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Article

Synthesis and Structures of *cis*- and *trans*-Bis(alkyneselenolato)platinum(II) Complexes

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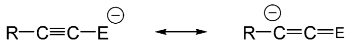
The reaction of 2 equiv of LiSeCC-*n*-C_5H_{11} **(1)** with *cis*-$PtCl_2(Ph_3P)_2$ **(2)** gives a mixture of the cis and trans isomers of $Pt(Ph_3P)_2(SeCC\text{-}n\text{-}C_5H_{11})_2$ **(3),** which slowly isomerizes in CH_2Cl_2 to the preferred trans form *trans*-**3**. The closely related *cis*-[$Pt(dppf)_2(SeCC\text{-}n\text{-}C_5H_{11})_2$] **(4)** (dppf = bis(diphenylphosphino)ferrocene) was prepared by a similar metathetical reaction using the platinum chloride complex of the chelating dppf to impose the cis geometry. The structures of the cis and trans complexes have been investigated in solution by heteronuclear NMR (^{31}P, ^{77}Se, and ^{195}Pt) and, in the cases of *trans*-**3** and **4**, characterized in the solid state by single-crystal X-ray diffraction. Changing the coordination geometry from cis to trans induces significant changes in the structural and spectroscopic parameters, which do not comply with the previously anticipated donor–acceptor properties of selenolate ligands.

Introduction

Alkynechalcogenolates (**A**) can be described as chalcogeno ketene anions **(B)** and are capable of showing unique ambident rectivity.[1] This ambident behavior has been mainly explored toward organic or main group based electrophiles in the case of alkynelthiolates, mostly aiming at thioketenes. In contrast, much less information is available about the reactivity and coordination chemistry of alkynelthiolates toward transition metals, which started to develop only recently.[2] Even less information is available for their selenium analogues, i.e., the alkyneselenolates, despite the favorable NMR properties of the ^{77}Se nucleus. The first examples exploring the coordination behavior of these unusual ligands have been described by Tatsumi and coworkers.[3,4] The growing interest in the chemistry and coordination behavior of alkyneselenolates stems from their structural flexibility, their unique electronic situation, and the antioxidative activity of biomimetic models based on structurally related organoselenium compounds.[5,6]



$$\underset{\textbf{A}}{R{-}C{\equiv}C{-}E^{\ominus}} \longleftrightarrow \underset{\textbf{B}}{R{-}\overset{\ominus}{C}{=}C{=}E}$$

In this contribution we describe our results dealing with the coordination behavior of alkyneselenolates toward platinum. Using an alkyl-substituted alkyneselenolate, we synthesized cis and trans platinum complexes of this ligand which were characterized by heteronuclear NMR spectroscopy and X-ray diffraction. While the coordination chemistry of alkyneselenolates itself is rather unexplored, these compounds represent the first (alkyneselenolato)platinum complexes. The structural and spectroscopic comparison of closely related *cis*- and *trans*-bis(alkyneselenolato) complexes shows that the electronic situation differs from that of other selenolate ligands.

Results and Discussion

Generally two routes are available for the coordination of alkyneselenolates. The first approach proceeds via salt

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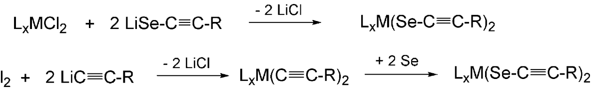
10.1021/ic048454a CCC: $30.25

Scheme 1. Synthetic Routes to Alkyneselenolate Complexes



$$L_xMCl_2 + 2\,LiSe\text{-}C{\equiv}C\text{-}R \xrightarrow{-2\,LiCl} L_xM(Se\text{-}C{\equiv}C\text{-}R)_2$$

$$L_xMCl_2 + 2\,LiC{\equiv}C\text{-}R \xrightarrow{-2\,LiCl} L_xM(C{\equiv}C\text{-}R)_2 \xrightarrow{+2\,Se} L_xM(Se\text{-}C{\equiv}C\text{-}R)_2$$

metathesis from the corresponding metal halide and an alkali alkyneselenolate (metathesis route) (Scheme 1, top).[3,4] The second approach takes advantage of an insertion of selenium into an alkyne−metal bond (insertion route), where the metal is cadmium and mercury (Scheme 1, bottom).[7,8]

Recently we reported some alkyneselenolates carrying substituents with different electronic and steric properties.[9,10] To minimize electronic interaction of the substituent with the adjacent CCSe unit, we have chosen an alkyl derivative, i.e., heptyneselenolate, as designated ligand for complexation. Therefore, we explored both of the above-mentioned synthetic routes to obtain complexes of the formula $(PenCCSe)_2Pt(PR_3)_2$ (Pen = pentyl). The insertion route starting from $(PenCC)_2Pt(PR_3)_2$ failed in our hands, and under various conditions frequently resulted in the formation of the corresponding selenophosphorane $SePR_3$ as the main product (Scheme 2). The identity of the latter is established on the basis of the ^{31}P and ^{77}Se NMR spectra of the reaction mixture as well as mass spectrometry. One might assume that the relatively high Pt−C bond strength could be the reason for the failure of this route.[11] However, unlike the only about half as weak Cd−C bond,[12] the Hg−C bond is of similar strength and undergoes this reaction.[13]

In contrast, the metathesis route turned out to be successful for our purpose. Thus, the reaction of lithium heptyneselenolate **(1)** with *cis*-dichlorobis(triphenylphosphine)platinum(II) (*cis*-$(Ph_3P)_2PtCl_2$) **(2)** at −78 °C furnishes the desired bis(alkyneselenato)platinum complex **3** as an orange solid (λ_{max} = 212 nm). As in related cases,[14] starting from *cis*-**2** results in the formation of a mixture of *cis*-**3** and *trans*-**3**, whereof *trans*-**3** is the dominant form (ratio 4:1) (Scheme 3). In the ^{31}P NMR spectra *trans*-**3** shows a resonance at 28.0 ppm with a $^{1}J_{PPt}$ coupling constant of 2858 Hz and a $^{2}J_{PSe}$ coupling constant of 26 Hz. The cis isomer of **3** has a chemical shift of 23.6 ppm with larger coupling constants than found for *trans*-**3** (i.e., *cis*-**3**: $^{1}J_{PPt}$ = 3220 Hz and $^{2}J_{PSe}$ = 42 Hz). Relevant NMR spectroscopic data for *cis*- and *trans*-**3** are summarized in Table 3.

Recrystallization from dry methylene chloride affords pure crystalline *trans*-**3** for which we were able to obtain a crystal structure. The asymmetric unit of *trans*-**3** contains a planar coordinated Pt(II) center, which is also an inversion center, and two molecules of methylene chloride. As already derived from the NMR spectra the alkyneselenolato ligands adopt a trans configuration in the approximately square planar coordination environment around platinum (Figure 1). The phosphane and the alkyneselenolate units in *trans*-**3** show Pt(1)−P(1) (2.348(2) Å) and Pt(1)−Se(2) (2.4902(9) Å) distances which are slightly longer than the values reported for the related *trans*-$[Pt(PPh_3)_2(SePh)_2]$ and even more so compared to *cis*-$[Pt(PPh_3)_2(SePh)_2]$.[14]

Table 1. Comparison of Selected Bond Lengths (Å) and Angles (deg) in *trans*-**3** and **4**

trans-**3**		**4**	
Pt1−P1	2.348(2)	Pt1−P1	2.2819(13)
		Pt1−P2	2.2882(12)
Pt1−Se1	2.4902(9)	Pt1−Se1	2.4639(5)
		Pt1−Se2	2.4608(6)
Se1−C19	1.811(4)	Se1−C35	1.831(5)
		Se2−C42	1.817(6)
C19−C20	1.177(5)	C35−C36	1.199(7)
		C42−C43	1.205(8)
C20−C21	1.446(6)	C36−C37	1.477(9)
		C43−C44	1.489(10)
P1−Pt1−P1a	180.00(4)	P1−Pt1−P2	97.98(4)
Se2a−Pt1−Se2	180.00(2)	Se1−Pt1−Se2	85.07(2)
P1−Pt1−Se2a	83.37(3)	P1−Pt1−Se2	170.34(3)
P1$^{\#1}$−Pt1−Se2	83.37(3)	P2−Pt1−Se1	176.55(3)
P1a1−Pt1−Se2a	96.63(3)	P2−Pt1−Se2	91.53(3)
P1−Pt1−Se2	96.63(3)	P1−Pt1−Se1	85.44(3)
C19−Se2−Pt1	100.6(1)	C35−Se1−Pt1	110.0(2)
		C42−Se2−Pt1	112.8(2)
C20−C19−Se2	176.9(4)	C36−C35−Se1	170.3(6)
		C43−C42−Se2	175.5(7)
C19−C20−C21	177.5(5)	C35−C36−C37	178.1(10)
		C42−C43−C44	175.6(10)
		Cp(1)−Fe−Cp(2)	178.8(3)

Table 2. Crystal and Structure Refinement Data for *trans*-**3** and **4**

	trans-**3**	**4**
formula	$C_{50}H_{52}P_2PtSe_2{\cdot}2CH_2Cl_2$	$C_{48}H_{50}FeP_2PtSe_2{\cdot}C_6H_6$
fw	1237.72	1175.79
temp, K	213	123
wavelength, Å	0.710 73	0.710 73
cryst system	triclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
unit cell dimens		
a, Å	11.188(2)	11.4545(1)
b, Å	11.425(2)	22.1938(2)
c, Å	11.828(2)	19.1997(2)
α, deg	99.34(3)	90
β, deg	99.05(3)	104.241(1)
γ, deg	119.17(3)	90
V, Å^3	1252.7(4)	4730.93(8)
Z	1	4
d(calcd), Mg/m^3	1.641	1.651
μ, mm^{-1}	4.565	4.903
θ range for data collcn, deg	2.09−25.66	2.96−27.48
goodness-of-fit on *F*^{2}	1.013	1.040
R1 (obsd data)	0.0257	0.0365
wR2 (all data)	0.0599	0.1047

Table 3. Relevant NMR Spectroscopic Data for *cis-/trans*-**3** and **4**

	trans-**3**	*cis*-**3**	*cis*-**4**
$\delta(^{31}P)$, ppm	28.0	23.6	19.4
$\delta(^{77}Se)$, ppm			330
$\delta(^{195}Pt)$, ppm	−4985		−5009
$^{1}J_{PPt}$, Hz	2858	3220	3287
$^{1}J_{PtSe}$, Hz	198		240
$^{2}J_{PSe}$, Hz	26	42	

This is surprising, because in related work dealing with (areneselenolato)platinum complexes longer Pt−P bonds in

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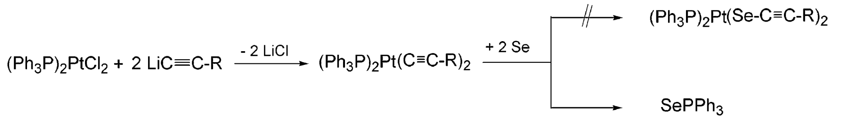
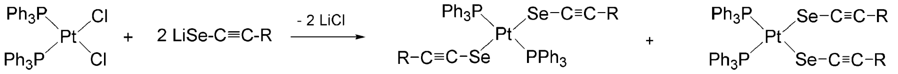
Scheme 2. Attempted Synthesis of **3** via the Insertion Route (R = Pentyl; Ph = Phenyl)

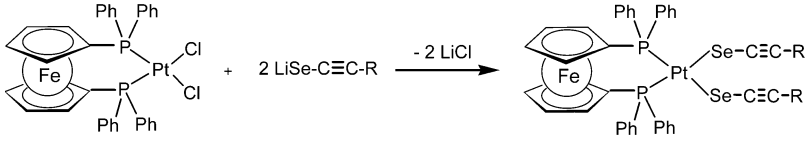


Scheme 3. Synthesis of **3** (R = Pentyl)



2 **1** *trans*-**3** *cis*-**3**

Scheme 4. Synthesis of **4** (R = Pentyl)



1 **4**

trans relative to cis complexes have been interpreted as a result of slightly stronger trans influence of $^{-}$SeR compared to that of PPh_3.[14] On the other hand, this concept should be concomitant with a decrease of the Se−Pt bond length in the trans form compared to the cis form, which has not been observed and is also not supported by our findings.

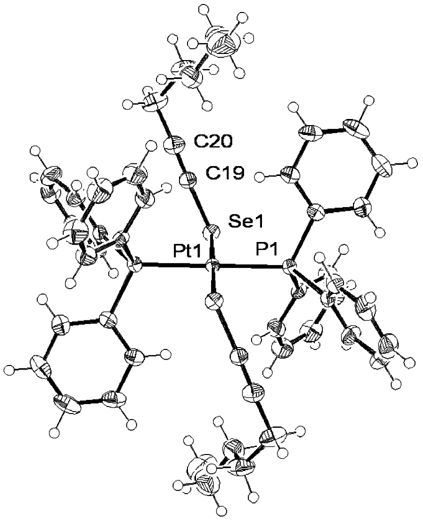


Figure 1. Molecular structure of *trans*-**3** with thermal ellipsoids (50% probability level). Solvent molecules were omitted for clarity.

Within the C≡C−Se unit, the C(19)−C(20) bond length of 1.177(5) Å is characteristic for a C≡C triple bond, while the Se(2)−C(19) distance is with 1.811(4) Å at the shorter end of the range (1.828(7)−1.851(7) Å) observed for a Se−C bond in alkyneselenolates so far.[3,4,7] The angle between Se(2)−C(19)−C(20) is almost linear (176.9(4)°), which indicates that the contribution of the selenoketenyl resonance structure is negligible. The square planar geometry around platinum is slightly distorted. While the sum of the bond angles necessarily is 360° due to the inversion center, the P(1)−Pt(1)−Se(2) and the P(1a)−Pt(1)−Se(2) angles differ by more than 10° (83.37(3)° vs 96.63(3)°). We attribute this feature to the steric repulsion between the heptynyl unit with preferably one of the triphenylphosphine groups as well as the electronic reasons quoted for metal thiolates.[15] Relevant geometric parameters and details of the experimental data collection for *trans*-**3** are listed in Tables 1 and 2, respectively.

We were interested to compare the structural results obtained for *trans*-**3** with its cis isomer. As in the case of the related (benzeneselenolate)platinum complexes, slow isomerization of *cis*-**3** to *trans*-**3** in solution precluded the growth of crystals of *cis*-**3** suitable for X-ray diffraction, however. To circumvent this issue, we replaced the triphenylphosphine ligands with a chelating diphosphine to enforce cis geometry. We have chosen bis(diphenylphosphino)ferrocene (dppf) rather than bis(diphenylphosphino)ethylene (dppe), which has been used in previous investigations,[2] because from its electronic and steric properties the ferrocenylene unit is closer to a phenyl group than alkylidene units.[16] To synthesize an analogous complex with cis geometry, we started from (dppf)$PtCl_2$, which we reacted with lithium heptyneselenolate **(1)** to give the *cis*-bis(alkyneselenato)platinum complex **4** (Scheme 4).

We determined the structure of **4** in the solid state by X-ray diffraction which confirms the cis arrangement of the alkyneselenolate ligands (Figure 2). The Pt−P distances (2.2819(13)−2.2882(12) Å) and the Pt−Se bond lengths (2.4608(6)−2.4639(5) Å) in **4** are both shorter than the respective ones in *trans*-**3**. In contrast, the bond lengths associated with the alkyneselenolate unit appear slightly elongated in the cis complex compared to the trans complex as for instance the C≡C triple bonds in **4** are 1.199(7)−1.205(8) Å relative to 1.177(5) Å in *trans*-**3**. As is evident from the C≡C−C angles (175.6(10)−178.1(10)°) the alkynyl groups show an arrangement close to linearity. Somewhat larger are the deviations from ideal linearity for the corresponding Se−C≡C angles, which range from 170.3(6) to 175.5(7)°. Within the approximately square planar coordination environment around platinum, the neighboring atoms show angles in the range between 85.07(2) and 97.98(4)°,

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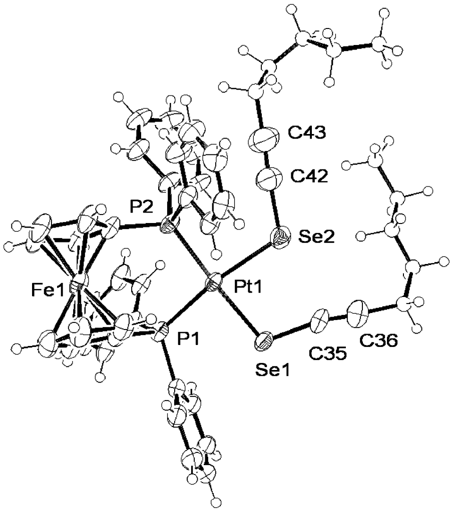

Figure 2. Molecular structure of one orientation of **4** with thermal ellipsoids (50% probability level), except for the disordered pentyl groups. For clarity, the solvent molecule and one site of the disordered pentyl groups have been omitted.

where the largest value corresponds to the P1−Pt1−P1 angle involving the bis(phosphine) ligand. To adjust the bite angle of the dppf ligand, the Cp rings of the ferrocenyl unit are twisted by 34.5° (P(1)−Cp(1)−Cp(2)−P(2)). The Cp−Fe−Cp system is almost linear with an angle of 178.8(3)°. The Pt−Fe distance of 4.299 Å significantly exceeds the sum of the van der Waals radii; therefore, any direct interaction between these atoms appears unlikely. Relevant geometric parameters and details of the experimental data collection for **4** in comparison to *trans*-**3** are summarized in Tables 1 and 2, respectively.

In addition to the structural changes that can be observed for *cis*-**3** and **4**, the heteronuclear NMR spectra reveal valuable information related to the bonding situation in (alkyneselenolato)platinum complexes. Relevant NMR spectroscopic data for *cis-/trans*-**3** and **4** are summarized in Table 3. It can be noted that the ^{31}P resonance of the phosphane unit in the trans form appears at lower field than in the cis form. In contrast the ^{195}Pt resonances show the opposite trend with the ^{195}Pt nucleus in the cis form being more shielded than in the trans form. Significant changes are observed for the coupling constants $^1J_{\mathrm{PPt}}$ and $^1J_{\mathrm{PtSe}}$, which reflect the metal−ligand interactions. Thus, in the order from trans to cis, these coupling constants increase by 15% ($^1J_{\mathrm{PPt}}$) and 21% ($^1J_{\mathrm{PtSe}}$), indicating an increased bond order.[17] This correlates clearly with the structural findings for compounds *trans*-**3** and **4** for which both the Pt−P and the Pt−Se distances decrease from trans to cis.

The fact that both the phosphine and the alkyneselenolate ligands experience a contraction of the metal−ligand bonds suggests that the supposedly stronger trans influence of the selenolate ligand might be only one among other factors. An alternative explanation might be that the steric situation in the trans form prevents shorter metal−ligand bond lengths, while in the cis form steric repulsion is reduced and consequently shorter metal−ligand distances are feasible.

In summary, we synthesized closely related cis and trans platinum complexes of SeCC-*n*-C_5H_{11} and elucidated their structures in solution and the crystalline state. In line with previous work, we find exclusive coordination of the selenium atom of the ambident alkyneselenolate ligand and a preference for the obviously more stable trans isomer. In contrast to previous work, we find a uniform increase of all metal−ligand bond lengths in the cis vs the trans isomers. This is an indication that the structural changes are more likely a consequence of steric repulsion than a stronger trans influence of alkyneselenolate ligands.

Experimental Section

^{1}H, ^{13}C, ^{31}P, ^{77}Se, and ^{195}Pt NMR spectra have been recorded on Bruker AMX 360 and Bruker DPX 250 instruments at room temperature. Chemical shift values are given in ppm and are referenced to external standards. Mass spectra have been measured on Kratos Concept 1-H and VG Autospec spectrometers using the FAB ionization technique with *m*-NBA matrix. Microanalysis were measured on a VarioEL v2.3. Compounds **1**, **2**, and (dppf)$PtCl_2$ have been prepared according to published procedures.[9,18,19] All experiments have been carried out under an argon atmosphere using standard Schlenk techniques. The resulting products are moderately air sensitive.

Synthesis of Bis(1-heptyneselenolato)(triphenylphosphine)-platinum(II) (3). A solution of lithium heptyneselenolate (0.36 g, 2 mmol) in ether (40 mL) was cooled to −78 °C. To this mixture solid *cis*-$PtCl_2(PPh_3)_2$ (0.79 g, 1 mmol) was added while stirring. The mixture was slowly warmed to room temperature, and stirring was continued for 12 h upon which white and yellow precipitates were observed. These were filtered under argon, and the supernatant liquid was discarded. The residue was extracted with methylene chloride, and the filtrate was separated. The solvent of the filtrate was evaporated in a vacuum, and the product was obtained as an oily residue which slowly crystallized (0.85 g, 80%). Prolonged evacuation of the crystalline material gave analytically pure samples. Anal. Calcd for $C_{50}H_{52}P_2PtSe_2 \cdot CH_2Cl_2$ ($M_r = 1152.83$): C, 53.13; H, 4.72. Found: C, 53.50; H, 5.04.

***trans*-3:** ^{31}P NMR (CD_2Cl_2) $\delta = 28.0$ (s, $^1J_{\mathrm{PPt}} = 2858$ Hz, $^2J_{\mathrm{PSe}} = 26$ Hz); ^{195}Pt NMR (CD_2Cl_2) $\delta = -4985$ (t, $^1J_{\mathrm{PtP}} = 2858$ Hz, $^1J_{\mathrm{PtSe}} = 198$ Hz); ^{1}H NMR (CD_2Cl_2) δ 7.7−7.1 (m, 30H), 1.8−0.9 (m, 22H); ^{13}C NMR (CD_2Cl_2) δ 133.0, 132.1, 130.9, 129 (m, phenyl), 93.0 (s, $^2J_{\mathrm{CPt}} = 28$ Hz, $-\mathrm{Se}-\mathrm{C}{\equiv}\mathit{C}$), 64.1 (t, $^3J_{\mathrm{CP}} = 6.7$ Hz, $-\mathrm{Se}\text{-}\mathit{C}{\equiv}\mathrm{C}$), 31.6, 29.1, 22.8, 20.9, 14.4 (s, pentyl); MS (FAB) *m/z* 893 (10%, ($M^+ - (\mathrm{Se}-\mathrm{C}{\equiv}\mathrm{C}-\mathrm{Pen})$)), 718 (65%, ($M^+ - 2(\mathrm{Se}-\mathrm{C}{\equiv}\mathrm{C}-\mathrm{Pen})$)), 455 (45%, $PtSeC_{13}H_{25}^+$), 357 (100%, $Ph_3PC_7H_{11}^+$), 263 (50%, $HPPh_3^+$); UV/vis 212.4 nm.

***cis*-3:** ^{31}P NMR (CD_2Cl_2) $\delta = 23.6$ (s, $^1J_{\mathrm{P-Pt}} = 3220$ Hz, $^2J_{\mathrm{P-Se}} = 42$ Hz).

Synthesis of Bis(1-heptyneselenolato)(1,1′-bis(diphenylphosphino)ferrococene)platinum(II) (4). (dppf)$PtCl_2$ (1.07 g, 1.3 mmol) was dissolved in THF (20 mL) and cooled to −78 °C. To this mixture a solution of lithium heptyneselenolate (0.41 g, 2.24 mmol) in THF (10 mL) was added slowly while stirring. The mixture was slowly warmed to room temperature, and stirring was continued for 60 h upon which the mixture turned red. The solvent was evaporated in a vacuum, and the residual solid was extracted with benzene. The product solution was separated from the

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eliminated LiCl by filtration through a filter funnel under an argon atmosphere and subsequently concentrated in a vacuum to incipient crystallization. From this solution **4** crystallized as an orange yellow solid at room temperature (0.9 g, 63%). Prolonged evacuation of the crystalline material gave analytically pure samples: mp 298.5 (dec); ^{31}P NMR (C_6D_6) $\delta = 19.4$ (s, $^{1}J_{\mathrm{PPt}} = 3287$ Hz); ^{195}Pt NMR (C_6D_6) $\delta = -5009$ (tt, $^{1}J_{\mathrm{PtP}} = 3287$ Hz, $^{1}J_{\mathrm{PtSe}} = 240$ Hz); ^{77}Se NMR (C_6D_6) $\delta = 330$; ^{1}H NMR (C_6D_6) δ 7.83−7.25 (m, 20H), 4.21 (s, 4H), 3.92 (s, 4H), 1.80−0.75 (m, 22H); ^{13}C NMR (C_6D_6) δ 135.3, 131.4, 130.7, 127.2 (phenyl), 100.4 (s, $-\mathrm{Se}-\mathrm{C}\equiv C$), 75.7, 73.8, 73.1 (m, Fc′), 60.6 (s, $-\mathrm{Se}\text{-}C\equiv\mathrm{C}$), 31.2, 28.7, 22.2, 20.8, 13.9 (s, pentyl); MS (FAB) *m*/*z* 1099 (M^+, 60%), 1003 ($M^+ -$ heptyne, 22%), 923 ($M^+ -$ heptyneselenol, 100%), 828 ($M^+ -$heptyneselenol $-$ heptyne, 60%), 748 ($M^+ - 2$ heptyneselenol, 50%); UV/vis 263.0 nm. Anal. Calcd for $C_{48}H_{50}FeP_2PtSe_2$ ($M_r = 1097.70$): C, 52.52; H, 4.59. Found: C, 52.08; H, 4.65.

Crystal Data for *trans*-3. An orange crystal of *trans*-**3** with dimensions 0.3 × 0.2 × 0.2 mm was coated in paraffin oil, mounted on a glass fiber, and placed under a cold stream of nitrogen. The measurements were performed on a Bruker AXS CCD 1000 diffractometer using graphite-monochromatized Mo Kα radiation at 213 K. A total of 6971 reflections were collected ($\theta_{\mathrm{max}} = 25.66°$), from which 4286 were unique ($R_{\mathrm{int}} = 0.0224$), with 3867 having $I > 2\sigma(I)$. Additional experimental details are given in Table 2. The structure has been solved by Patterson analysis and subsequent refinement by full-matrix least-squares techniques against F^2 (SHELXL-97).[20,21] The non-hydrogen atoms were refined with anisotropic displacement parameters without any constraints. For 277 parameters final R indices of R = 0.0257 and wR2 = 0.0599 (GOF = 1.013) were obtained.

Crystal Data for 4. An orange crystal of **4** with dimensions 0.4 × 0.3 × 0.3 mm was coated in paraffin oil, mounted on a glass fiber, and placed under a cold stream of nitrogen. The measurements were performed on a Nonius Kappa CCD diffractometer using graphite-monochromatized Mo Kα radiation at 123 K. A total of 71 779 reflections were collected ($\theta_{\mathrm{max}} = 27.48°$), from which 10 644 were unique ($R_{\mathrm{int}} = 0.0571$), with 8467 having $I > 2\sigma(I)$. Additional experimental details are given in Table 2. The structure was solved by direct methods (SHELXS-97) and refined by full-matrix least-squares techniques against F^2 (SHELXL-97).[20,21] The atoms C45, C46, C47, and C48 of the pentyl group are disordered over two sites with an occupancy factor of 0.5. All other non-hydrogen atoms were refined with anisotropic displacement parameters without any constraints. For 516 parameters final R indices of R = 0.0365 and wR2 = 0.1047 (GOF = 1.040) were obtained. An empirical absorption correction was applied.

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Supporting Information Available: Details of the X-ray crystallographic studies for *trans*-**3** and **4** in CIF format and complete ORTEP plots. This material is available free of charge via the Internet at http://pubs.acs.org.

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