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Complexation of Cage Thiones With Bisphosphine Platinum(0) Complexes

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ABSTRACT: *The syntheses of thiocarbonyl derivatives of pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,8}]-8,10-dione (***1***) using bis(trimethylsilyl)sulfide* **12** *or H_2S/HCl as a thionating agent are reported. The complexation reactions of monothioketone* **3**, *dimethoxythioketone* **5**, *and thioxoketone* **6** *with bisphosphine platinum(0) complexes were investigated. The formed complexes* **9a–c** *and* **11** *were characterized by ^{1}H, ^{31}P NMR, IR spectroscopy, as well as mass spectrometry and elemental analysis. X-ray crystal structure analyses of* **5** *and complexes* **9a** *and* **11** *were performed. The structure analyses show that thiocarbonyl derivatives are coordinated in the η^2-mode. In each case, only one isomer is formed, with the platinum complex fragment selectively coordinated in the exo-position.* © 2007 Wiley Periodicals, Inc. Heteroatom Chem 18:584–590, 2007; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20332

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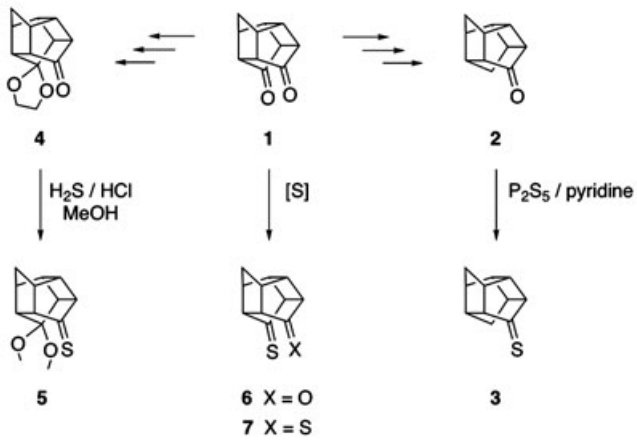
INTRODUCTION

Thioketones form a class of organic compounds with interesting chemical properties that enable their application as building blocks for the preparation of diverse sulfur-containing heterocycles. Especially important are reactions leading to three-membered thiiranes [1a] as well as [3+2]-cycloadditions with 1,3-dipoles, resulting in the formation of the diverse, five-membered heterocycles containing at least one sulfur atom [1b]. The superior reactivity observed in some reactions with dipoles allowed one to classify thioketones as superdipolarophiles [2].

Low stability of thioketones limits their exploration as useful starting materials. While simple aliphatic thioketones are unstable and odorous compounds, aromatic representatives are more stable and can be explored for the purpose of synthetic and coordination chemistry [3]. It is well known that increasing sterical hindrance in aliphatic and cycloaliphatic thioketones results in increased stability. Thus, such compounds as di(*tert*-butyl)thioketone [4a], 2,2,4,4-tetramethyl-3-thioxocyclobutanone [4b], and adamantanethione [4c] are more stable and can be explored without special precautions. In recent articles, the synthesis of novel stable and nonodorous thioketones **3** and **5** derived from a "cage" polycyclic diketone **1** has been reported [5,6]. There are known examples

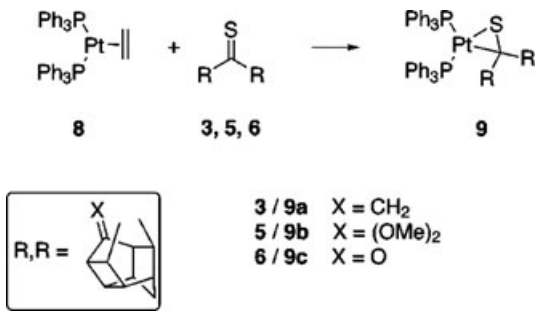


SCHEME 1 Thiocarbonyl derivatives of dione **1**.

of direct thionation of dione **1**, but attempts to isolate monothio **6** and/or dithio derivatives **7** were not successful [7].

The complex fragment $[(Ph_3P)_2Pt]$ shows good ability to form stable adducts with unstable sulfur-containing species (e.g., dithiirane and thioketone derivatives [3,8]). The first thioketone complex of type **9** with the general formula $[(Ph_3P)_2Pt(\eta^2\text{-}S{=}CR_2]$ was reported in 1967 [9]. This and further experimental examples show that $[(Ph_3P)Pt(\eta^2\text{-}C_2H_4)]$ instantly forms stable complexes, even with sterically hindered thioketones [8]. The thiones are coordinated in the η^2-mode and could be regarded as platina thiiranes [8c].

In this article, we report on the syntheses of thiocarbonyl derivatives of pentacyclo $[5.4.0.0^{2,6}.0^{3,10}.0^{5,8}]$-8,10-dione (**1**) (Scheme 1) and the complexation reaction of the C=S group containing compounds **3, 5**, and **6** with $[(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)]$ (**8**) (Scheme 2).



SCHEME 2 Complexation of thiocarbonyl derivatives with platinum complex **8**.

RESULTS AND DISCUSSIONS

Thioketone **3** is obtained by thionation of ketone **2** with P_2S_5 in pyridine solution [5]. Treatment of the solution of **3** in toluene with the platinum complex **8** at room temperature results in decolorization of the reaction mixture within few minutes. Instantaneous decolorization of the solution indicates a fast complexation reaction. After evaporation of the solvent, the residual solid was analyzed by ^{31}P NMR spectroscopy. The presence of only one AB system ($\delta = 27.0/24.1$ with $^2J(P,P) = 11.5$ Hz) revealed the selective formation of one isomer of the 1:1 complex. The coupling constants $^1J(P,Pt) = 4454/2858$ Hz indicated coordination in the η^2-mode. Both the molecular peak at $m/z = 895$ and elemental analysis confirmed the formula $C_{47}H_{42}P_2PtS$. Diffusion of pentane to a solution of complex **9a** in CH_2Cl_2/methanol allowed the isolation of colorless crystals that were suitable for the X-ray crystal structure analysis (Table 1).

The structure showed that as expected the platinum complex fragment is side-on coordinated in the *exo*-position (Fig. 1). The C—S bond length (1.778(4) Å) is remarkably longer than the typical C=S bond (1.544(5) Å [10]). The elongation of this bond indicates a strong interaction of the platinum complex fragment with the polarizable π-system of the C=S bond. The structure fits well with the previously postulated formation of the platina thiirane ring [8c] (Table 2).

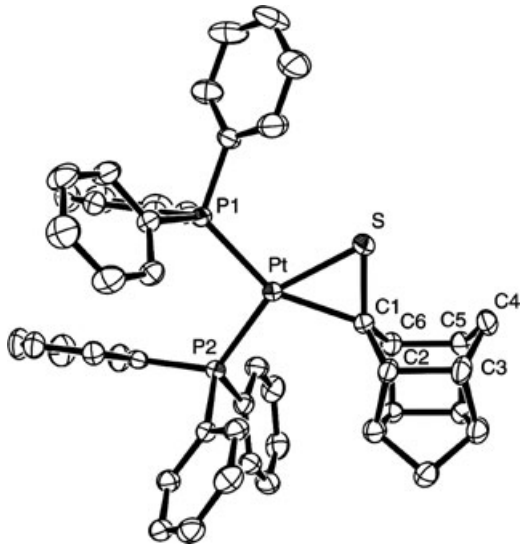


FIGURE 1 The molecular structure of the thioketone complex **9a**, with ellipsoids drawn at 50% probability level. Hydrogen atoms have been omitted for clarity.

TABLE 1 Summary of Data Collection and Refinement for **5, 9a**, and **11**

	5	**9a**	**11**
Empirical formula	$C_{13}H_{16}O_2S$	$C_{47}H_{42}P_2PtS \cdot 0.5\ CH_3OH$	$C_{45}H_{44}O_2P_2PtS \cdot 0.5$ THF
Formula weight (g/mol)	236.32	911.92	941.94
Color	Red	Colorless	Colorless
Crystal size (mm^3)	$0.08 \times 0.08 \times 0.06$	$0.04 \times 0.04 \times 0.03$	$0.04 \times 0.04 \times 0.03$
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$
a (Å)	12.6607(5)	12.3922(3)	12.5748(3)
b (Å)	7.4838(4)	12.4405(3)	16.0328(3)
c (Å)	12.5451(6)	14.1382(4)	22.0765(5)
α (°)	–	83.613(1)	–
β (°)	104.275(3)	75.245(1)	92.795(1)
γ (°)	–	70.880(1)	–
V ($Å^3$)	1,151.95(9)	3,849.2(2)	4,445.53(17)
Z	4	2	4
F(0 0 0)	504	914	1896
$\rho_{calcd.}$	1.363	1.521	1.407
μ (Mo-K_α) (cm^{-1})	2.63	36.92	33.12
Temperature (°C)	−90	−90	−90
Reflections collected	7,444	13,871	29,053
Absorption correction	Multiscan	Multiscan	Multiscan
Min/max transmission	0.9793/0.9844	0.7202/0.7797	0.7418/0.8446
Independent reflections (R_{int})	2597 (0.0293)	9029(0.0213)	10184 (0.0465)
h	−16/15	−16/16	−16/14
k	−9/9	−14/16	−20/20
l	−15/16	−18/16	−26/28
Θ range (°)	$3.19 \leq \Theta \geq 27.41$	$2.25 \leq \Theta \geq 27.46$	$2.24 \leq \Theta \geq 27.48$
Completeness Θ_{max} (%)	99.0	99.1	99.7
Reflections with $I > 2\sigma(I)$	2,054	8,065	7,742
No. of parameters, restraints	145, 0	470, 1	480, 0
R_1, wR_2 [$I > 2\sigma(I)$]	0.0388, 0.1016	0.0319, 0.0838	0.0371, 0.0900
R_2, wR_2 (all data)	0.0534, 0.1102	0.0391, 0.0883	0.0597, 0.0999
GoF	1.041	1.051	1.032
Extrema of final difference Fourier synthesis (e/$Å^3$)	0.243/−0.259	2.279/−0.902	1.104/−1.111

TABLE 2 Selected Bond Lengths (Å) and Angles (°) for **5, 9a**, and **11**

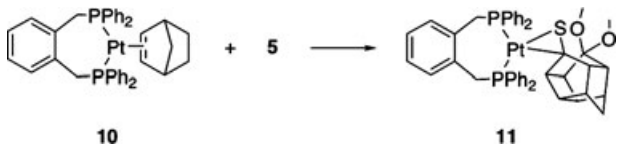
	Dimethoxy ketone **5**	*Thioketone complex* **9a**	*Dimethoxy thioketone complex* **11**
Pt—P(1)	–	2.2559(10)	2.2527(12)
Pt—P(2)	–	2.2974(10)	2.2815(12)
Pt—S(1)	–	2.2833(11)	2.2851(11)
Pt—C(1)	–	2.145(4)	2.159(4)
S(1)—C(1)	1.6205(19)	1.778(4)	1.767(4)
C(1)—C(2)	1.502(2)	1.526(6)	1.516(6)
C(1)—C(5)	1.504(2)	1.517(6)	1.520(6)
C(2)—C(8)	1.587(2)	1.590(6)	1.586(6)
C(6)—C(5)	1.566(2)	1.589(6)	1.577(6)
C(8)—C(7)	1.527(2)	1.526(7)	1.518(7)
C(7)—C(6)	1.523(2)	1.508(7)	1.532(6)
O(1)—C(7)	1.4071(19)	–	1.404(5)
O(2)—C(7)	1.4177(18)	–	1.440(5)
P(1)—Pt—P(2)	–	101.86(4)	102.64(4)
S(1)—Pt—C(1)	–	46.22(11)	46.76(11)
P(1)—Pt—C(1)	–	106.02(11)	108.18(12)
P(2)—Pt—S(1)	–	104.86(4)	102.34(4)
O(1)—C(7)—O(2)	111.41(12)	–	108.4(3)
C(5)—C(1)—S(1)	127.41(13)	120.5(3)	121.0(3)
C(2)—C(1)—S(1)	127.33(12)	120.8(3)	124.1(3)
C(5)—C(1)—C(2)	104.57(13)	101.6(3)	101.2(3)
C(6)—C(7)—O(1)	116.86(13)	–	119.2(4)
C(8)—C(7)—O(1)	109.37(12)	–	111.1(4)

In extension of already discussed thionation of **1** with H_2S/HCl stream in methanolic solution [5], another method based on the application of monoacetal **4** was tested. In this case, reaction with H_2S/HCl stream carried out at room temperature provided the dimethoxy thioketone **5** as the exclusive product in good yield. After typical workup and column chromatography, **5** was isolated as an orange-colored oil that crystallizes at low temperature.

The spectroscopic data confirmed the identity of this product with the earlier described sample of **5** [5]. In analogy to **3**, coordinating reaction of **5** with **8** occurred smoothly in toluene at room temperature. Again the ^{31}P NMR data ($^1J(P,Pt) = 2843/4287$ Hz and $^2J(P,P) = 11.5$ Hz) confirmed the formation of only one isomer and the binding of the $(Ph_3P)_2Pt$ fragment in the η^2-mode. Both elemental analysis and the molar peak at $m/z = 955$ are in good conformity with the structure **9b**.

Apparently, the steric hindrance caused by the presence of two dimethoxy groups does not influence the attack of the Pt atom on to the C=S bond. In contrast to the reported reaction of **3** with Ph_2CN_2 [11], under comparable conditions, the analogous reaction with thioketone **5** did not occur. (A solution of Ph_2CN_2 and dimethoxy thioketone **5** in 1:3 ratio in diethyl ether was allowed to stand at room temperature for 24 h, but no decolorization of the intense violet color of Ph_2CN_2 was observed. This result suggests no conversion under applied reaction conditions.) This result can be plausibly explained by steric factors that hindered Ph_2CN_2 to approach the C=S dipolarophile.

To get more information on the structure of **5**, its X-ray crystal structure analysis was performed (Fig. 2). While the oxygen atom O(1) is closely located at the thiocarbonyl carbon atom C(1) (O(1)—C(1) = 2.698 Å), the sulfur atom S(1) is not efficiently shielded. The distance between S(1) and O(1) was estimated to be 3.451 Å.



10 11

SCHEME 3 Syntheses of thioketone complex **11**.

Similar to the complexation of **5** with **8,** treatment of **5** with platinum complex [(dpp(*o*-xyl)Pt(η^2-nb)] **10** (nb = norbornene) in toluene solution yielded analogous 1:1 complex (Scheme 3). Spectroscopic data proved the expected structure of **11**, which was finally confirmed by X-ray crystal structure analysis (Fig. 3).

The structure shows that the complexation of a platinum complex fragment by sulfur atom results in significant changes in geometry of the cage fragment. For example, the intramolecular distance C(1)···O(1) is elongated from 2.698 Å to 2.966 Å. On the other hand, the distance O(1)···S(1) in **11** (2.811 Å) is shorter than that in the thioketone **5**, by approximately 0.5 Å below the sum of the van de Waals radius [12]. This is slightly shorter than those reported for intermolecular S···O interactions in oxidized thioethers and disulfides [13].

Some earlier attempts of thionation of **1** have already been reported [7]. Bis(trimethylsilyl) sulfide

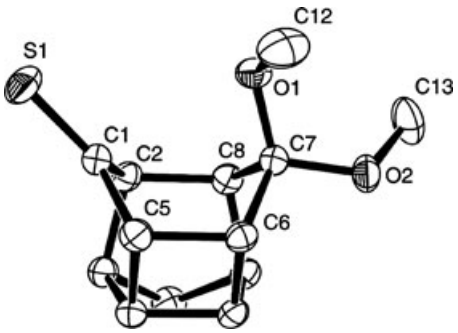


FIGURE 2 The molecular structure of dimethoxy thioketone **5**, with ellipsoids drawn at 50% probability level. Hydrogen atoms have been omitted for clarity.

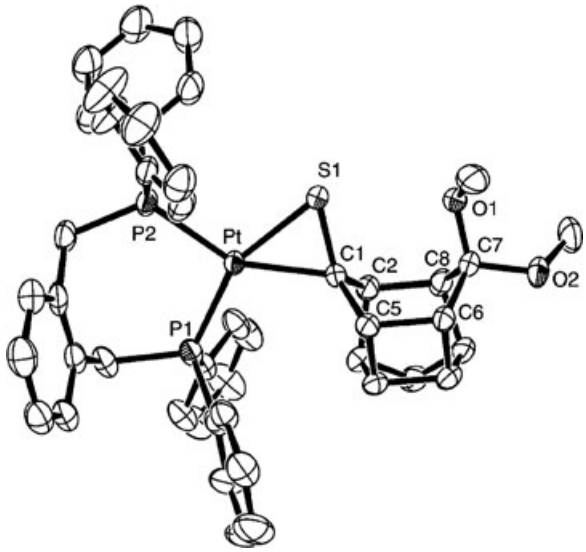
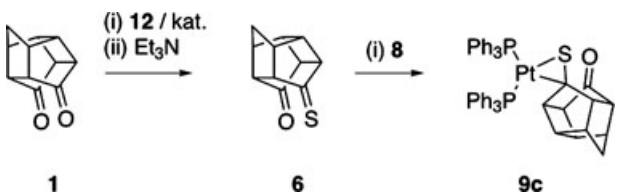


FIGURE 3 The molecular structure of the dimethoxy thioketone complex **11**, with ellipsoids drawn at 50% probability level. Hydrogen atoms have been omitted for clarity.

(**12**) was used to exchange oxygen by sulfur atom under conditions described by Degl'Innocenti et al. (CH_2Cl_2/$(Me_3Si)_2S$ **12**/CF_3-SO_2-O-$Si(CH_3)_3$ **13**/room temperature) [14]. Dione **1** and thionating agent **12** were used in 2.5:1 ratio to form the thioxoketone **6** exclusively. After several minutes, the reaction solution turned orange/red, and after 1 h of additional stirring, the reaction was stopped by the addition of triethylamine. Subsequently, the colored solution was treated with **8** dissolved in toluene. Flash chromatography followed by recrystallization led to the isolation of colorless solid, which was analyzed spectroscopically.

The ^{31}P NMR spectrum showed the presence of a characteristic AB system analogous to that described for **9a**, **9b**, and **11** (^1J(P,Pt) = 4367/2906 Hz and ^2J(P,P) = 6 Hz). In addition, the presence of the C=O group was evidenced by a strong absorption in the IR spectrum (ν = 1735 cm^{-1}). The corresponding signal in the ^{13}C NMR spectrum appeared at δ = 219.4. In the same spectrum, the *C*=S group shows a resonance at δ = 87.6 with ^2J(P,C) = 61 Hz. The 1:1 stoichiometry of **9c** was confirmed by mass spectrometry (*m*/*z* = 909). In another experiment, the thionation of **1** was carried out using two-fold excess of **12** in MeCN solution. In this case, an intense coloration of the reaction mixture was observed after the addition of the catalyst. The initial colorless solution turned to red and then to orange. However, attempted complexation with **8** did not yield the expected complex under the described reaction conditions. Instead, decomposition leading to a mixture of unidentified products was observed.

In conclusion, this study shows that thiocarbonyl derivatives of sterically hindered "cage" dione **1** with different substitution patterns easily undergo complexation with platinum(0) complexes to yield the 1:1 adducts (Scheme 2). The X-ray studies of complexes **9a** and **11** obtained with **3** and **5**, respectively, showed that the platinum complex fragment approaches the C=S bond exclusively from the *exo*-side. *In situ* formed thioxoketone **6** was trapped by complexation with **8** (Scheme 4).



SCHEME 4 Syntheses of thioxoketone complex **9c**.

EXPERIMENTAL

All reactions were performed under argon atmosphere. **2, 4** [15], **3** [5], **12** [16], platinum(0) complexes **8** [17], and **10** [18] were prepared as described in the literature. NMR spectra were recorded on a Brucker DRX 200 spectrometer. ^1H NMR chemical shifts were referenced to residual protons in deuterated solvents at 200 MHz. ^{13}C NMR chemical shifts were referenced to solvent carbon atoms as internal standards at 50 MHz. ^{31}P NMR chemical shifts were referenced to external H_3PO_4 at 81 MHz. IR spectra were recorded on a Perkin Elmer System 2000 FT-IR spectrometer. Mass spectra were recorded on a Finnigan MAT SSQ 710 mass spectrometer. Elemental analyses were performed on a Leco CHNS-932 analyzer.

Synthesis of Dimethoxy Thioketone **5**

The monoacetal **4** (1g, 4.5 mmol) was dissolved in anhydrous MeOH (20 mL), and a stream of H_2S/HCl was passed through the stirred solution for 1 h. The orange reaction mixture was transferred to a vigorously stirred mixture of ice, water, and excess of KOH. Extraction with diethyl ether (3 × 20 mL) followed by removal of the solvent afforded crude product, which was purified by column chromatography (silica gel/CH_2Cl_2). Dimethoxy thioketone **5** was obtained as a red or an orange solid in 60% yield.

Dimethoxy thioketone **5**. Yield: 60%; mp 62°C (orange plates) or 44°C (red rhombohedra). Anal. calcd. for $C_{13}H_{16}O_2S$: C, 66.07%; H, 6.82%; S, 13.57%. Found: C, 66.14%; H, 6.85%; S, 13.83%. ^1H NMR ($CDCl_3$): δ = 3.18 (m, 1H), 3.14 (s, 3H, —O—*Me*), 3.12 (m, 1H), 3.02 (s, 3H, —O—*Me*), 2.94 (m, 2H), 2.83 (m, 1H), 2,81 (m, 1H), 2.67 (m, 1H), 2.62 (m, 1H), 1.80 (d, ^2J(H,H) = 11 Hz, 1H, CH_aH_b), 1.46 (d, ^2J(H,H) = 11 Hz, 1H, CH_aH_b); ^{13}C NMR ($CDCl_3$): δ = 264.6 (*C*=S), 108.4 (*C*(O—Me)$_2$), 62.5, 53.5, 53.1, 50.7 (—O—*Me*), 46.4, 45.2, 44.2, 40.8, 39.8, 37.3 ppm (CH_aH_b). IR (KBr): 2979, 2864, 1457, 1351, 1320, 1274, 1186, 1153, 1135, 1098, 1065, 1017, 937, 900, 849, 825, 756, 589, 508 cm^{-1}.

Synthesis of Thioketone Complexes **9a, 9b**, *and* **11**

The corresponding thiocarbonyl derivative (0.12 mmol) was dissolved in toluene (5 mL). A solution of the platinum(0) complex (0.1 mmol) in toluene (10 mL) was added dropwise. After decolorization, the solvent was evaporated to dryness. The crude product was washed with diethyl ether and dissolved

in THF. The solution was filtrated over silica gel. The thioketone complexes were obtained as crystalline material by slow diffusion of pentane into this solution.

Complex **9a**. Yield: 45% of a colorless microcrystalline solid; mp 230°C (decomp.). Anal. calcd. for $C_{47}H_{42}P_2PtS$: C, 63.01%; H, 4.73%; S, 3.58%. Found: C, 63.05%; H, 5.02%; S, 3.28%. ^{1}H NMR ($CDCl_3$): δ = 7.32–7.10 (m, 30H), 2.37 (m, 1H), 2.29 (m, 2H), 2.10 (m, 4H), 1.65 (s, 1H), 1.19 (d, ^2J(H,H) = 11.5 Hz, 1H, CH_aH$_b$), 1.00 (m, 1H), 0.59 (d, ^2J(H,H) = 11.5 Hz, 1H, CH$_a$$H_b$), 0.46 (m, 1H); ^{31}P NMR ($CDCl_3$): 27.0 (d with ^{195}Pt satellites, ^2J(P,P) = 11.5 Hz, ^1J(P,Pt) = 4454 Hz), 24.1 ppm (d with ^{195}Pt satellites, ^2J(P,P) = 11.5 Hz, ^1J(P,Pt) = 2858 Hz). MS (FAB in nba): *m/z* (%) = 895 (1.5) [M$^+$], 719 (16) [$(Ph_3P)_2Pt^+$], 307 (100, nba). IR (KBr): 3071, 3052, 2948, 2856, 1965, 1898, 1815, 1630, 1479, 1434, 1310, 1302, 1181, 1095, 1068, 948, 742, 694, 540, 520, 511, 498 cm^{-1}.

Complex **9b**. Yield: 60% of pale yellow crystals; mp 218°C (decomp.). Anal. calcd. for $C_{49}H_{46}O_2P_2PtS$: C, 61.56%; H, 4.85%; S, 3.03%. Found: C, 61.44%; H, 4.92%; S, 3.35%. ^{1}H NMR ($CDCl_3$): δ = 7.34–7.09 (m, 30H), 3.23 (s, 3H, —O—*Me*), 3.08 (s, 3H, —O—*Me*), 2.6–2.3 (m, 5H), 2.2–2.0 (m, 2H), 1.14 (d, ^2J(H,H) = 10.5 Hz, 1H, CH_aH$_b$), 0.55 (d, ^2J(H,H) = 10.5 Hz, 1H, CH$_a$$H_b$), 0.39 (m, 1H); ^{31}P NMR ($CDCl_3$): 28.3 (d with ^{195}Pt satellites, ^2J(P,P) = 11.5 Hz, ^1J(P,Pt) = 4287 Hz), 23.9 ppm (d with ^{195}Pt satellites, ^2J(P,P) = 11.5 Hz, ^1J(P,Pt) = 2843 Hz). MS (FAB in nba): *m/z* (%) = 955 (8) [M$^+$], 924 (8) [(M—OMe)$^+$], 719 (100) [$(Ph_3P)_2Pt^+$]. IR (KBr): 3052, 2968, 2858, 2823, 1635, 1479, 1434, 1330, 1183, 1120, 1094, 1052, 1013, 990, 742, 694, 540, 521, 511 cm^{-1}.

Complex **11**. Yield: 55% of colorless crystals; mp 198°C (decomp.). Anal. calcd. for $C_{45}H_{44}O_2P_2PtS \cdot$ THF: C, 60.17%; H, 5.36%; S, 3.28%. Found: C, 59.91%; H, 5.47%; S, 3.03%. ^{1}H NMR ($CDCl_3$): δ = 7.94 (m, 2H), 7.80 (m, 2H), 7.60 (m, 2H), 7.36 (m, 14H), 6.88 (m, 2H), 6.42 (d, J = 7.5 Hz, 1H), 6.23 (d, J = 7 Hz, 1H), 3.87 (m, 3H), 3.69 (m, 1H), 3.20 (s, 3H, —O—*Me*), 3.04 (s, 3H, —O—*Me*), 2.44 (t, J = 6 Hz, 1H), 2.30 (m, 2H), 2.18 (m, 1H), 2.03 (m, 2H), 1.92 (m, 1H), 1.05 (d, ^2J(H,H) = 10.5 Hz, 1H, CH_aH$_b$), 0.51 (d, ^2J(H,H) = 10.5 Hz, 1H, CH$_a$$H_b$); ^{13}C NMR ($CDCl_3$): δ = 136.3 (m), 135.5 (m), 135.2 (m), 134.9 (m), 134.0 (m), 133.7, 133.2, 131.6 (m), 131.3, 130.8, 130.6, 129.6 (m), 128.1 (m), 127.7 (m), 126.2 (m), 108.7, 78.3 (d, ^2J(C,P) = 57 Hz, *C*=S), 57.0, 51.4, 49.7, 49.3, 47.9 (d, J(C,P) = 9 Hz), 46.5, 45.1, 42.3, 41.9 (d, J(C,P) = 12 Hz), 41.5 (d, J(C,P) = 28 Hz), 39.2, 37.1 (d, J(C,P) = 19 Hz); ^{31}P NMR ($CDCl_3$): 10.6 (s with ^{195}Pt satellites, ^1J(P,Pt) = 4617 Hz), 6.9 ppm (s with ^{195}Pt satellites, ^1J(P,Pt) = 2744 Hz). MS (DEI): *m/z* (%) = 906 (9) [M$^+$], 875 (7) [(M-OMe)$^+$], 759 (12) [(M-OMe$_2$)$^+$], 701 (100) [((dpp(*o*-xyl)PtS)$^+$] (Scheme 3).

Synthesis of Thioketone Complexes **9c**

Dione **1** (200 mg, 1.14 mmol) and $((CH_3)_3Si)_2S$ **12** (80 mg, 0.45 mmol) were dissolved in CH_2Cl_2 (10 mL). After the addition of three drops of timethylsilyl triflate **13** (CF_3—SO_2—O—Si$(CH_3)_3$), the reaction mixture slowly turned red. After 1 h of additional stirring, thionation was stopped by adding 10 drops of triethylamine followed by dropwise addition of platinum complex **8**, dissolved in toluene (10 mL). After 30 min, solvents were evaporated to dryness and preliminary flash chromatography (silica gel with THF/hexane 1:1) yielded the crude product. This material was washed with diethyl ether and recrystallized from THF/pentane to yield complex **9c** as white microcrystalline solid (Scheme 4).

Complex **9c**. Yield: 43%; mp 215°C (decomp.) (colorless solid). Anal. calcd. for $C_{47}H_{40}OP_2PtS$: C, 62.04%; H, 4.43%; S, 3.39%. Found: C, 61.40%; H, 4.43%; S, 3.52%. ^{1}H NMR ($CDCl_3$): δ = 7.30–7.11 (m, 30H), 2.99 (m, 1H), 2.59 (m, 2H), 2.45 (m, 2H), 2.26 (m, 1H), 1.90 (m, 1H), 1.43 (d, ^2J(H,H) = 11 Hz, 1H, CH_aH$_b$), 0.93 (d, ^2J(H,H) = 11 Hz, 1H, CH$_a$$H_b$); ^{13}C NMR ($CDCl_3$): δ = 219.4 (C=O), 134.3 (m), 129.4 (m), 127.8 (m), 87.6 (d, ^2J(C,P) = 61 Hz, 63.8, 57.8 (d, J(C,P) = 10 Hz), 52.5, 50.0 (d, J(C,P) = 11 Hz), 49.0, 43.8, 43.5, 37.6, 35.0; ^{31}P NMR ($CDCl_3$): 26.2 (d with ^{195}Pt satellites, ^1J(P,Pt) = 4367 Hz), 24.3 ppm (d with ^{195}Pt satellites, ^1J(P,Pt) = 2906 Hz); MS (FAB in nba): *m/z* (%) = 909 (9) [M$^+$], 719 (100) [$(Ph_3P)_2Pt^+$]. IR (KBr): 3053, 2974, 2861, 1969, 1902, 1815, 1735 (C=O), 1629, 1479, 1434, 1310, 1182, 1158, 1137, 1095, 1027, 998, 965, 742, 694, 541, 520, 511 cm^{-1}.

X-Ray Data

X-ray Structure Determination of **5, 9a**, *and* **11** *[19].* The intensity data were collected on a Nonius Kappa CCD diffractometer using graphite-monochromated Mo-K$_\alpha$ radiation. Data were corrected for Lorentz polarization and for absorption effects [20–22]. Crystallographic data as well as structure solution and refinement details are summarized in Table 1.

The structure was solved by direct methods (SHELXS [23]) and refined by full-matrix least-squares techniques against $|F_o|^2$ (SHELXL-97 [24]).

The hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms except for the solvent molecules were refined anisotropically [24]. XP (Siemens Analytical X-ray Instruments, Inc.) and Ortep-3 for Windows [25] were used for structure representations.

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[19] CCDC-626630 (**5**), CCDC-626631 (**9a**), and CCDC-626632 (**11**) contain the supplementary crystallographic data excluding structure factors. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223–336-033; or deposit@ccdc.cam.ac.uk).

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