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On the Reactivity of the Platina-β-diketone $[Pt_2\{(COMe)_2H\}_2(\mu\text{-}Cl)_2]$ Towards $Ph_2PCH_2CH_2CH_2SO_xPh$ ($x = 0, 2$)

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Abstract. The reaction of the electronically unsaturated platina-β-diketone $[Pt_2\{(COMe)_2H\}_2(\mu\text{-}Cl)_2]$ (**1**) with $Ph_2PCH_2CH_2CH_2SPh$ (**2**) leads selectively to the formation of the acetyl(chlorido) platinum(II) complex (*SP*-4-3)-$[Pt(COMe)Cl(Ph_2PCH_2CH_2CH_2SPh\text{-}\kappa P,\kappa S)]$ (**4**) having the γ-phosphinofunctionalized propyl phenyl sulfide coordinated in a bidentate fashion (κ*P*,κ*S*). In boiling benzene complex **4** undergoes decarbonylation yielding the methyl(chlorido) platinum(II) complex (*SP*-4-3)-$[PtMeCl(Ph_2PCH_2CH_2CH_2SPh\text{-}\kappa P,\kappa S)]$ (**6**). However, the reaction of **1** with the analogous γ-diphenylphosphinofunctionalized propyl phenyl sulfone $Ph_2PCH_2CH_2CH_2SO_2Ph$ (**3**) affords the acetyl(chlorido) platinum(II) complex (*SP*-4-4)-$[Pt(COMe)Cl(Ph_2PCH_2CH_2CH_2SO_2Ph\text{-}\kappa P)_2]$ (**5**). In boiling benzene complex **5** undergoes a CO extrusion yielding (*SP*-4-4)-$[PtMeCl(Ph_2PCH_2CH_2CH_2SO_2Ph\text{-}\kappa P)_2]$ (**8**) whereas in presence of **1** the formation of the carbonyl complex (*SP*-4-3)-$[PtMeCl(CO)(Ph_2PCH_2CH_2CH_2SO_2Ph\text{-}\kappa P)]$ (**7**) is observed. Addition of $Ag[BF_4]$ to complex **5** leads to the formation of the cationic methyl(carbonyl) platinum(II) complex (*SP*-4-1)-$[PtMe(CO)(Ph_2PCH_2CH_2CH_2SO_2Ph\text{-}\kappa P)_2][BF_4]$ (**9**). All complexes were characterized by microanalysis and NMR spectroscopy (^1H, ^{13}C, ^{31}P) and complexes **4** and **6** additionally by single-crystal X-ray diffraction analyses.

1 Introduction

Reactions of hexachloridoplatinic acid with *n*-butyl alcohol and trimethylsilyl-substituted alkynes lead to the formation of platina-β-diketones $[Pt_2\{(COR)_2H\}_2(\mu\text{-}Cl)_2]$ (R = alkyl) which may be described as hydroxycarbene complexes stabilized by strong intramolecular hydrogen bonds to acyl ligands, as shown in Scheme 1 for the formation of the parent complex **1** (R = Me).[1] In contrast to *Lukehart*'s metalla-β-diketones $[L_xM\{(COR)_2H\}]$ (L = CO, Cp; M = Mo, Re, Fe,..; R = alkyl, aryl),[2] platina-β-diketones exhibit a unique reactivity due to their electronic unsaturation (16 valence electron complexes) and their kinetically labile ligand sphere.[3] Thus, the platina-β-diketone $[Pt_2\{(COMe)_2H\}_2(\mu\text{-}Cl)_2]$ (**1**) is found to react with numerous monodentate and chelating donors L and L^L yielding, respectively, diacetyl(hydrido) platinum(IV) complexes of type **A** and acetyl platinum(II) complexes of type **B** (Scheme 1). In the case of hard/hard N^N donors, the platinum(IV) complexes of type **A** proved to be thermally extraordinarily stable,[4, 5] whereas with soft donors (P, P^P, S^S) type **A** complexes could be detected NMR spectroscopically only or remained unseen at all, thus only type **B** complexes could be isolated.[6–8] The formation of the diacetyl platinum(II) complexes of type **C** can be induced by addition of bases to complexes **A**.[9, 10]

Here we report on reactions of the dinuclear platina-β-diketone $[Pt_2\{(COMe)_2H\}_2(\mu\text{-}Cl)_2]$ (**1**) with $P^\wedge SO_x$ ($x = 0, 2$) type ligands $Ph_2PCH_2CH_2CH_2SPh$ (**2**) and $Ph_2PCH_2CH_2CH_2SO_2Ph$ (**3**) yielding mononuclear acetyl(chlorido) platinum(II) complexes of type **B** as well as on their decarbonylation.

2 Results and Discussion

2.1 Syntheses

The dinuclear platina-β-diketone $[Pt_2\{(COMe)_2H\}_2(\mu\text{-}Cl)_2]$ (**1**) was found to react in dichloromethane with $Ph_2PCH_2CH_2CH_2SPh$ (**2**) and $Ph_2PCH_2CH_2CH_2SO_2Ph$ (**3**) to yield mononuclear acetyl(chlorido) platinum(II) complexes (**4**, **5**, routes **a**/**c**, Scheme 2). In these reactions as well as in the reactions described in the following, as a side product traces of a black solid, most likely platinum black, were formed. Complexes **4** and **5** were isolated in yields of > 70 % as colorless air-stable products, which were characterized by NMR (^1H, ^{13}C, ^{31}P) and IR spectroscopy as well as by microanalyses and single-crystal X-ray diffraction analysis (**4**).

The platinum complexes **4** and **5** were found to undergo a decarbonylation reaction in boiling benzene within 2 hours, thus yielding the methyl(chlorido) platinum(II) complexes **6** and **8** (routes **b**/**d**). The addition of $Ag[BF_4]$ to complex **5** (route **e**) led with precipitation of AgCl to the formation of the methyl(carbonyl)platinum(II) complex **9**. Complexes **6**, **8** and **9** were isolated as colorless air-stable solids in yields between 70 and 78 % and fully characterized by microanalysis, ^1H, ^{13}C, and ^{31}P NMR spectroscopy as well as by single-crystal X-ray diffraction analysis (**6**).

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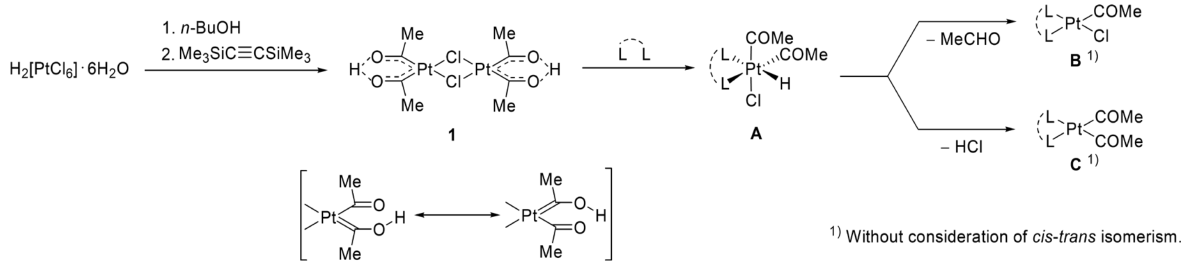
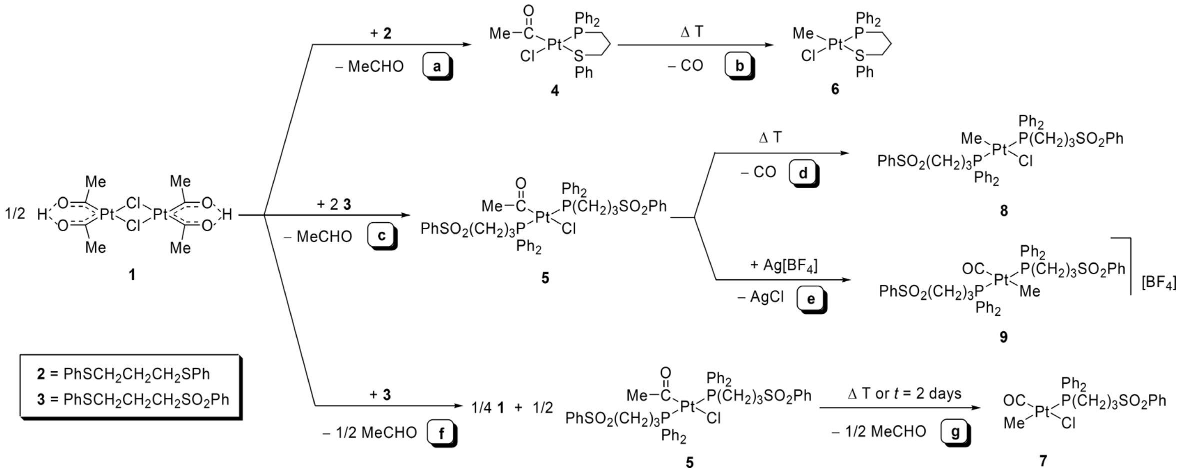


Scheme 1. Synthesis of the platina-β-diketone **1** and its reactivity towards monodentate and chelating ligands L and L^L, respectively.



Scheme 2. Reactions of the platina-β-diketone **1** with γ-phosphinofunctionalized propyl phenyl sulfides and sulfones.

The reaction of the platina-β-diketone **1** with a deficiency of the phosphinofunctionalized sulfone **3** (molar ratio 1:2) led – in a fast reaction – to the formation of **5**, whereas the half of complex **1** remained unreacted (route **f**). This obtained mixture was found to undergo – in a slow reaction within two days – a decarbonylation reaction yielding the methyl(chlorido)carbonyl platinum(II) complex **7** (route **g**). In boiling benzene this reaction proceeded within two hours. Complex **7** was isolated (yield 82 %) as colorless air-stable solid and fully characterized analytically and spectroscopically. Noteworthy, the pure complex **5**, prepared according to route **c**, proved to be stable in dichloromethane solution at room temperature and reacted only in boiling benzene according to route **d**.

2.2 Spectroscopic Investigations

Selected NMR spectroscopic parameters of complexes **4–9** are given in Table 1. The magnitudes of the $^1J_{Pt,P}$ couplings in complexes **4–9** are fully consistent with the trans influence order Cl < PR_3 < Me because they were found to decrease from about 4500 Hz (**4**, **6**) over 2500–3400 Hz (**5**, **8**, **9**) to ca 1450 Hz (**7**). In the two acetyl(chlorido) platinum(II) complexes the ^{13}C resonances of the methyl groups exhibited d+dd (**4**) and t+dt (**5**) patterns showing $^3J_{P,C}$ and $^2J_{Pt,C}$ couplings of about 5/6 Hz and 165/215 Hz, respectively. However, in the ^1H NMR spectra the protons of the methyl groups appeared as singlet signals (δ_H = 1.84/1.16) only. The carbonyl carbon atoms showed shifts in the

Table 1. Selected NMR spectroscopic data (δ in ppm, J in Hz) of complexes **4–9** bearing the ligands L1 ($Ph_2PCH_2CH_2CH_2SPh$) and L2 ($Ph_2PCH_2CH_2CH_2SO_2Ph$), respectively.

Complex		δ_C (COMe) ($^2J_{P,C}$)	δ_C (COCH$_3$) ($^2J_{Pt,C}$/$^3J_{P,C}$)	δ_C (CO) ($^2J_{P,C}$)	δ_C (CH$_3$) ($^1J_{Pt,C}$/$^2J_{P,C}$)	δ_P ($^1J_{Pt,P}$)
[Pt(COMe)Cl(L1-κ*P*,κ*S*)]	(**4**)	213.5 (6.8)	40.7 (167.0/4.7)	–	–	–4.1 (4765)
[Pt(COMe)Cl(L2-κ*P*)$_2$]	(**5**)	215.3 (5.6)	44.2 (216.1/6.2)	–	–	15.7 (3366)
[PtMeCl(L1-κ*P*,κ*S*)]	(**6**)	–	–	–	–1.7 (616.0/5.9)	4.0 (4407)
[PtMeCl(CO)(L2-κ*P*)]	(**7**)	–	–	165.1 (7.4)	2.4 (479.7/87.4)	22.1 (1442)
[PtMeCl(L2-κ*P*)$_2$]	(**8**)	–	–	–	–13.0 (661.8/5.6)	23.2 (3056)
[PtMe(CO)(L2-κ*P*)$_2$][BF$_4$]	(**9**)	–	–	178.3 (5.3)	2.4 ($^{a)}$/6.5)	17.3 (2538)

a) Not detected.

expected range (213.5/215.3 ppm, **4**/**5**), but only $^2J_{P,C}$ couplings (ca 6 Hz) due to weak intensity. The ^{1}H and ^{13}C resonances of the methyl ligands in complexes **6** and **8** exhibited strong highfield shifts by, respectively, 1.2 and more than 40 ppm compared to the resonances of the methyl group of the acetyl ligand in complexes **4** and **5**. Besides the expected coupling patterns in complexes **6** (d+dd) and **8** (t+dt) the magnitudes of the $^2J_{Pt,H}$ couplings in the region of 70–80 Hz and of the $^1J_{Pt,C}$ coupling constants (600–700 Hz) unambiguously prove that the methyl groups are directly bound to the platinum atom.

As expected, the shifts of the methyl ligands (^{1}H, ^{13}C) in complexes **7** and **9** were also found in the highfield region (δ_H = 1.10/0.50; δ_C = 2.4/2.4). Whereas the $^1J_{Pt,C}$ coupling constant of **7** (480 Hz) is decreased by, respectively, 136 and 182 Hz compared to the couplings in **6** and **8**, it could not be detected in **9** due to bad signal-to-noise ratio. Noteworthy, the $^2J_{P,C}$ coupling in the methyl(chlorido) carbonyl platinum(II) complex **7** is with 87.4 Hz very large but in the same region as reported for other platinum(II) complexes bearing a methyl and a phosphane ligand in mutual *trans* position.[11–13] The resonances of the carbonyl carbon atoms in **7** and **9** are in the expected region (δ_C ca. 170) showing $^2J_{P,C}$ couplings of 7.4 and 5.3 Hz, respectively.

2.3 Structures

Crystals of **4** and **6** suitable for X-ray diffraction analyses were obtained from dichloromethane solutions with a layer of *n*-pentane at room temperature. In crystals monomeric complexes without unusual intermolecular contacts (shortest intermolecular distance between non-hydrogen atoms: 3.46(2) Å, C4···C14', **4**; 3.44(2) Å, C20···C20', **6**) were found. The molecular structures are shown in Figure 1 and Figure 2. Selected structural parameters are given in the Figure captions.

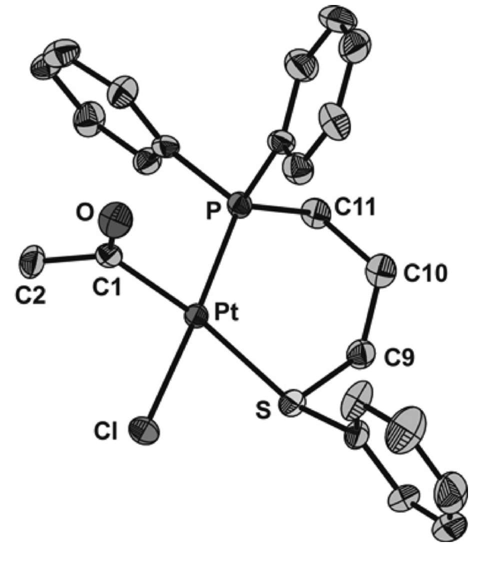


Figure 1. Molecular structure of (*SP*-4-3)-[Pt(COMe)Cl($Ph_2PCH_2CH_2CH_2SPh$-κ*P*,κ*S*)] (**4**). The ellipsoids are shown with a probability of 50 %. Hydrogen atoms were omitted for clarity. Selected structural parameters (distances in Å, angles in °): Pt–Cl 2.378(3), Pt–S 2.435(3), Pt–P 2.217(3), Pt–C1 2.02(1), C1–C2 1.50(2), C1–O 1.226(1), Cl–Pt–S 84.58(9), Cl–Pt–C1 88.5(3), S–Pt–P 98.90(9), P–Pt–C1 88.1(3), Cl–Pt–P 176.5 (1), S–Pt–C1 172.9(3).

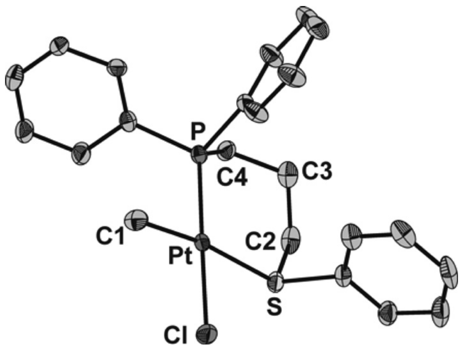


Figure 2. Molecular structure of (*SP*-4-3)-[PtMeCl($Ph_2PCH_2CH_2CH_2SPh$-κ*P*,κ*S*)] (**6**). The ellipsoids are shown with a probability of 50 %. Hydrogen atoms were omitted for clarity. Selected structural parameters (distances in Å, angles in °): Pt–Cl 2.379(2), Pt–S 2.377(2), Pt–P 2.204(2), Pt–C1 2.056(9), Cl–Pt–S 84.36(8), S–Pt–P 97.50(7), P–Pt–C1 90.4(3), C1–Pt–Cl 87.8(3), Cl–Pt–P 176.52(8), S–Pt–C1 171.9(3).

In the two complexes the platinum atoms adopt an almost ideal square-planar configuration; only the S–Pt–P angles are somewhat enlarged (98.90(9)°/97.50(7)°) due to the bite of the chelating P^S ligand. As expected, the Pt–Cl bonds (2.378(3)/2.379(2) Å) are of the same length. The *trans* influence order COMe > Me is reflected in a markedly longer Pt–S bond in **4** (2.435(3) Å) compared to that in **6** (2.377(2) Å). The Pt–C bond lengths in **4** (2.02(1) Å) and **6** (2.056(9) Å) are analogous to those in other platinum(II) complexes bearing a thioether ligand in *trans* position to an acyl ligand[7, 14, 15] and a methyl ligand,[16–18] respectively.

2.4 Conclusion

Reactions of the dinuclear platina-β-diketone $[Pt_2\{(COMe)_2H\}_2(\mu\text{-}Cl)_2]$ (**1**) with the γ-phosphinofunctionalized propyl phenyl sulfide ($Ph_2PCH_2CH_2CH_2SPh$, **2**) and sulfone ($Ph_2PCH_2CH_2CH_2SO_2Ph$, **3**) lead via an unseen platinum(IV) intermediate of type **A** with reductive elimination of acetaldehyde[4, 19] (detected ^{1}H NMR spectroscopically) to the formation of type **B** acetyl(chlorido) platinum(II) complexes (**4**, **5**) (Scheme 1). In complex **4**, ligand **2** acts as a chelating P^S donor; analogous reactions were found with other bidentate P^P[4] or N^S[7] donors. In contrast, in complex **5** the phosphinofunctionalized sulfone **3** acts only as monodentate ligand (κ*P*), obviously due to a too low donor capability of the sulfonyl group. Its reactivity against **1** is analogous to that of non-functionalized phosphanes P*R*$_3$.[10]

In boiling benzene complexes **4** and **5** underwent an extrusion of CO yielding the respective methyl(chlorido) platinum(II) complexes **6** and **8**, respectively. This decarbonylation proceeds already at room temperature, if a "vacant" coordination site is generated by reaction of **5** either with Ag[BF$_4$] or with the (unreacted) platina-β-diketone **1** (routes **e**/**g**, Scheme 2). Here, the latter reaction was found to be diastereoselective yielding the (*SP*-4-3) isomer whereas the analogous reaction using PPh_3 instead of **3** proceeded non-diastereoselective since the (*SP*-4-3) and the (*SP*-4-2) isomers of complex $[PtClMe(CO)(PPh_3)]$ were isolated in a ratio of 7:3.[6] On the other hand, in an analogous reaction using a phosphane with a low donor capability ($P(C_6F_5)_3$) only the decarbonylated product was formed.[11] Analogous decarbonylation reactions have also been reported on α-ketoacyl[20] and formyl platinum(II) complexes.[21] The results presented here give further insight into the reactivity of platina-β-diketones towards mono- and bidentate ligands and readily access to novel acetyl, methyl and carbonyl platinum(II) complexes.

3 Experimental Section

3.1 General Remarks

All reactions were performed in an argon atmosphere using the standard Schlenk techniques. Solvents were dried (Et_2O, benzene and *n*-pentane over Na/benzophenone, CH_2Cl_2 over CaH_2) and distilled prior to use. NMR spectra were recorded at 27 °C with Varian Gemini 200, VXR 400 and Unity 500 spectrometers. Solvent signals (^{1}H, ^{13}C) were used as internal references; $\delta(^{31}P)$ is relative to external H_3PO_4 (85 %). Multiplet signals in NMR spectra of higher order resulting in pseudo triplets are denoted by 't'. IR spectra were recorded with a Bruker Tensor 28 spectrometer with a Platinum ATR unit. Microanalyses were performed by the University of Halle microanalytical laboratory using CHNS-932 (LECO) elemental analyzer. The complex $[Pt_2\{(COMe)_2H\}_2(\mu\text{-}Cl)_2]$ (**1**) as well as the γ-phosphinofunctionalized sulfide (**2**) and sulfone (**3**) were prepared according to literature methods.[1, 22, 23]

3.2 Synthesis of $[Pt(COMe)Cl(Ph_2PCH_2CH_2CH_2SPh\text{-}\kappa P,\kappa S)]$ (4) and $[Pt(COMe)Cl(Ph_2PCH_2CH_2CH_2SO_2Ph\text{-}\kappa P)_2]$ (5)

To a stirred suspension of **1** (100 mg, 0.16 mmol) in CH_2Cl_2 (5 mL) a solution of, respectively, **2** (108 mg, 0.32 mmol) and **3** (236 mg, 0.64 mmol) in CH_2Cl_2 (3 mL) was added at –78 °C and allowed to warm to room temperature. After the addition of *n*-pentane (5 mL), the precipitated solid was filtered off, washed with *n*-pentane (3 × 3 mL) and dried in vacuo.

(**4**) Yield: 150 mg (77 %). Anal. $C_{23}H_{24}ClOPPtS$ (610.01 g·mol^{-1}): C, 45.29; H, 3.97; Found: C, 44.61; H, 4.01. **IR**: ν = 1648 (s, CO) cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 1.84 (s, 3 H, CH_3), 1.93–2.04 (m, 2 H, CH_2CH_2SPh), 2.55 (m, 2 H, CH_2PPh_2), 3.15 (m, 2 H, CH_2SPh), 7.23–7.73 (m, 15 H, H_{Ph}). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 21.8 (s, CH_2CH_2SPh), 25.2 (d, $^1J_{P,C}$ = 32.7 Hz, CH_2PPh_2), 36.0 (d, $^3J_{P,C}$ = 2.9 Hz, CH_2SPh), 40.7 (d+dd, $^3J_{P,C}$ = 4.7, $^2J_{Pt,C}$ = 167.0 Hz, CH_3), 128.5–133.2 (C_{Ph}), 213.5 (d, $^2J_{P,C}$ = 6.8 Hz, Pt–C). **^{31}P NMR** (81 MHz, $CDCl_3$): δ = –4.1 (s+d, $^1J_{Pt,P}$ = 4765 Hz, PPh_2).

(**5**) Yield: 232 mg (72 %). Anal. $C_{44}H_{45}ClO_5P_2PtS_2$ (1010.44 g·mol^{-1}): C, 52.30; H, 4.49; Found: C, 52.01; H, 4.65. **IR**: ν = 1625 (s, CO) cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 1.16 (s, 3 H, CH_3), 2.22 (m, 4 H, $CH_2CH_2SO_2Ph$), 2.73 (m, 4 H, CH_2PPh_2), 3.28 (m, 4 H, CH_2SO_2Ph), 7.36–7.82 (m, 30 H, H_{Ph}). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 18.7 (s, $CH_2CH_2SO_2Ph$), 25.1 ('t', N = 35.0 Hz, CH_2PPh_2), 44.2 (t+dt, $^3J_{P,C}$ = 6.2, $^2J_{Pt,C}$ = 216.1 Hz CH_3), 56.5 ('t', N = 14.8 Hz, CH_2SO_2Ph), 128.0–139.1 (C_{Ph}), 215.3 (t, $^2J_{P,C}$ = 5.6 Hz, Pt–C). **^{31}P NMR** (81 MHz, $CDCl_3$): δ = 15.7 (s+d, $^1J_{Pt,P}$ = 3366 Hz, PPh_2).

3.3 Synthesis of $[PtMeCl(Ph_2PCH_2CH_2CH_2SPh\text{-}\kappa P,\kappa S)]$ (6), $[PtMeCl(CO)(Ph_2PCH_2CH_2CH_2SO_2Ph\text{-}\kappa P)]$ (7) and $[PtMeCl(Ph_2PCH_2CH_2CH_2SO_2Ph\text{-}\kappa P)_2]$ (8)

To a stirred suspension of **1** (100 mg, 0.16 mmol) in CH_2Cl_2 (5 mL) a solution of, respectively, **2** (108 mg, 0.32 mmol) and **3** (0.32 mmol for the preparation of **7**; 0.64 mmol for the preparation of **8**) in CH_2Cl_2 (2 mL) was added at –78 °C, allowed to warm to room temperature and stirred for further 30 minutes. After the solvent was evaporated in vacuo, the residue was dissolved in benzene (2 mL) and the reaction mixture was heated under reflux for two hours. After cooling to room temperature the reaction mixture was filtered, *n*-pentane (5 mL) was added to the filtrate, the precipitated solid was filtered off and washed with *n*-pentane (3 × 3 mL). The crude products were re-precipitated from chloroform/*n*-pentane (1:2), filtered off and dried in vacuo.

(**6**) Yield: 136 mg (73 %). Anal. $C_{22}H_{24}ClPPtS$ (582.00 g·mol^{-1}): C, 45.40; H, 4.16; Found: C, 45.29; H, 4.28. **^{1}H NMR** (400 MHz, CD_2Cl_2): δ = 0.59 (d+dd, $^3J_{P,H}$ = 4.15, $^2J_{Pt,H}$ = 71.81 Hz, 3 H, CH_3), 1.95–2.04 (m, 2 H, CH_2CH_2SPh), 2.49 (m, 2 H, CH_2PPh_2), 3.19 (m, 2 H, CH_2SPh), 7.06–7.88 (m, 15 H, H_{Ph}). **^{13}C NMR** (100 MHz, CD_2Cl_2): δ = –1.7 (d+dd, $^2J_{P,C}$ = 5.9, $^1J_{Pt,C}$ = 616.0 Hz, CH_3), 22.0 (s, CH_2CH_2SPh), 25.4 (d, $^1J_{P,C}$ = 39.5 Hz, CH_2PPh_2), 36.9 (d, $^3J_{P,C}$ = 2.7 Hz, CH_2SPh), 128.5–133.5 (C_{Ph}). **^{31}P NMR** (81 MHz, CD_2Cl_2): δ = 4.0 (s+d, $^1J_{Pt,P}$ = 4407 Hz, PPh_2).

(**7**) Yield: 168 mg (82 %). Anal. C_{23}H24ClO_3PPtS (642.01 g·mol^{-1}): C, 43.03; H, 3.77; Found: C, 42.87; H, 3.71. **IR**: ν = 2075 (s, CO) cm^{-1}. **^{1}H NMR** (400 MHz, CD_2Cl_2): δ = 1.10 (d+dd, $^3J_{P,H}$ = 7.65, $^2J_{Pt,H}$ = 56.88 Hz, 3 H, CH_3), 1.91–2.02 (m, 2 H, $CH_2CH_2SO_2Ph$), 2.76–2.82 (m, 2 H, CH_2PPh_2), 3.19 (m, 2 H, C*H2*SO_2Ph), 7.42–7.84 (m, 15 H, H_{Ph}). **^{13}C NMR** (100 MHz, CD_2Cl_2): δ = 2.4 (d+dd, $^2J_{P,C}$ = 87.4, $^1J_{Pt,C}$ = 479.7 Hz, CH_3), 18.5 (d, $^2J_{P,C}$ = 2.7 Hz, $CH_2CH_2SO_2Ph$), 24.3 (d, $^1J_{P,C}$ = 29.0 Hz, CH_2PPh_2), 56.7 (d, $^3J_{P,C}$ = 14.8 Hz, CH_2SO_2Ph), 128.3–139.3 (C_{Ph}), 165.1 (d, $^2J_{P,C}$ = 7.4 Hz, *C*O). **^{31}P NMR** (81 MHz, CD_2Cl_2): δ = 22.1 (s+d, $^1J_{Pt,P}$ = 1442 Hz, PPh_2).

(**8**) Yield: 123 mg (78 %). Anal. $C_{43}H_{45}ClO_4P_2PtS_2$ (982.43 g·mol^{-1}): C, 52.57; H, 4.62; Found: C, 52.42; H, 4.77. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = –0.08 (t+dt, $^3J_{P,H}$ = 6.45, $^2J_{Pt,H}$ = 80.64 Hz, 3 H, CH_3), 2.08 (m, 4 H, $CH_2CH_2SO_2Ph$), 2.74 (m, 4 H, CH_2PPh_2), 3.27 (m, 4 H, CH_2SO_2Ph), 7.36–7.77 (m, 30 H, H_{Ph}). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = –13.0 (t+dt, $^2J_{P,C}$ = 5.6, $^1J_{Pt,C}$ = 661.8 Hz, CH_3), 18.4 (s, $CH_2CH_2SO_2Ph$), 24.7 ('t', N = 35.2 Hz, CH_2PPh_2), 56.5 ('t', N = 14.6 Hz, CH_2SO_2Ph), 127.9–139.2 (C_{Ph}). **^{31}P NMR** (81 MHz, $CDCl_3$): δ = 23.2 (s+d, $^1J_{Pt,P}$ = 3056 Hz, PPh_2).

3.4 Synthesis of $[PtMe(CO)(Ph_2PCH_2CH_2CH_2SO_2Ph\text{-}\kappa P)_2][BF_4]$ (9)

To a stirred suspension of **1** (100 mg, 0.16 mmol) in CH_2Cl_2 (5 mL) a solution of **3** (236 mg, 0.64 mmol) in CH_2Cl_2 (3 mL) was added at –78 °C and allowed to warm to room temperature. Afterwards, the solution was cooled to –78 °C again before a suspension of $Ag[BF_4]$ (31 mg, 0.16 mmol) in CH_2Cl_2 (1 mL) was added. After warming to room temperature and stirring for 30 minutes, the precipitated AgCl was filtered off and the filtrate was stirred for 12 hours. The volume was reduced to its half under reduced pressure, diethyl ether (5 mL) was added, the precipitated solid was filtered off, washed with diethyl ether (3 × 3 mL) and dried in vacuo.

Yield: 119 mg (70 %). Anal. $C_{44}H_{45}O_5P_2PtS_2BF_4$ (1061.79 g·mol^{-1}): C, 49.77; H, 4.27; Found: C, 49.66; H, 4.33. **IR**: ν = 2077 (s, CO) cm^{-1}. **^{1}H NMR** (400 MHz, CD_2Cl_2): δ = 0.50 (t+dt, $^2J_{P,H}$ = 8.71, $^1J_{Pt,H}$ = 61.97 Hz, 3 H, CH_3), 2.06–2.15 (m, 4 H, $CH_2CH_2SO_2Ph$), 2.98–3.04 (m, 4 H, CH_2PPh_2), 3.27 (m, 2 H, CH_2SO_2Ph), 7.52–7.83 (m, 30 H, H_{Ph}). **^{13}C NMR** (50 MHz, CD_2Cl_2): δ = 2.4 (t, $^2J_{P,C}$ = 6.5 Hz, CH_3), 18.7 ('t', N = 25.7 Hz, $CH_2CH_2SO_2Ph$), 25.5 ('t', N = 35.7 Hz, CH_2PPh_2), 55.8 ('t', N = 15.9 Hz, CH_2SO_2Ph), 126.7–139.2 (C_{Ph}), 178.3 (t, $^2J_{P,C}$ = 5.3 Hz, CO). **^{31}P NMR** (81 MHz, CD_2Cl_2): δ = 17.3 (s+d, $^1J_{Pt,P}$ = 2538 Hz, PPh$_2$).

3.5 X-ray Crystallography

Single-crystals suitable for X-ray diffraction measurements of **4** and **6** were obtained from CH_2Cl_2 solutions with a layer of *n*-pentane. Intensity data were collected with STOE diffractometers STADI-4 at 293(2) K (**4**) and IPDS 2T at 200(2) K (**6**) using Mo-K_α radiation (λ = 0.7103 Å, graphite monochromator). A summary of the crystallographic data, the data collection parameters and the refinement parameters is given in Table 2. Absorption corrections were applied numerically with X-RED32[24] (T_{min}/T_{max} 0.57/0.63, **4**; 0.18/0.51, **6**). The structures were solved with direct methods using SHELXS-97[25] and refined using full-matrix least-square routines against F^2 with SHELXL-97.[26] All non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen atoms with isotropic ones. Hydrogen atoms were placed in calculated positions according to the riding model.

Crystallographic data (excluding structure factors) have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-793818 (**4**), CCDC-793819 (**6**). Copies of the data can be obtained free of charge on application to http://www.ccdc.cam.ac.uk/cgi-bin/catreq.cgi or from the Business & Administration, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK; Fax: +44-1223-336033; or E-Mail: admin@ccdc.cam.ac.uk.

Table 2. Crystallographic data, data collection parameters and refinement parameters for **4** and **6**.

	4	**6**
Empirical formula	$C_{23}H_{24}ClOPPtS$	$C_{22}H_{24}ClPPtS$
M_r	609.99	581.98
Crystal system	monoclinic	triclinic
Space group	$C2/c$	$P\bar{1}$
a /Å	24.687(3)	9.2840(7)
b /Å	8.5402(8)	9.7000(8)
c /Å	21.348(2)	12.844(1)
α /°		75.047(6)
β /°	91.460(9)	86.022(6)
γ /°		70.351(6)
V /Å^3	4499.5(8)	1052.3(1)
Z	8	2
D_{calc} /g·cm^{-3}	1.801	1.837
μ(Mo-K_α) /mm^{-1}	6.531	6.973
F(000)	2368	564
θ range /°	1.65–25.05	2.82–29.22
Rfln. collected	4648	18522
Rfln. observed [$I > 2\sigma(I)$]	3006	4625
Rfln. independent	3978 (R_{int} = 0.0373)	5650 (R_{int} = 0.0620)
Data/restraints/parameters	3978/0/253	5650/0/237
Goodness-of-fit on F^2	1.099	1.190
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.0483, 0.1031	0.0415, 0.0975
$R1$, $wR2$ (all data)	0.0762, 0.1220	0.0546, 0.0994
Largest diff. peak and hole / e·Å^{-3}	1.852 and –2.014	1.998 and –2.802

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