	12.67(16)	3.587(6)	0.173(6)	3.583(6)
[(dppb)Pt(C_6F_5)(SC_6F_4H-4)]	Intra SR_F::R_F	16.52(20)	3.546(5)	0.861(5)	3.440(5)
	Intra R_F::Ph	22.63(29)	3.635(5)	0.689(5)	3.569(5)
	Inter SR_F	0.00(30)	3.614(5)	1.358(5)	3.349(5)
[(dppe)Pt($SC_6F_4H\text{-}4)_2$]	Intra SR_F	4.39(16)	3.869(5)	1.183(5)	3.684(5)
cis-[$(PPh_3)_2Pt(SC_6F_4H\text{-}4)_2$]·3acetone	Intra SR_F	9.26(16)	3.888(3)	1.686(3)	3.504(3)
	Intra Ph	7.68(19)	3.845(3)	0.271(3)	3.844(3)

Table 5
Electrochemical and UV–Vis absorption data of [(N^N)Pt($SC_6F_4H\text{-}4)_2$] and related complexes.[a]

	Electrochemical data		UV–Vis data λ_{max} [nm] (ε [10^3 M^{-1} cm^{-1}])
	Oxidation	Reductions/$E_{red1} - E_{red2}$	
[(bpy)Pt($SC_6F_5)_2$]	0.79	−1.64, −2.27/0.63	408 (3.0)
[(bpy)Pt($SC_6F_4H\text{-}4)_2$]	0.76	−1.62, −2.26/0.64	416 (3.7)
[(dppz)Pt($SC_6F_4H\text{-}4)_2$]	0.66	−1.62, −2.18/0.56	430 (3.0)
[(CF_3dppz)Pt($SC_6F_4H\text{-}4)_2$]	0.62	−1.56, −2.20/0.64	463 (2.8)
[(bpy)Pt($SC_6F_5)_2$] [27]	0.77	−1.60, −2.29/0.69	414 (3.2)[b]
[(bpy)Pt(SC_6F_4(CN)-4)$_2$] [27]	0.95	−1.54, −2.14/0.60	383 (3.0)[b]
[(bpy)Pt($SC_6H_5)_2$] [26,27]	0.22	−1.72, −2.37/0.65	498 (2.1)[b]

[a] Electrochemical potentials [V], measured in 0.1 M nBu$_4$NPF$_6$/MeCN at 298 K, scan rate 100 mV/s and long-wavelength absorption maxima λ_{max} [nm] with extinction coefficients ε [10^3 M^{-1} cm^{-1}], measured in MeCN.
[b] In DMF.

[(bpy)Pt(SC_6F_5)$_2$] exhibits a slightly greater reduction potential, a higher oxidation potential and higher absorption energy than the SC_6F_4H-4 derivative, although the differences are far smaller than those observed for different N^N ligands. For the SC_6H_5 Pt complex the oxidation potential is markedly lowered, by about 0.5 V, compared with the SC_6F_5 derivative, while the introduction of the SC_6F_4(CN)-4 coligand results in a higher oxidation potential (+0.2 V). This clearly underlines that the LUMO is essentially $\pi^*_{(N^N)}$-centred, while the HOMO is metal-centred, although with appreciable contributions from the thiolate coligand [26,27]. When comparing the Pt complexes with the Pd derivative [(bpy)Pd(SC_6F_4H-4)$_2$], for the latter both the difference of first oxidation and reduction potential (0.88 V; −1.54 V in MeCN) and the absorption energy (363 nm) is larger. This larger HOMO–LUMO gap is in line with the second ionisation potential of the two metals (18.6 eV for Pt and 19.4 eV for Pd) and the electron binding energy of the valence p electrons (51.7 eV for Pt 5p and 50.9 eV for Pd 4p) [38,70], in other words, the slightly less noble character of Pd compared with Pt. At the same time the extinction coefficient of the Pd derivative is markedly bigger (~10000 compared with ~3000 M^{-1} cm^{-1}), which might be due to a larger contribution of π–π^* or $L'_{(SRF)}$-to-$L_{(N^N)}$-charge transfer character to this absorption [14,26,27].

4. Conclusions and outlook

In this work we explored formation reactions leading to Pt complexes [$(L)_2Pt(SR_F)_2$] with COD (cycloocta-1,5-diene), diimine, or phosphine ligands (L) and the SC_6F_4H-4 coligand (SR_F). Direct reaction of HSC_6F_4H-4 with the corresponding [$(L)_2PtCl_2$] precursor complexes was accelerated by addition of traces of KO*t*Bu for the COD complexes. For the diimine or phosphine derivatives equimolar amounts of KO*t*Bu were necessary to ensure rapid conversion (~2 h) and reasonable yields (60–80%). The one-pot procedure using [$(DMSO)_2PtCl_2$] the diimine ligand and HSC_6F_4H-4 / KO*t*Bu gave excellent yields (>90%). Thus, a number of previously reported and new COD, diimine or phosphine Pt complexes with the SC_6F_4H-4 coligand were prepared in high yields and purity without the use of sophisticated or toxic precursors such as $(NBu_4)_2[Pt(SC_6F_4H\text{-}4)_4]$, $Tl(SC_6F_4H\text{-}4)$ or $Pb(SC_6F_4H\text{-}4)_2$. Remarkably, these metathetical reactions (exchange of Cl-coligand for SC_6F_4H-4) tolerate also rather labile ligands such as COD and DMSO and allow the preparation of such complexes in high yield in contrast to the corresponding Pd derivatives which undergo rapid cleavage of COD and DMSO with formation of oligomers or polymers $[Pd(SR_F)_2]_m$ under the same reaction conditions. Most of the compounds could be structurally characterised by single crystal XRD in the solid and all of them by multi-nuclear NMR spectroscopy in solution. The previously unreported structure of $K_2[Pt(SC_6F_4H\text{-}4)_4]$ (prepared from KSC_6F_4H-4 and K_2PtCl_4) revealed an almost perfect square planar PtS_4 coordination with Pt–S distances at ~2.33 Å, which is longer than found for the COD complexes or diimine derivatives but markedly shorter than Pt–S distances in phosphine complexes. Thus, Pt–S distances markedly reflect the donor strength of the *trans* ligand. At the same time, the Pt–S bond length in such $[Pt(SR)_4]^{2-}$ dianions seems to be rather invariant concerning substituents (R = C_6F_5 or C_6H_5), and provides a highly stable scaffold. The absorption spectroscopy and electrochemistry of the diimine complexes [(N^N)Pt(SC_6F_4H-4)$_2$] with N^N = bpy and the better π-accepting derivatives dppz (dipyrido[3,2-*a*:2′,3′-*c*]phenazine) and CF_3dppz (11-CF_3 substituted) have been investigated and compared with related Pt complexes and the previously reported Pd derivative [(bpy)Pd(SC_6F_4H-4)$_2$]. In order to tune the photophysical and electrochemical properties of such complexes, three parameters were thus at hand; (i) better π-accepting N^N ligands lower the LUMO energy, (ii) substitution on the thiolate ligand by electron-demanding F atoms decreases the HOMO energy, while (iii) Pt derivatives exhibit intrinsically smaller HOMO–LUMO gaps compared with Pd complexes and also provide more stable binding in corresponding [$(L)_2M(SR)_2$] or [(L^L)$M(SR)_2$] (L or L^L, any ligand or chelate ligand; M = Pd or Pt) complexes with respect to unwanted formation of oligomeric or polymeric $[M(SR)_2]_m$. In the latter respect fluorinated derivatives (SR_F) proved to be superior to non-fluorinated compounds (SR). Thus from the viewpoint of the application of such complexes in photoactive materials the Pt (compared with Pd) derivatives with per-fluorinated ligands (compared with non-fluorinated) are quite promising. Thus, in future investigation we will explore such possibilities.

Acknowledgements

We are indebted to Dr. Wieland Tyrra for NMR experiments (University of Cologne). We are also grateful for a loan of K_2PtCl_4 by Johnson Matthey (J.M.) and for financial support by Deutsche Forschungsgemeinschaft KL 1194/11-1 (A.L. and A.K.). V.L. acknowledges a grant from Heinrich Hertz-Stiftung.

Appendix A. Supplementary material

CCDC 943480 for [(COD)Pt(SC_6F_4H-4)$_2$], 943481 for [(COD)Pt(Me)(SC_6F_4H-4)], 943482 for $K_2[Pt(SC_6F_4H\text{-}4)_4]\cdot 2EtOH$, 943483 for *cis*-$[(PPh_3)_2Pt(SC_6F_4H\text{-}4)_2]\cdot 3$acetone, 943484 for [(dppe)Pt(SC_6F_4H-4)$_2$] and 943485 for [(dppb)Pt(C_6F_5)(SC_6F_4H-4)] contains the full crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2014.07.058.

References

[1] W. Beck, K. Stetter, Inorg. Nucl. Chem. Lett. 2 (1966) 383.
[2] (a) W. Beck, K.H. Stetter, S. Tadros, K.E. Schwarzhans, Chem. Ber. 100 (1967) 3944;
(b) W. Beck, W.P. Fehlhammer, K.H. Stetter, S. Tadros, Chem. Ber. 100 (1967) 3955;
(c) W. Beck, S. Tadros, Z. Anorg. Allg. Chem. 375 (1970) 231.
[3] R.S. Nyholm, J.F. Skinner, M.H.B. Stiddard, J. Chem. Soc. A (1968) 38.
[4] R.H. Fenn, G.R. Segrott, J. Chem. Soc. A (1970) 2781.
[5] (a) J.A. Mahar, M.E. Peach, J. Fluorine Chem. 31 (1986) 121;
(b) M.E. Peach, J. Inorg. Nucl. Chem. 35 (1973) 1046;
(c) C.R. Lucas, M.E. Peach, Can J. Chem. 48 (1970) 1869;
(d) M.E. Peach, Can. J. Chem. 46 (1968) 2699.
[6] A. Singhal, V.K. Jain, B. Varghese, E.R.T. Tiekink, Inorg. Chim. Acta 285 (1999) 190.
[7] (a) J. Chatt, F.A. Hart, J. Chem. Soc. (1960) 2807;
(b) J. Chatt, F.A. Hart, J. Chem. Soc. (1953) 2363.
[8] (a) P.H. Kreutzer, K.T. Schorpp, W. Beck, Z. Naturforsch. B 30 (1975) 544;
(b) B. Kreutzer, P. Kreutzer, W. Beck, Z. Naturforsch. B 27 (1972) 461;
(c) W. Beck, K. von Werner, Chem. Ber. 104 (1971) 2901.
[9] R. Zanella, R. Ros, M. Graziani, Inorg Chem. 12 (1973) 2736.
[10] (a) V.K. Jain, S. Kannan, R.J. Butcher, J.P. Jasinski, J. Chem. Soc., Dalton Trans. (1993) 1509;
(b) C. Xu, J.W. Siria, G.K. Anderson, Inorg. Chim. Acta 206 (1993) 123.
[11] Q. Chen, F. Boeheim, J. Dabrowiak, J. Zubieta, Inorg. Chim. Acta 216 (1994) 83.
[12] (a) S. Archer, J.A. Weinstein, Coord. Chem. Rev. 256 (2012) 2530;
(b) M.Ya. Mel'nikov, J.A. Weinstein, High Energy Chem. 42 (2008) 287.
[13] (a) S.F. Parker, K. Refson, R.D. Bennett, J. Best, M. Ya, Inorg. Chem. 51 (2012) 9748;
(b) J.A. Weinstein, M.T. Tierney, E.S. Davies, K. Base, A.A. Robeiro, M.W. Grinstaff, Inorg. Chem. 45 (2006) 4544.
[14] (a) W. Paw, R.J. Lachicotte, R. Eisenberg, Inorg. Chem. 37 (1998) 4139;
(b) S.D. Cummings, L.-T. Cheng, R. Eisenberg, Chem. Mater. 9 (1997) 440;
(c) J.A. Zuleta, J.M. Bevilaqua, J.M. Rehm, R. Eisenberg, Inorg Chem. 31 (1992) 1332;
(d) J.A. Zuleta, J.M. Bevilaqua, R. Eisenberg, Coord. Chem. Rev. 111 (1991) 237.
[15] (a) V.W.W. Yam, R.P.L. Tang, K.M.C. Wong, C.C. Ko, K.K. Cheung, Inorg. Chem. 40 (2001) 571;
(b) B.C. Tzeng, W.F. Fu, C.-M. Che, H.Y. Chao, K.K. Cheung, S.M. Peng, J. Chem. Soc., Dalton Trans. (1999) 1017.

[16] F. Pevny, M. Zabel, R.F. Winter, A.F. Rausch, H. Yersin, F. Tuczek, S. Zális, Chem. Commun. 47 (2011) 6302.
[17] M. Kato, T. Okamura, H. Yamamoto, N. Ueyama, Inorg. Chem. 44 (2005) 1966.
[18] (a) E.L. Crossley, J.B. Aitken, S. Vogt, H.H. Harris, L.M. Rendina, Angew. Chem., Int Ed. 49 (2010) 1231;
(b) P.B. Glover, P.R. Ashton, L.J. Childs, A. Rodger, M. Kercher, R.M. Williams, L. De Cola, Z. Pikramenou, J. Am. Chem. Soc. 125 (2003) 9918.
[19] B.-C. Tzeng, C.-S. Ding, T.-Y. Chang, C.-C. Hu, G.-H. Lee, Cryst. Eng. Commun. 14 (2012) 8228.
[20] (a) H. Kuniyasu, K. Takekawa, F. Yamashita, K. Miyafuji, S. Asano, Y. Takai, A. Ohtaka, A. Tanaka, K. Sugoh, H. Kurosawa, N. Kambe, Organometallics 27 (2008) 4788;
(b) H. Kuniyasu, F. Yamashita, J. Terao, N. Kambe, Angew. Chem., Int. Ed. 46 (2007) 5929;
(c) H. Kuniyasu, F. Yamashita, T. Hirai, J.-H. Ye, S.-I. Fujiwara, N. Kambe, Organometallics 25 (2006) 566;
(d) T. Kato, H. Kuniyasu, T. Kajiura, Y. Minami, A. Ohtaka, M. Kinomoto, J. Terao, H. Kurosawa, N. Kambe, Chem. Commun. (2006) 868.
[21] (a) I.P. Beletskaya, V.P. Ananikov, Pure Appl. Chem. 79 (2007) 1041;
(b) J. Forniés-Cámer, A.M. Masdeu-Bultó, C. Claver, C. Tejel, M.A. Ciriano, C.J. Cardin, Organometallics 21 (2002) 2609;
(c) J.C. Bayón, C. Claver, A.M. Masdeu-Bultó, Coord. Chem. Rev. 193–195 (1999) 73;
(d) J. Forniés-Cámer, A. Aaliti, N. Ruiz, A.M. Masdeu-Bultó, C. Claver, C.J. Cardin, J. Organomet. Chem. 530 (1997) 199.
[22] (a) V.K. Jain, L.B. Kumbhare, S. Dey, N.D. Ghavale, Phosphorus Sulfur 183 (2008) 1003;
(b) S. Dey, V.K. Jain, Plat. Met. Rev. 48 (2004) 16;
(c) M. Bochmann, Chem. Vap. Depos. 2 (1996) 85.
[23] (a) M. Howe-Grant, S.J. Lippard, Inorg. Synth. 20 (1980) 101;
(b) M. Howe-Grant, K.C. Wu, W.R. Bauer, S.J. Lippard, Biochemistry 15 (1976) 4339.
[24] (a) R.T.C. Brownlee, W.D. McFadyen, M.J. O'Connor, T.J. Rook, I.A.G. Roos, L.P.G. Wakelin, Magn. Reson. Chem. 25 (1987) 492;
(b) W.D. McFadyen, L.P.G. Wakelin, I.A.G. Roos, V.A. Leopold, J. Med. Chem. 28 (1985) 1113.
[25] (a) A. Zarkadoulas, E. Koutsouri, C.A. Mitsopoulou, Coord. Chem. Rev. 256 (2012) 2424;
(b) J.S. Pap, F.L. Benedito, E. Bothe, E. Bill, S. DeBeer George, T. Weyhermüller, K. Wieghardt, Inorg. Chem. 46 (2007) 4187;
(c) W. Paw, S.C. Cummings, M.A. Mansour, W.B. Connick, D.K. Geiger, R. Eisenberg, Coord. Chem. Rev. 171 (1998) 125;
(d) W.B. Connick, H.B. Gray, J. Am. Chem. Soc. 119 (1997) 11620;
(e) Y. Zhang, K.D. Ley, K.S. Schanze, Inorg. Chem. 35 (1996) 7102.
[26] J.A. Weinstein, N.N. Zheligovskaya, M.Ya. Mel'nikov, F. Hartl, J. Chem. Soc., Dalton Trans. (1998) 2459.
[27] J.A. Weinstein, A.J. Blake, E.S. Davies, A.L. Davis, M.W. George, D.C. Grills, I.V. Lileev, A.M. Maksimov, P. Matousek, M.Y. Mel'nikov, A.W. Parker, V.E. Platonov, M. Towrie, C. Wilson, N.N. Zheligovskaya, Inorg. Chem. 42 (2003) 7077.
[28] V.C. Gibson, N.J. Long, C.K. Williams, M. Fontani, P. Zanello, Dalton Trans. (2003) 3599.
[29] (a) S. Bernès, L. Villanueva, H. Torrens, J. Chem. Crystallogr. 38 (2008) 123;
(b) A. Garcés-Rodríguez, D. Morales-Morales, S. Hernández-Ortega, Acta Crystallogr., Sect. E 63 (2007) m479;
(c) G. Rivera, S. Bernès, H. Torrens, Polyhedron 26 (2007) 4276.
[30] F. Estudiante-Negrete, R. Redón, S. Hernández-Ortega, R.A. Toscano, D. Morales-Morales, Inorg. Chim. Acta 360 (2007) 1651.
[31] (a) M.A. Usón, J.M. Llanos, J. Organomet. Chem. 663 (2002) 98;
(b) R. Usón, J. Forniés, M.A. Usón, M. Tomas, M.A. lbanez, J. Chem. Soc., Dalton Trans. (1994) 401;
(c) R. Usón, J. Forniés, M.A. Usón, S. Herrero, J. Organomet. Chem. 447 (1993) 137.
[32] S.-K. Lee, D.-Y. Noh, Inorg. Chem. Commun. 13 (2010) 183.
[33] M. Corona-Rodríguez, S. Hernández-Ortega, J. Valdés-Martínez, D. Morales-Morales, Supramol. Chem. 19 (2007) 579.
[34] R. Usón, M.A. Usón, S. Herrero, L. Rello, Inorg. Chem. 37 (1998) 4437.
[35] (a) E. Martin, B. Toledo, H. Torrens, F.J. Lahoz, P. Terreros, Polyhedron 17 (1998) 4091;
(b) D. Cruz-Garritz, E. Martin, H. Torrens, K.A. Mayoh, A.J. Smith, Transition Met. Chem. 16 (1991) 236;
(c) D. Cruz-Garritz, E. Martin, H. Torrens, K.A. Mayoh, A.J. Smith, Acta Crystallogr., Sect. C 46 (1990) 2377.
[36] (a) B. Rivera, H. Torrens, S. Bernès, Acta Crystallogr., Sect. E 62 (2006) m3287;
(b) J. García, E. Martin, D. Morales, H. Torrens, F. del Río, Inorg. Chim. Acta 207 (1993) 93.
[37] G. Rivera, S. Bernès, C. Rodriguez de Barbarin, H. Torrens, Inorg. Chem. 40 (2001) 5575.
[38] V. Lingen, A. Lüning, C. Strauß, I. Pantenburg, G.B. Deacon, A. Klein, G. Meyer, Eur. J. Inorg. Chem. (2013) 4450.
[39] (a) V.K. Jain, L. Jain, Coord. Chem. Rev. 254 (2010) 2848;
(b) V.K. Jain, L. Jain, Coord. Chem. Rev. 249 (2005) 3075;
(c) H. Torrens, Coord. Chem. Rev. 196 (2000) 331.
[40] G.T. Morgan, F.H. Burstall, J. Chem. Soc. (1934) 965.
[41] (a) A.L. Sanger, J. Chem. Soc., Dalton Trans. (1977) 1971;
(b) A.D. Westland, J. Chem. Soc. (1965) 3060.
[42] H.C. Clark, L.E. Manzer, J. Organomet. Chem. 59 (1973) 411.
[43] K. Butsch, R. Gust, A. Klein, I. Ott, M. Romanski, Dalton Trans. 39 (2010) 4331.
[44] (a) W. Kaim, Angew. Chem., Int. Ed. Engl. 22 (1983) 171;
(b) W. Kaim, Rev. Chem. Intermed. 8 (1987) 247.
[45] (a) M. Atsumi, L. González, C. Daniel, J. Photochem. Photobiol. A 190 (2007) 310;
(b) K.E. Erkkila, D.T. Odomand, J.K. Barton, Chem. Rev. 99 (1999) 2777;
(c) X.-H. Zou, J.L.-N. Xia-Hua, Trends Inorg. Chem. 7 (2001) 99;
(d) A.E. Friedman, J.-C. Chambron, J.-P. Sauvage, N.J. Turro, J.K. Barton, J. Am. Chem. Soc. 112 (1990) 4960;
(e) D. Villagra, R. López, S.A. Moya, C. Claver, A. Bastero, Organometallics 27 (2008) 1019.
[46] N. Hernandez-Gil, W.E. Wentworth, E.C.M. Chen, J. Phys. Chem. 88 (1984) 6181.
[47] G.B. Deacon, P.W. Elliot, A.P. Erven, G. Meyer, Z. Anorg. Allg. Chem. 631 (2005) 843.
[48] J.C. Bailar Jr., H. Itatani, Inorg. Chem. 4 (1965) 1618.
[49] J.H. Price, A.N. Williamson, R.F. Schramm, B.B. Wayland, Inorg. Chem. 11 (1972) 1280.
[50] G.M. Sheldrick, SHELXS-97, Program for the Solution of Crystal Structures, University of Göttingen, Germany, 1997.
[51] G.M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1997.
[52] P. Espinet, A.C. Albéniz, J.A. Casares, J.M. Martínez-Ilarduya, Coord. Chem. Rev. 252 (2008) 2180.
[53] B. Still, P.G.A. Kumar, J.R. Aldrich-Wright, W.S. Price, Chem. Soc. Rev. 36 (2007) 665.
[54] (a) A. Klein, A. Lüning, I. Ott, L. Hamel, M. Neugebauer, K. Butsch, V. Lingen, F. Heinrich, S. Elmas, J. Organomet. Chem. 695 (2010) 1898;
(b) K. Butsch, S. Elmas, N. Sen Gupta, R. Gust, F. Heinrich, A. Klein, Y. von Mering, M. Neugebauer, I. Ott, M. Schäfer, H. Scherer, T. Schurr, Organometallics 28 (2009) 3906;
(c) A. Klein, T. Schurr, H. Scherer, N. Sen Gupta, Organometallics 26 (2007) 230;
(d) A. Klein, K.-W. Klinkhammer, T. Scheiring, J. Organomet. Chem. 592 (1999) 128.
[55] C.E. Keefer, R.D. Bereman, S.T. Purrington, B.W. Knight, P.D. Boyle, Inorg. Chem. 38 (1999) 2294.
[56] M. Hirano, S. Tatesawa, M. Yabukami, Y. Ishihara, Y. Hara, N. Komine, S. Komiya, Organometallics 30 (2011) 5110.
[57] (a) P.G. Waddell, A.M.Z. Slawin, J.D. Woollins, Dalton Trans. 39 (2010) 8620;
(b) D. Gudat, V.K. Jain, A. Klein, T. Schurr, S. Zalis, Eur. J. Inorg. Chem. (2005) 4056;
(c) A.L. Rieger, G.B. Carpenter, P.H. Rieger, Organometallics 12 (1993) 842;
(d) H. Motschi, P.S. Pregosin, L.M. Venanzi, Helv. Chim. Acta 62 (1979) 667;
(e) T.G. Appleton, H.C. Clark, L.E. Manzer, Coord. Chem. Rev. 10 (1973) 335.
[58] (a) T.G. Appleton, J.R. Hall, S.F. Ralph, Inorg. Chem. 24 (1985). 673–677 and 4685–4693;
(b) P.S. Pregosin, H. Omura, L.M. Venanzi, J. Am. Chem. Soc. 95 (1973) 2047.
[59] E. Pizzo, P. Sgarbossa, A. Scarso, R.A. Michelin, G. Strukul, Organometallics 25 (2006) 3056.
[60] A. Klein, T. Schurr, A. Knödler, D. Gudat, K.-W. Klinkhammer, V.K. Jain, S. Zalis, W. Kaim, Organometallics 24 (2005) 4125.
[61] S.J. Berners-Price, L. Ronconi, P.J. Sadler, Prog. Nucl. Magn. Reson. Spectrosc. 49 (2006) 65.
[62] (a) C.A. Hunter, K.R. Lawson, J. Perkins, C.J. Urch, J. Chem. Soc., Perkin Trans. 2 (2001) 651;
(b) C. Janiak, J. Chem. Soc., Dalton Trans. (2000) 3885.
[63] K. Osakada, T. Hosoda, T. Yamamoto, Bull. Chem. Soc. Jpn. 73 (2000) 923.
[64] (a) S. Otto, Inorg. Chim. Acta 363 (2010) 3316;
(b) Y. Suzaki, K. Osakada, Organometallics 23 (2004) 5081;
(c) D.C. Smith Jr., C.M. Haar, E.D. Stevens, S.P. Nolan, Organometallics 19 (2000) 1427;
(d) R. Wyrwa, W. Poppitz, H. Görls, Z. Anorg. Allg. Chem. 623 (1997) 649.
[65] A. Castellanos, J.J. Garcia, H. Torrens, N. Bailey, C.O. Rodriguez de Barbarin, A. Gutierrez, F. del Rio, J. Chem. Soc., Dalton Trans. (1994) 2861.
[66] I. Nakanishi, K. Matsumoto, S. Ooi, Acta Crystallogr., Sect. C 47 (1991) 2073.
[67] A. Singhal, V.K. Jain, A. Klein, M. Niemeyer, W. Kaim, Inorg. Chim. Acta 357 (2004) 2134.
[68] The Shannon radii differ only by 0.04 Å (Pd > Pt): R.D. Shannon, Acta Crystallogr., Sect. A 32 (1976) 751-767. For examples see: (a) M.R. Warren, S.K. Brayshaw, L.E. Hatcher, A.L. Johnson, S. Schiffers, A.J. Warren, S.J. Teat, J.E. Warren, C.H. Woodall, R.R. Raithby, Dalton Trans. 41 (2012) 13173;
(b) S. Dey, L.B. Kumbhare, V.K. Jain, T. Schurr, W. Kaim, A. Klein, F. Belaj, Eur. J. Inorg. Chem. (2004) 4510;
(c) K. Herbst, B. Rink, L. Dahlenburg, M. Brorson, Organometallics 20 (2001) 3655.
[69] S. Scarso, M. Colladon, P. Sgarbossa, C. Santo, R.A. Michelin, G. Strukul, Organometallics 29 (2010) 1487.
[70] J.C. Fuggle, N. Mårtensson, J. Electron Spectrosc. Relat. Phenom. 21 (1980) 275.