

Platinum(II) and Palladium(II) Dichalcogenolene Complexes Containing the Ligand Tri(1-cyclohepta-2,4,6-trienyl)phosphane. Molecular Structure, Intramolecular Dynamics in Solution, and the Absolute Signs of Coupling Constants $^1J(^{195}\text{Pt}, ^{77}\text{Se})$ and $^2J(^{77}\text{Se}, \text{Pt}, ^{31}\text{P})$

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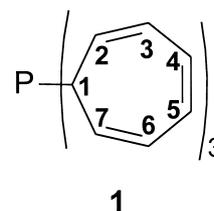
Platinum, Palladium, Dithiolenes

Tri(1-cyclohepta-2,4,6-trienyl)phosphane, $\text{P}(\text{C}_7\text{H}_7)_3$ (**1**), serves as a bidentate chelating ligand [P] in platinum(II) and palladium(II) complexes. Here the synthesis of the four dichalcogenolene complexes $[\text{P}]\text{M}[\text{E}_2\text{C}_2(\text{CO}_2\text{Me})_2]$ (**4**) ($\text{M} = \text{Pt}$) and **5** ($\text{M} = \text{Pd}$) with $\text{E} = \text{S}$ (**a**) and Se (**b**) from the reaction of the respective dicyclopentadienylytitanium dichalcogenolenes, $\text{Cp}_2\text{Ti}[\text{E}_2\text{C}_2(\text{CO}_2\text{Me})_2]$, and $[\text{P}]\text{MCl}_2$ with $\text{M} = \text{Pt}$ (**2**) and Pd (**3**) is reported. At room temperature, the complexes **4** and **5** are fluxional with respect to the NMR time scale, and the nature of the dynamic process is discussed. The complexes have been characterised by ^1H , ^{13}C , ^{31}P , ^{77}Se and ^{195}Pt NMR spectroscopy. The signs of the coupling constants $^1J(^{195}\text{Pt}, ^{77}\text{Se})$ (< 0) and $^2J(^{77}\text{Se}, ^{31}\text{P})$ (> 0) were obtained by selective $^{31}\text{P}\{^{195}\text{Pt}\}$ and $^{31}\text{P}\{^{77}\text{Se}\}$ spin tickling experiments. The crystal structure of **4b** was determined by X-ray analysis.

Introduction

Phosphanes containing one or more olefinic double bonds in pending side-arms are attractive chelating ligands in transition metal chemistry [1]. For example, tri(1-cyclohepta-2,4,6-trienyl)phosphane, $\text{P}(\text{C}_7\text{H}_7)_3$ **1** [2] ([P] when it is coordinated to a metal), can offer up to four sites for coordination to a transition metal counting the phosphorus atom and one central $\eta^2\text{-C}=\text{C}$ bond of each C_7H_7 ring [3]. In the rich Pt(II) and Pd(II) chemistry, complexes of the type $[\text{P}]\text{MX}_2$ are of particular interest with respect to further transformations, considering the different reactivity of M-X bonds. We have recently reported on the synthesis and some reactions of the dichlorides $[\text{P}]\text{MCl}_2$ **2** ($\text{M} = \text{Pt}$) and **3** ($\text{M} = \text{Pd}$) [4]. In this context, the synthesis of dithiolenes or diselenolenes is attractive, considering the properties of transition metal dichalcogenolenes [5]. Previously, such complexes of platinum and palladium have been obtained from the reaction of bis(phosphane)metal polychalcogenides and activated alkynes such as dimethyl acetylenedicarboxylate [6, 7], or from the reaction of dicyclopentadienylytitanium dichalcogenolates,

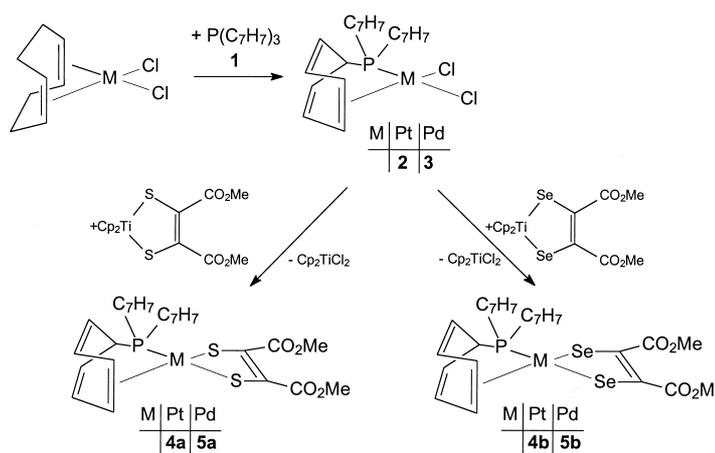
$\text{Cp}_2\text{Ti}[\text{E}_2\text{C}_2(\text{CO}_2\text{Me})_2]$, with $(\text{Ph}_3\text{P})_2\text{PtCl}_2$ [8]. However, complexes of this type bearing a phosphane and an η^2 -coordinated $\text{C}=\text{C}$ double bond at the metal are unknown, to the best of our knowledge. In the present work, the reaction of **2** and **3** with $\text{Cp}_2\text{Ti}[\text{E}_2\text{C}_2(\text{CO}_2\text{Me})_2]$ was investigated, focusing on structural characterisation of the resulting platinum and palladium complexes in the solid state by X-ray analysis, and on NMR spectroscopic studies, in particular of the selenium derivatives taking advantage of the presence of ^{77}Se (natural abundance 7.58%; $I = 1/2$) in addition to the other prominent spin-1/2 nuclei such as ^1H , ^{13}C , ^{31}P and ^{195}Pt .



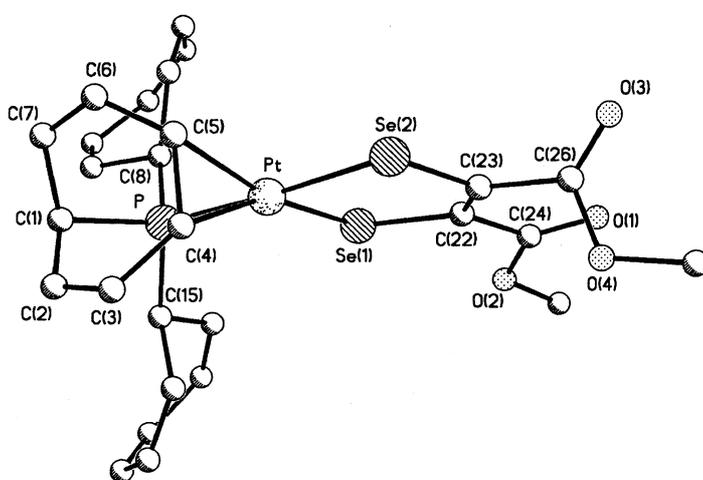
Results and Discussion

Synthesis

The preparation of the compounds **4** and **5** is summarised in Scheme 1. The complexes **2** and **3**,



Scheme 1.

Fig. 1. Molecular structure of the platinum complex $[P]Pt[Se_2C_2(CO_2Me)_2]$ (**4b**). Selected bond lengths and angles are given in Table 1.Table 1. Selected bond lengths [pm] and angles [$^\circ$] in **4b**.

Pt-P	226.27(19)	Pt-Se(1)	236.98(9)
Pt-Se(2)	243.10(8)	Pt-C(4)	221.6(8)
Pt-C(5)	225.3(8)	C(4)-C(5)	141.8(12)
C(11)-C(12)	131.1(19)	C(18)-C(19)	133.7(17)
C(22)-C(23)	134.2(11)	Se(1)-C(22)	189.6(7)
Se(2)-C(23)	187.6(8)	P-C(1)	185.0(8)
P-C(8)	184.1(7)	P-C(15)	185.2(8)
Se(1)-Pt-Se(2)	89.77(3)	P-Pt-Se(1)	90.15(6)
P-Pt-Se(2)	176.61(5)	C(4)-Pt-Se(1)	155.4(2)
C(5)-Pt-Se(1)	167.5(2)	C(4)-Pt-Se(2)	90.5(2)
C(5)-Pt-Se(2)	88.3(2)	C(4)-Pt-P	91.0(2)
C(5)-Pt-P	91.0(2)	C(4)-Pt-C(5)	37.0(3)
C(22)-Se(1)-Pt	102.3(3)	C(23)-Se(2)-Pt	101.8(2)

the most versatile starting materials, are readily obtained from the reaction of (cod)PtCl₂ (cod = cycloocta-1,5-diene) with the phosphane **1** [4]. The reaction of **2** and **3** with the respective titanium complex

Cp₂Ti[E₂C₂(CO₂Me)₂] affords the compounds **4** and **5** in pure state and in high yield. The complexes can be separated by chromatography over silica gel from the small excess of Cp₂Ti[E₂C₂(CO₂Me)₂] and from CpTiCl₂, which is formed during the reaction. They were isolated as yellow (**4a**, **4b**) or brown (**5a**, **5b**) powders, which are moderately air-stable and can be stored under argon atmosphere for several months without decomposition.

X-ray structural analysis of the platinum(II) complex 4b

The molecular structure of **4b** (Fig. 1; for selected structural parameters see Table 1) shows that the platinum atom occupies the centre of a planar coordination sphere (mean deviation from the best plane 7.5 pm), forming bonds of significantly differ-

No	4a	5a	4b	5b
$\delta^{31}\text{P}^{\text{b,d}}$	110.2 (s) {3206}	122.5 (s)	110.6 (s) {3225} [88.3 / 35.2]	115.5 (s) [96.6 / 22.0]
$\delta^{195}\text{Pt}^{\text{b,d}}$	-63.0 (d) {3206}	–	-205.5 (d) {3224 Hz}	–
$\delta^{77}\text{Se}^{\text{b,e}}$	–	–	590.1 (d, Se ^{cis}) {326.5} [35] 610.2 (d, Se ^{trans}) {92}[90]	658.8 (d, Se ^{cis}) [22.4] 676.2 (d, Se ^{trans}) [96.1]
$\delta^{13}\text{C}^{\text{f}}$	b	c		
C ¹	33.8 (d) {38.8} [34.9]	35.1 (d) [25.5]	34.6 (d) {40.3} [35.2]	36.5 (d) [19.9]
C ^{2,7}	106.7 (s) 107.1 (s)	111.2 (br) 111.8 (br)	111.5 (br)	120.1 (s)
C ^{3,6}	127.2 (d) [9.1] 127.4 (d) [10.4]	127.5 (br) 129.1 (br)	127.0 (d) [10.7] 127.2 (d) [11.3]	128.2 (d) [9.6]
C ^{4,5}	129.7 (s) 130.1 (s)	130.0 (s) 130.5 (s)	130.3 (s) 130.6 (s)	115.1 (br)
C ^{1'}	34.7 (d) [20.7]	37.6(d) [21.7]	34.1 (d) [20.7]	
C ^{2',7'}	128.7 (s) {51.2}	128.5 (s)	128.1 (s) {50.2}	
C ^{3',6'}	129.0 (d) [8.7]	128.8 (s)	129.2 (d) [11.3]	dynamic
C ^{4',5'}	73.7 (s) {94.0}	94.4 (s)	73.9 (s) {86.3}	
C ^{OCH₃}	52.5 / 52.7 (s/s)	53.0 / 53.7 (s/s)	53.2 / 53.4 (s/s)	52.5 / 52.7 (s/s)
C ^{C=C-trans}	138.4 (d) [14.5]	135.5 (d) [15.7]	133.9 (d) [14.3]	128.8 (d) [9.8]
C ^{C=C-cis}	143.4 (d) [2.5]	142.4 (s)	144.2 (d) [2.4]	140.5 (s)
C ^{C=O}	165.1(s) / 167.0 (d) [3.8]	164.4 / 167.1 (s/s)	165.4 (s) / 169.8 (d) [2.7]	165.5 / 168.4 (s/s)

Table 2. ^{31}P , ^{195}Pt , ^{77}Se and ^{13}C NMR data of the complexes **4a**, **4b**, **5a** and **5b** in CDCl_3 solution^a.

^a The primed positions belong to the cyclohepta-2,4,6-trienyl ring which is η^2 coordinated via $\text{C}^4=\text{C}^5$; *cis* and *trans* denote the positions with respect to the phosphorus atom; ^b measurements at 25 °C; ^c measurements at -30 °C; ^d { } / [] coupling constants $^1J(^{195}\text{Pt}, ^{31}\text{P})$ / $^2J(^{77}\text{Se}, ^{31}\text{P})$; ^e { } / [] coupling constants $^1J(^{195}\text{Pt}, ^{77}\text{Se})$ / $^2J(^{77}\text{Se}, ^{31}\text{P})$; ^f { } / [] coupling constants $^nJ(^{195}\text{Pt}, ^{13}\text{C})$ / $^nJ(^{31}\text{P}, ^{13}\text{C})$.

ent lengths to the two selenium atoms, to the phosphorus atom, and to the central $\eta^2\text{-C}=\text{C}$ unit of one of the C_7H_7 rings (Pt-Z(C(4)C(5)) 211.9 pm). The bond distance C(4)-C(5) (141.8(12) pm) is elongated as compared with the non-coordinated C=C bonds (131 - 136 pm). The C=C axis of the η^2 -coordinated double bond in **4b** is arranged almost perpendicular to the coordination plane, the angle of the C(4)-C(5) vector relative to the best (coordination) plane being 84.9° (in other examples [4, 9] this angle is closer to 90°).

The phosphorus atom occupies equatorial positions at both non-coordinated C_7H_7 rings which are not in close proximity to the platinum atom. The arrangement of the non-coordinated C_7H_7 rings must be different in solution, taking into account the fluxional character of the compounds **2** - **5** (vide infra).

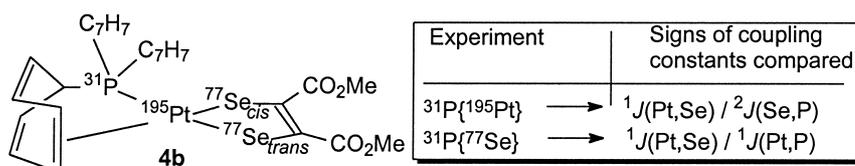
The Pt-Se(1) bond (236.98(9) pm; selenium *trans* to the $\eta^2\text{-C}=\text{C}$ unit) is slightly shorter than the Pt-Se(2) bond (243.10(8) pm; selenium *trans* to phosphorus), a trend which has been observed now for several examples of the type [P]PtLL' (L = L' = I [4], C≡C-Fc [9]; L = Cl, L' = C≡C-^tBu [9]). The range of the Pt-Se bond lengths is similar to data reported

in the literature (243 - 246 pm) [10, 11]. The bond lengths Pt-P change with the polarising ability of the ligand L in *trans* position, *e. g.* 220.89(14) pm (L = Cl) [9], 223.9(2) (L = I) [4], 226.27(19) (L = Se, **4b**), 227.81(18) [9] (L = C≡C-Fc), following the magnitude of the coupling constants $^1J(^{195}\text{Pt}, ^{31}\text{P})$ (vide infra, and Fig. 3). Similarly, the distances between Pt and the carbon atoms of the $\eta^2\text{-C}^4=\text{C}^5$ bond are shorter in the presence of more strongly polarising *trans* ligands, and this is again becoming apparent in the magnitude of the coupling constants $^1J(^{195}\text{Pt}, ^{13}\text{C}^{4,5'})$ (86.3 Hz for **4b**, and 58.9 Hz for [P]Pt(C≡C-Fc)₂ [9]), although the data set is still too limited for a more detailed discussion.

The five-membered ring [Pt-Se(1)-C(22)-C(23)-Se(2)] deviates from planarity as indicated by a dihedral (folding) angle between the planes PtSe(1)Se(2) and Se(1)C(22)C(23)Se(2) of 172.2°.

NMR spectroscopic results

The ^{31}P , ^{195}Pt , ^{77}Se and ^{13}C NMR data of the complexes **4** and **5** are listed in Table 2; ^1H NMR data are given in the experimental section.



Scheme 2. Compound **4b** with the relevant isotopomers, containing ^{31}P , ^{195}Pt , and ^{77}Se either in *cis* or in *trans* positions relative to the phosphorus atom. The spin tickling experiments enable to compare the signs of coupling constants as indicated, with the result that both $^1J(^{195}\text{Pt}, ^{77}\text{Se}) < 0$ and both $^2J(^{77}\text{Se}, ^{31}\text{P}) > 0$.

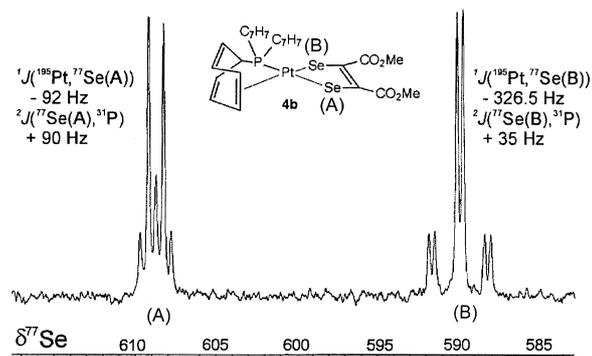


Fig. 2. 95.4 MHz ^{77}Se NMR spectrum of **4b** in CDCl_3 (at 25 °C). The $\delta^{77}\text{Se}$ values and the magnitude of the coupling constants $^1J(^{195}\text{Pt}, ^{77}\text{Se})$ are assigned. The determination of the signs given requires selective heteronuclear $^{31}\text{P}\{^{77}\text{Se}\}$ and $^{31}\text{P}\{^{195}\text{Pt}\}$ double resonance experiments (see text and Scheme 2).

Dynamic properties

For all complexes **2** - **5**, the ^1H and ^{13}C NMR spectra, measured at room temperature, reveal dynamic processes involving the C_7H_7 rings of the phosphane ligand, since broadening of several ^1H and ^{13}C resonance signals is observed (*e.g.* in the case of **4a**) or only four averaged ^1H and ^{13}C NMR signals of the C_7H_7 rings are visible. The ^{31}P and ^{195}Pt NMR spectra show the pattern typical of scalar ^{195}Pt - ^{31}P coupling, indicating that the Pt-P bond is not cleaved in the course of the dynamic process. Therefore, a specific intramolecular exchange of the C_7H_7 rings must take place. In the cases of **2** and **3**, there is no straightforward way to obtain further information from NMR spectra, except that the dynamic process can be slowed down at low temperature. In contrast, in the cases of **4** and **5**, the NMR spectroscopic properties, in particular of the diselenolene group in **4b** and **5b** (^{13}C , ^{77}Se NMR), provide additional information. In spite of the dynamic process involving the C_7H_7 rings of

the phosphane ligand [P], the nuclei in the diselenolene group remain chemically non-equivalent (see Fig. 2 for the ^{77}Se NMR spectrum). This observation excludes a purely dissociative mechanism leading to an intermediate in which the platinum atom becomes three-coordinate, and therefore, the two selenium sites are equivalent on average. Similarly, an associative mechanism leading to an intermediate with five-coordinate Pt is unlikely. Such an intermediate has been claimed previously on the basis of ^1H NMR data for complexes of the type $[\text{tbp}]\text{MX}_2$ (where [tbp] is the chelating tri(3-butenyl)phosphane, $\text{P}(\text{CH}_2\text{CH}_2\text{-CH}=\text{CH}_2)_3$, which is coordinated by the phosphorus atom and one C=C bond; M = Pt, Pd, X = Cl, Br I [12]). However, considering the small energy barrier generally encountered for the interconversion of square pyramidal and trigonal bipyramidal structures, the assumption of a long-lived intermediate is questionable, since a trigonal bipyramidal structure would not allow to differentiate between the selenium sites. This leaves a mechanism in which the Pt centre stays in a planar surrounding, and each leaving C_7H_7 ring is immediately replaced by the next one via a transition state. From the low temperature NMR spectra, the energy of activation for this process can be evaluated [13] as 42 ± 2 kJ/mol in the platinum complex **4b**, and somewhat less in the palladium analogue **5b**. Since the chelate-like coordination of the C_7H_7 ring together with the phosphorus atom requires that the latter occupies an axial ring position (in contrast to the equatorial positions occupied in solid **4b**, vide supra), the conformation of the two non-coordinated rings has to be highly fluxional in order to let them participate in the exchange with the coordinated ring. This fluxionality was found for **1** itself [14], where the barrier to axial / equatorial conversion was too low to be assessed by simple 1D NMR measurements (+23 to -90 °C), and the same is true for the complexes studied in the present work.

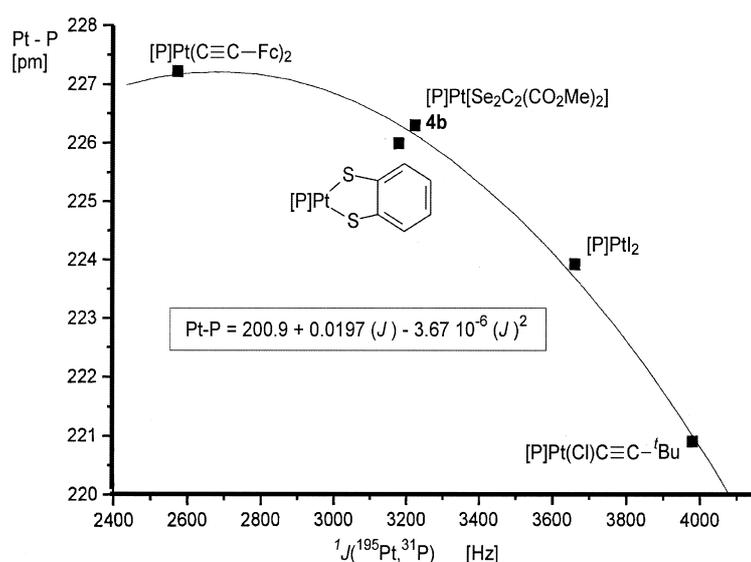


Fig. 3. Correlation of the Pt-P bond lengths in five [Pt]PtLL' complexes, including **4b**, with the magnitude of $^1J(^{195}\text{Pt}, ^{31}\text{P})$; the polynomial fit with $y = a + bx + cx^2$ is given (errors: a : ± 6.75 ; b : $\pm 4.2 \cdot 10^{-3}$; c : $\pm 6.35 \cdot 10^{-7}$).

Signs of coupling constants $^2J(^{77}\text{Se}, ^{31}\text{P})$ and $^1J(^{195}\text{Pt}, ^{77}\text{Se})$ in **4b**

The determination of relative coupling signs by selective double resonance experiments is possible if there is a pair of active spins and one passive spin [15]. In the case of **4b**, both the combinations $^{31}\text{P}/^{195}\text{Pt}$ as the active spins and ^{77}Se as the passive spin, and $^{31}\text{P}/^{77}\text{Se}$ as the active spins and ^{195}Pt as the passive spin, take advantage of the comparatively high NMR receptivity of ^{31}P as the observed nucleus. By selective irradiation of ^{195}Pt transitions and observing differential effects on the ^{77}Se satellites in the ^{31}P NMR spectra ($^{31}\text{P}\{^1\text{H}, ^{195}\text{Pt}_{\text{selective}}\}$ experiment), the signs of the coupling constants $^2J(^{77}\text{Se}, ^{31}\text{P})$ and $^1J(^{195}\text{Pt}, ^{77}\text{Se})$ were compared and found to be opposite both for *cis* and *trans* positions of the ^{77}Se nuclei with respect to phosphorus. Since a positive sign of $^1J(^{195}\text{Pt}, ^{31}\text{P})$ can be assumed [16] (there is no exception known so far), absolute coupling signs become available from a second series of experiments in which the ^{195}Pt nucleus serves as the passive spin ($^{31}\text{P}\{^1\text{H}, ^{77}\text{Se}_{\text{selective}}\}$ experiment). This compares the known positive sign of $^1J(^{195}\text{Pt}, ^{31}\text{P})$ with the unknown sign of $^1J(^{195}\text{Pt}, ^{77}\text{Se})$. The differential effects observed for the ^{195}Pt satellites were typical of opposite signs, which means that $^1J(^{195}\text{Pt}, ^{77}\text{Se}) < 0$. This is remarkable, since all signs, with one exception, of $^1J(^{195}\text{Pt}, ^{77}\text{Se})$ have been found positive [17]. However, all cases stud-

ied so far were selenoether complexes of platinum [17, 18], in which negative contributions to the spin-spin coupling, arising from the lone pairs of electrons at the selenium [19], are probably less pronounced (just one lone pair) when compared with selenolates (two lone pairs). This trend is also borne out in the data $^1J(^{77}\text{Se}, ^{13}\text{C})$ of organoselenium compounds where the selenium is present in different formal oxidation states [20].

The magnitude of $^1J(^{195}\text{Pt}, ^{31}\text{P})$ in the complexes [Pt]PtLL' changes according to the polarising ability of L *trans* to phosphorus, and there is a smooth non-linear relationship between $^1J(^{195}\text{Pt}, ^{31}\text{P})$, measured in solution, and the bond lengths Pt-P determined here for **4b** and for four other examples with L = I [4], Cl [9], C \equiv C-Fc [9] and S (in [Pt]Pt[S₂C₆H₄] [21] in the solid state (Fig. 3).

The magnitude of $^2J(^{77}\text{Se}, ^{31}\text{P})$ is larger than in other Pt(II) complexes studied [7, 22]. In the case of *cis*-[(Ph₃P)₂Pt(Se₂CH₂)] [22] it was found, in agreement with our results for **4b**, that $^2J(^{77}\text{Se}, ^{31}\text{P})_{\text{cis}}$ and $^2J(^{77}\text{Se}, ^{31}\text{P})_{\text{trans}}$ (11.0 and 31.0 Hz) have the same sign.

Chemical shifts $\delta^{13}\text{C}$, $\delta^{31}\text{P}$, $\delta^{195}\text{Pt}$ and $\delta^{77}\text{Se}$

The ^{13}C NMR spectra provide conclusive structural information if they are measured with dynamic processes slow on the NMR time scale (Fig. 4). All $\delta^{13}\text{C}$ values are found in the expected range for coordinated and non-coordinated C₇H₇ rings [23].

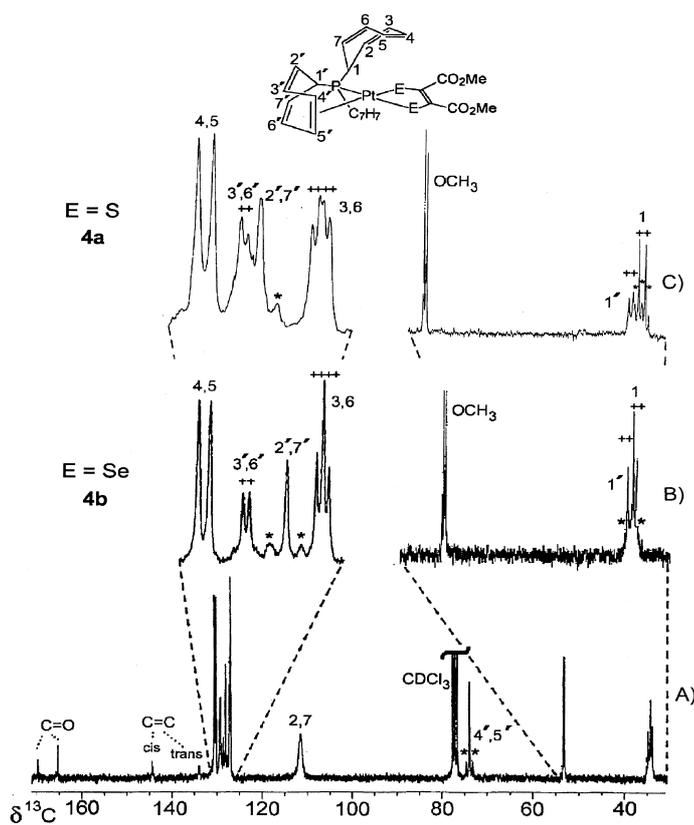


Fig. 4. 62.9 MHz $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **4b** in CDCl_3 (-30°C). The assignment is given in A) and in the expansions B). In C), the respective expansions of the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **4a** in CDCl_3 (at 23°C) are shown. The beginning of dynamic processes on the NMR time scale becomes evident by broadening of some of the ^{13}C resonance signals. Overlapping doublets due to $J(^{31}\text{P}, ^{13}\text{C})$ and $J(^{195}\text{Pt}, ^{13}\text{C})$ are marked by (+) and (*), respectively.

The $\delta^{31}\text{P}$ data are consistent with the usual trend found [24] for the influence of Pt-P and Pd-P bonds, by which the ^{31}P nuclei are better shielded in the case of a Pt-P bond. The influence of the atom (sulfur or selenium) in *trans* position is noticeable only in the case of the palladium complexes **5a** and **5b**, where the ^{31}P nucleus in **5a** is less shielded (7 ppm) as compared to **5b**. In the cases of **4a** and **4b**, the $\delta^{31}\text{P}$ values are almost identical, and this is also observed for the magnitude of the coupling constants $^1J(^{195}\text{Pt}, ^{31}\text{P})$. The ^{77}Se chemical shifts [17, 25] are much more sensitive to the metal when compared with the $\delta^{31}\text{P}$ data, although the direction of the effect is the same. Thus, considerable deshielding (*ca.* 60 - 70 ppm) of the ^{77}Se nuclei is observed in the palladium complex **5b** with respect to the platinum analogue **4b**. The $\delta^{195}\text{Pt}$ values of **4a** and **4b** follow established trends [26] (*c.f.* the normal halogen dependence in the case of halides), that the ^{195}Pt nuclei are better shielded (by 142 ppm) in the Pt-Se complex **4b** with respect to the Pt-S complex **4a**.

Experimental Section

General and physical methods

All reactions were carried out under argon atmosphere and in dried solvents. The starting materials (cod)PtCl₂ [27], P(C₇H₇)₃ (**1**) [2], [P]PtCl₂ (**2**), [P]PdCl₂ (**3**) [4], and Cp₂Ti[E₂C₂(CO₂Me)₂] [8] were prepared according to published methods, or were used as commercial products [(cod)PdCl₂] without further purification.

NMR: Bruker ARX 250 and Bruker DRX 500 ($\delta^1\text{H}$ (CHCl₃/CDCl₃) = 7.24; $\delta^{13}\text{C}$ (CDCl₃) = 77.0; $\delta^{31}\text{P}$ = 0 for ext. H₃PO₄, 85% aq. with $\Xi(^{31}\text{P})$ = 40.480747 MHz; $\delta^{77}\text{Se}$ = 0 for ext. Me₂Se with $\Xi(^{77}\text{Se})$ = 19.071523 MHz; $\delta^{195}\text{Pt}$ = 0 for $\Xi(^{195}\text{Pt})$ = 21.4 MHz). The Bruker DRX 500 instrument was equipped with three independent frequency channels. A triple resonance probehead, tuned to ^{31}P with ^1H decoupling and tuneable to ^{77}Se or ^{195}Pt , served for $^{31}\text{P}\{^1\text{H}, ^{77}\text{Se}_{\text{selective}}\}$ and $^{31}\text{P}\{^1\text{H}, ^{195}\text{Pt}_{\text{selective}}\}$ experiments. The power levels for the spin tickling experiments were carefully adjusted to produce the desired differential effects.

IR: Perkin Elmer Spectrum 2000 FT-IR Spectrometer. EI-MS: Finnigan MAT 8500 (Ionisation energy 70eV);

the *m/e* data refer to the isotopes ^1H , ^{12}C , ^{16}O , ^{31}P , ^{35}Cl , ^{79}Br , ^{80}Se , ^{127}I and ^{195}Pt . Decomposition points were determined using a Büchi 510 melting point apparatus.

General procedure for the synthesis of

$[\text{P}]\text{M}[\text{S}_2\text{C}_2(\text{CO}_2\text{Me})_2]$ ($M = \text{Pt } \mathbf{4a} / M = \text{Pd } \mathbf{5a}$)

$\text{Cp}_2\text{Ti}[\text{S}_2\text{C}_2(\text{CO}_2\text{Me})_2]$ (135 mg, 0.32 mmol) was added to a solution of **2** or **3** (0.30 mmol) in toluene (15 ml). After the mixture had been heated under reflux for several hours, the solvent was removed under high vacuum. The resulting residue was dissolved in CH_2Cl_2 (2 ml) and chromatographed on silica gel. Elution with CH_2Cl_2 and CH_2Cl_2 / acetone (10:1) gave an orange-brown (**4a**) or brown (**5a**) solution, which was brought to dryness. The solid residue was dissolved in CH_2Cl_2 (2 ml), and MeOH (30 ml) was added. The precipitate formed was separated and dried in a high vacuum.

$[\text{P}]\text{Pt}[\text{S}_2\text{C}_2(\text{CO}_2\text{Me})_2]$ (**4a**): (reaction time 2 h), yellow powder, dec. 200 °C, yield 173 mg (81%), $\text{C}_{27}\text{H}_{27}\text{O}_4\text{PPtS}_2$. – ^1H NMR (250.1 MHz, 25 °C, CDCl_3): $\delta = 2.40$ (dt, 2H, H^1 ; $^2J(^{31}\text{P}, ^1\text{H}) = 8.4$ Hz, $^3J(^1\text{H}, ^1\text{H}) = 6.9$ Hz), 3.76 / 3.83 (s/s, 3H/3H, OCH_3), 4.68 (dt, 1H, H^1 ; $^2J(^{31}\text{P}, ^1\text{H}) = 12.4$ Hz, $^3J(^1\text{H}, ^1\text{H}) = 8.8$ Hz), 4.87 (m, 2H, $\text{H}^{2,7}$; $^3J(^{31}\text{P}, ^1\text{H}) = 6.3$ Hz), 5.04 (m, 2H, $\text{H}^{2,7}$; $^3J(^{31}\text{P}, ^1\text{H}) = 6.5$ Hz), 5.79 (m, 2H, $\text{H}^{2,7}$), 5.86 (m, 2H, $\text{H}^{4,5}$; $^2J(^{195}\text{Pt}, ^1\text{H}) = 43.1$ Hz), 6.23 (m, 4H, $\text{H}^{3,6}$), 6.37 (m, 2H, $\text{H}^{3,6}$), 6.47 (m, 4H, $\text{H}^{4,5}$). – IR(CsI): $\nu = 1431$ (s) (C=C), 1534(s) (C-O), 1702 (vs) (C=O), 1725 (vs) (C=O) cm^{-1} .

$[\text{P}]\text{Pd}[\text{S}_2\text{C}_2(\text{CO}_2\text{Me})_2]$ (**5a**): (reaction time 8 h), brown powder, dec. 187 °C, yield 163 mg (88%), $\text{C}_{27}\text{H}_{27}\text{O}_4\text{PPdS}_2$. – ^1H NMR (250.1 MHz, –30 °C, CDCl_3): $\delta = 2.43$ (br, 2H, H^1), 3.70/3.79 (s/s, 3H/3H, OCH_3), 4.53 (br, 1H, H^1), 4.95 (br, 2H, $\text{H}^{2,7}$), 5.12 (br, 2H, $\text{H}^{2,7}$), 5.84 (br, 2H, $\text{H}^{4,5}$), 6.20 (br, 4H, $\text{H}^{3,6}$), 6.48 (br, 2H, $\text{H}^{2,7}$), 6.50 (m, 4H, $\text{H}^{4,5}$), 6.69 (m, 2H, $\text{H}^{3,6}$). – IR(CsI): $\nu = 1430$ (s) (C=C), 1541(s) (C-O), 1701 (vs) (C=O), 1720 (vs) (C=O) cm^{-1} .

General procedure for the synthesis of

$[\text{P}]\text{M}[\text{Se}_2\text{C}_2(\text{CO}_2\text{Me})_2]$ ($M = \text{Pt } \mathbf{4b} / M = \text{Pd } \mathbf{5b}$)

$\text{Cp}_2\text{Ti}[\text{Se}_2\text{C}_2(\text{CO}_2\text{Me})_2]$ (152 mg, 0.34 mmol) was added to a solution of **2** or **3** (0.30 mmol) in CH_2Cl_2 (50 ml), and the mixture was heated under reflux for 4 d. The solvent was removed, the residue was dissolved in a small quantity of CH_2Cl_2 (2 ml) and chromatographed on silica gel. Elution with CH_2Cl_2 and CH_2Cl_2 / acetone (10:1) gave an orange-brown solution, which was concentrated under vacuum. Addition of pentane caused precipitation of a yellow (**4b**) or red-brown solid (**5b**) which was filtered off and dried under high vacuum.

Recrystallisation of **4b** from CH_2Cl_2 gave single crystals suitable for X-ray structural analysis.

$[\text{P}]\text{Pt}[\text{Se}_2\text{C}_2(\text{CO}_2\text{Me})_2]$ (**4b**): yellow powder, dec. 203 °C, yield 114 mg (76%), $\text{C}_{27}\text{H}_{27}\text{O}_4\text{PPtSe}_2$. – ^1H NMR (250.1 MHz, –30 °C, CDCl_3): $\delta = 2.43$ (dt, 2H, H^1 ; $^2J(^{31}\text{P}, ^1\text{H}) = 8.2$ Hz, $^3J(^1\text{H}, ^1\text{H}) = 6.3$ Hz), 3.73/3.79 (s/s, 3H/3H, OCH_3), 4.90 (dt, 1H, H^1 ; $^2J(^{31}\text{P}, ^1\text{H}) = 12.7$ Hz, $^3J(^1\text{H}, ^1\text{H}) = 8.2$ Hz), 5.07 (m, 2H, $\text{H}^{2,7}$; $^3J(^{31}\text{P}, ^1\text{H}) = 7.0$ Hz), 5.17 (m, 2H, $\text{H}^{2,7}$; $^3J(^{31}\text{P}, ^1\text{H}) = 7.6$ Hz), 5.90 (m, 2H, $\text{H}^{2,7}$), 5.98 (m, 2H, $\text{H}^{4,5}$; $^2J(^{195}\text{Pt}, ^1\text{H}) = 46.9$ Hz), 6.33 (m, 4H, $\text{H}^{3,6}$), 6.34 (m, 2H, $\text{H}^{3,6}$), 6.61 (m, 4H, $\text{H}^{4,5}$). – IR(CsI): $\nu = 1431$ (s) (C=C), 1534(s) (C-O), 1696 (vs) (C=O), 1722 (vs) (C=O) cm^{-1} . – MS (EI): *m/z* (%) = 799 (1) [M^+]; 770 (1) [$\text{P}(\text{C}_7\text{H}_7)_3\text{PtSe}_2\text{C}_2(\text{CO}_2)_2^+$], 677 (1) [$\text{P}(\text{C}_7\text{H}_7)_2\text{PtSe}_2\text{C}_2(\text{CO}_2)_2^+$], 91 (100) [C_7H_7^+].

$[\text{P}]\text{Pd}[\text{Se}_2\text{C}_2(\text{CO}_2\text{Me})_2]$ (**5b**): red-brown powder, dec. 188 °C, yield 155 mg (73%), $\text{C}_{27}\text{H}_{27}\text{O}_4\text{PPdSe}_2$. – ^1H NMR (250.1 MHz, 25 °C, CDCl_3): $\delta = 3.02$ (br, 3H, H^1), 3.71/3.78 (s/s, 3H/3H, OCH_3), 5.27 (m, 6H, $\text{H}^{2,7}$), 6.25 (m, 6H, $\text{H}^{3,6}$), 6.55 (m, 6H, $\text{H}^{4,5}$). – IR(CsI): $\nu = 1431$ (s) (C=C), 1544(s) (C-O), 1701 (vs) (C=O), 1718 (vs) (C=O). – MS (EI): *m/z* (%) = 710 (1) [M^+], 695 (1) [$\text{P}(\text{C}_7\text{H}_7)_3\text{PdSe}_2\text{C}_2(\text{CO}_2)_2^+$], 677 (1) [$\text{P}(\text{C}_7\text{H}_7)_2\text{PdSe}_2\text{C}_2(\text{CO}_2)_2^+$], 91 (100) [C_7H_7^+].

Crystal structure analysis of 4b

The intensity data were collected on a Siemens P4 diffractometer with Mo- K_α -radiation ($\lambda = 71.073$ pm, graphite monochromator) at room temperature. All non-hydrogen atoms were refined with anisotropic temperature factors. The hydrogen atoms were placed in calculated positions and refined applying the riding model with fixed isotropic temperature factors.

4b, $\text{C}_{27}\text{H}_{27}\text{O}_4\text{PPtSe}_2 \cdot \text{CH}_2\text{Cl}_2$, yellow prism of dimensions 0.40 × 0.15 × 0.08 mm, monoclinic, space group $P2_1/c$; $a = 1397.0(2)$, $b = 1433.69(17)$, $c = 1591.2(3)$ pm, $\beta = 104.375(12)^\circ$, $Z = 4$, $\mu = 7.159$ mm^{-1} ; 5364 reflections collected in the range 1.94 – 25.00° in ϑ , 5136 reflections assigned to be observed ($I > 2\sigma(I)$); full matrix least squares refinement with 344 parameters, $R1/wR2$ -values 0.0475/0.1342, absorption correction (ψ -scans), min./max. transmission factors 0.1623/0.6345; max./min. residual electron density 1.873/–1.789 $\text{e} \cdot 10^{-6} \cdot \text{pm}^{-3}$. Supplementary material has been deposited with the Cambridge Crystallographic Data Center (CCDC). The data are available on request on quoting CCDC No. 173511.

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