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Reaction of 3,3,5,5-Tetraphenyl-1,2,4-trithiolane with Pt^0(bisphosphane)(η^2-nbe) Complexes Bearing Bridged Bisphosphane Ligands with Various Bite Angles

Thomas Weisheit,[a] Holm Petzold,[b] Helmar Görls,[a] Grzegorz Mloston,[c] and Wolfgang Weigand*[a]

Dedicated to Professor Juzo Nakayama on the occasion of his 65th birthday

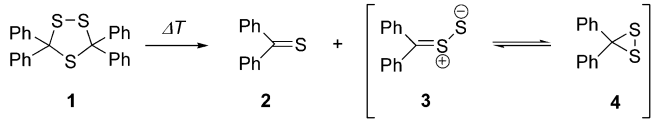
Keywords: P ligands / S ligands / Rearrangement / Thiosulfines / Platinum

A series of $Pt^0(\eta^2$-nbe) complexes [nbe = norbornene (bicyclo[2.2.1]hept-2-ene)] bearing bridged bisphosphane ligands with various bite angles (**5a–c**) was treated with 3,3,5,5-tetraphenyl-1,2,4-trithiolane (**1**) at 50 °C in a toluene solution. These reactions resulted in the formation of the appropriate dithiolato complexes **6a–c** as well as the η^2-thioketone complexes **7a–c** with respect to the $^{31}P\{^1H\}$ NMR spectroscopic data. All isolated complexes were fully characterized. Kinetic investigations using $^{31}P\{^1H\}$ NMR spectroscopy revealed first-order kinetics in **1**, pointing to the known cycloreversion of **1** as the initial and rate-determining step for these reactions. The formation of dithiolato complexes **6a–c** suggests 1,3-dipolar electrocyclization of diphenylthiosulfine (**3**) to diphenyldithiirane (**4**) in solution. On the basis of these results a plausible mechanism for the overall reaction is developed.

Introduction

Although evidence for the existence of thiosulfines was found nearly 30 years ago,[1] isolation of a stable member of this class remains a continuous challenge. Huisgen and Rapp used the thermal cycloreversion of 3,3,5,5-tetraphenyl-1,2,4-trithiolane (**1**) to generate diphenylthiosulfine (**3**) and confirmed its existence by interception reactions with diverse dipolarophiles.[2] In recent years, developments in flash vacuum pyrolysis (FVP) allowed the study of thiosulfines in an argon matrix at 10 K[3] and provided more insight into the rearrangement of thiosulfines[4] to dithiiranes or dithiocarboxylates,[3a,3c] as well as [1,4]-H shifts to form vinyl disulfanyls.[3b]

Although experimental results and theoretical calculations suggest fast electrocyclization of thiosulfines to dithiiranes[5] (Scheme 1), there still is a lack of evidence for this reaction at ambient temperature in solution. Nearly 15 years ago, Ishii et al. prepared the first stable and isolable dithiirane 1-oxide as well as the corresponding dithiirane.[6] Interestingly, it is still an open question if these dithiiranes undergo thermal ring opening to thiosulfines, because interception with dipolarophiles failed.[6a]



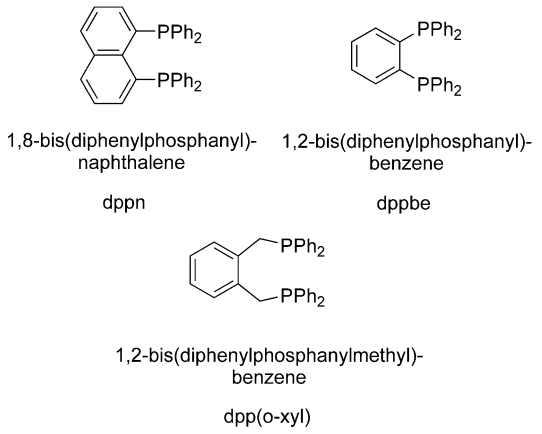
Scheme 1. Thermal cycloreversion of **1** and the proposed equilibrium between diphenylthiosulfine (**3**) and diphenyldithiirane (**4**).

The best proof for the presence of dithiiranes as reactive intermediates is the interception with the $Pt^0(PPh_3)_2$ complex fragment to form stable dithiolato complexes.[5b,6e,6f,7] In contrast, the oxidative addition of the $Pt^0(PPh_3)_2$ complex fragment into the sulfur–sulfur bond of 1,2,4-trithiolanes does not allow the generation of thiosulfines by cycloreversion from this common type of precursor molecule.[7a,8] In this context, a mechanism of the formation of the dithiolato complex $Pt^{II}(PPh_3)_2(S_2CPh_2)$ as well as the η^2-thioketone complex $Pt^0(PPh_3)_2(\eta^2$-S=$CPh_2)$ by reaction of $Pt^0(PPh_3)_2(\eta^2$-$C_2H_4)$ with **1** was proposed. After addition of the Pt^0 complex fragment to the sulfur–sulfur bond, thiobenzophenone (**2**) is eliminated, which subsequently reacts with the excess amount of $Pt^0(PPh_3)_2(\eta^2$-$C_2H_4)$ present in the reaction mixture.[8a]

[a] Institut für Anorganische und Analytische Chemie, Friedrich-Schiller-Universität,
07743 Jena, Germany
Fax: +49-3641-948102
E-mail: wolfgang.weigand@uni-jena.de
[b] TU Chemnitz, Institut für Chemie,
Straße der Nationen 62, 09111 Chemnitz, Germany
[c] University of Łódź, Department of Organic and Applied Chemistry,
Narutowicza 68, 90-136 Łódź, Poland

However, recently we showed that upon formal replacement of the PPh_3 ligands by bridged bisphosphanes, especially those exhibiting a small bite angle at the metal center, attack of the platinum complex fragment along the disulfide bond of tetrasubstituted 1,2,4-trithiolanes is hindered.[9] Therefore, treatment of 1,2,4-trithiolanes with this type of Pt^0(bisphosphane) complex fragment should allow investigations of their thermal cycloreversion in solution at ambient or even elevated temperatures.

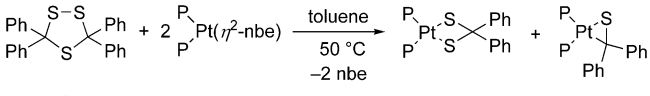
Here we report on the reaction of 3,3,5,5-tetraphenyl-1,2,4-trithiolane (**1**) with a series of Pt^0(bisphosphane)(η^2-nbe) complexes bearing bisphosphane ligands with various bite angles (Scheme 2).



Scheme 2. Nomenclature of the bidentate phosphanes used within this contribution.

Results and Discussion

Despite the high stability of the Pt^0(bisphosphane)(η^2-nbe) complexes, as a result of the relatively small bite angles of the bisphosphanes[10] and the steric shielding of the sulfur–sulfur bond in **1** they smoothly react in a toluene solution above 35 °C. Decolorization of the solutions to pale yellow as well as the precipitation of a yellow solid indicates the consumption of the Pt^0 starting material and formation of new complexes. The typical $^1J_{P,Pt}$ values found in the $^{31}P\{^1H\}$ NMR spectra point to the formation of a 1:1 mixture of the appropriate dithiolato complex **6** and η^2-thioketone complex **7** (Scheme 3).



Scheme 3. Formation of dithiolato complexes **6a**–**c** and η^2-thioketone complexes **7a**–**c** [**a**: P = 1/2 dppn; **b**: P = 1/2 dppbe; **c**: P = 1/2 dpp(o-xyl)].

In order to get pure samples of dithiolato complexes **6a**–**c**, a solution of the corresponding complex **5** and **1** in toluene was stirred for 3 h at 50 °C, and the solvents were then evaporated to dryness. The residues were washed with diethyl ether and dissolved in thf. Pure dithiolato complexes **6a**–**c** were obtained as yellow crystals by slow diffusion of pentane into these solutions. The molecular structures of **6b** and **6c** were confirmed by X-ray structure determination (Figures 1 and 2, respectively). Both complexes exhibit a distorted square-planar geometry. The found bond lengths and angles are comparable to those reported for similar dithiolato complexes.[5b,7a]

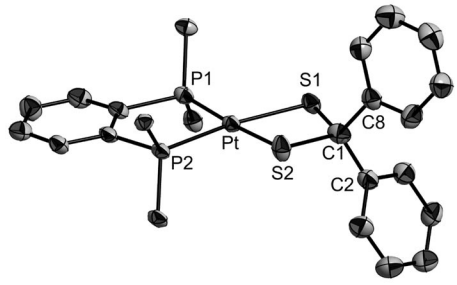


Figure 1. Molecular structure of **6b** at 50% probability level. Hydrogen atoms and solvent molecules have been omitted for clarity. The phenyl groups of the dppbe ligand are represented by their *ipso*-carbon atoms. Selected bond lengths [Å] and angles [°]: Pt–P1 2.257(2), Pt–P2 2.2323(19), Pt–S1 2.324(2), Pt–S2 2.318(2), S1–C1 1.872(9), S2–C1 1.865(8), P1–Pt–P2 87.12(8), S1–Pt–S2 75.86(8), P1–Pt–S1 102.56(8), P2–Pt–S2 94.57(8), S1–C1–S2 99.6(4).

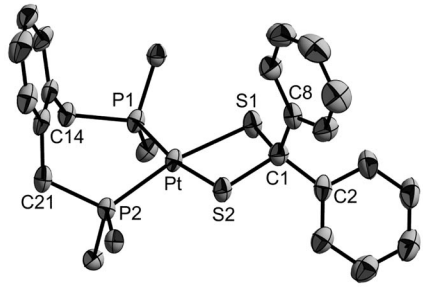
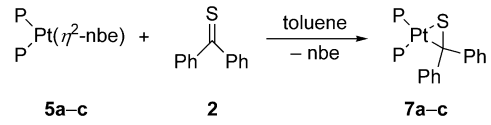


Figure 2. Molecular structure of **6c** at 50% probability level. Hydrogen atoms and solvent molecules have been omitted for clarity. The phenyl groups of the dpp(o-xyl) ligand are represented by their *ipso*-carbon atoms. Selected bond lengths [Å] and angles [°]: Pt–P1 2.2624(12), Pt–P2 2.2613(13), Pt–S1 2.3173(13), Pt–S2 2.3149(12), C1–S1 1.856(5), C1–S2 1.856(5), P1–Pt–P2 95.42(5), S1–Pt–S2 75.99(4), P1–Pt–S1 95.09(5), P2–Pt–S2 93.82(5), S1–C1–S2 100.4(2).

The $^{31}P\{^1H\}$ NMR spectra of **6a**–**c** show a singlet along with ^{195}Pt satellites, which confirms the symmetrical conformation of these complexes in solution. The value of $^1J_{P,Pt}$ increases with the P–Pt–P angle. Whereas complex **6a** exhibits a $^1J_{P,Pt}$ coupling constant of 2666 Hz, the value increases to 2847 and 2931 Hz for **6b** and **6c**, respectively. These values are in good agreement with the corresponding P–Pt–P angle, enlarged from 87.12(8)° for **6b** to 95.42(5)° for **6c**. A similar correlation concerning the $^1J_{P,Pt}$ values was already reported for the corresponding Pt^0(bisphosphane)(η^2-nbe) complexes.[9]

In order to prove the formation of complexes **7a**–**c** in the reaction of **5a**–**c** with **1**, authentic samples of **7a**–**c** were synthesized independently from thiobenzophenone **2** and **5a**–**c** (Scheme 4).



Scheme 4. Syntheses of η^2-thioketone complexes **7a**–**c** [**a**: P = 1/2 dppn; **b**: P = 1/2 dppbe; **c**: P = 1/2 dpp(o-xyl)].

Diffusion of pentane into thf solutions of **7b** and **7c** yielded crystals suitable for X-ray structure determination. The constitution and purity of **7a**–**c** were confirmed by the molecular peaks in the mass spectra as well as the correct elemental analysis. The molecular structures of **7b** and **7c** are presented in Figures 3 and 4, respectively. For both complexes the arrangement of the ligands around the platinum center is distorted square planar. The nonequivalent Pt–P bond lengths in **7b** and **7c** can be explained by the different *trans* influence of the sulfur and the carbon atom, respectively, as reported for similar structures.[5b,7a,8b] The side-on coordination of **2** to the Pt^0(bisphosphane) moiety is clearly visible. By virtue of π back donation, the C1–S bonds are elongated in comparison to a uncoordinated thiobenzophenone (**2**), exhibiting a sulfur–carbon bond length of 1.64 Å.[11] In the $^{13}C\{^1H\}$ NMR spectra of **7a**–**c** the signal of the C=S group is remarkably shifted upfield (81–86 ppm) relative to that of free **2** (δ = 238.5 ppm).[12] These large shifts as well as the determined Pt–S, Pt–C1 and C1–S bond lengths identify complexes **7a**–**c** as platina–thiirane cycles rather than classical π complexes. The $^{31}P\{^1H\}$ NMR spectra of **7a**–**c** reveal a typical AB spin system pattern (two doublets with appropriate ^{195}Pt satellites) according to the unsymmetrical conformation of these complexes. As a result of the different *trans* influence of the sulfur and the carbon atom, the two coupling constants are conspicuously different. Again, there is an obvious trend in the $^1J_{P,Pt}$ coupling constants. The values of both $^1J_{P,Pt}$ increase with the bite angle P–Pt–P [for **7b**: P–Pt–P 87.35(7)°, $^1J_{P,Pt}$ = 2909/4070 Hz; for **7c**: P–Pt–P 102.58(5)°, $^1J_{P,Pt}$ = 3062/4333 Hz].

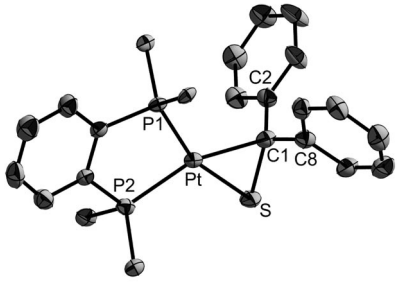


Figure 3. Molecular structure of **7b** at 50% probability level. Hydrogen atoms and solvent molecules have been omitted for clarity. The phenyl groups of the dppbe ligand are represented by their *ipso*-carbon atoms. Selected bond lengths [Å] and angles [°]: Pt–P1 2.2492(18), Pt–P2 2.260(2), Pt–S 2.295(2), Pt–C1 2.156(7), C1–S 1.815(11), P1–Pt–P2 87.34(7), S–Pt–C1 48.0(3), P1–Pt–C1 113.2(3), P2–Pt–S 111.36(7), C2–C1–C8 116.4(7).

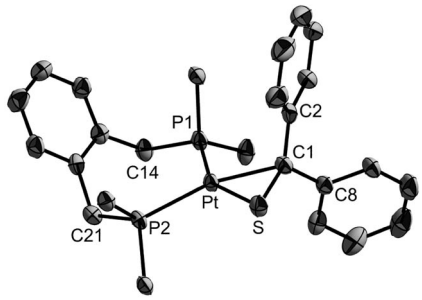


Figure 4. Molecular structure of **7c** at 50% probability level. Hydrogen atoms and solvent molecules have been omitted for clarity. The phenyl groups of the dpp(o-xyl) ligand are represented by their *ipso*-carbon atoms. Selected bond lengths [Å] and angles [°]: Pt–P1 2.2475(13), Pt–P2 2.2733(11), Pt–S 2.2990(14), Pt–C1 2.157(5), C1–S 1.787(5), P1–Pt–P2 102.58(5), S–Pt–C1 47.14(14), P1–Pt–C1 104.07(14), P2–Pt–S 106.21(5), C2–C1–C8 115.4(4).

On the one hand, the formation of complexes **6** and **7** could be reasonably explained by insertion of the Pt^0 complex fragment into the sulfur–sulfur bond of **1** followed by expulsion of thiobenzophenone.[8a,8c] On the other hand, however, the failed reaction of **5a** with spirocyclohexyl-1,2,4-trithiolane[9] suggests a different mechanism for the reaction of Pt^0 complexes bearing bisphosphanes with small bite angles with 1,2,4-trithiolanes.

In order to gain more information on the reaction rate and reaction order, we performed kinetic measurements by using $^{31}P\{^1H\}$ NMR spectroscopy. In a first experiment, we focused on Pt^0(bisphosphane)(η^2-nbe) complex **5a** and investigated the influence of the molar ratios on the rate constant of its reaction with **1** (Table 1, Runs 1–3). The observed rate constants of the consumption of **1** and **5a** as well as the corresponding molar concentration of **1** and **5a** are summarized in Table 1.

Table 1. Parameters concerning the kinetic measurements and the observed rate constants for the reactions of **5a**–**c** with **1**.

Run	Pt^0	$[P_2Pt(\eta^2$-nbe)][a]	[**1**][a]	k_{obs} (Pt^0)[b]	k_{obs} (**1**)[c]
1	**5a**	2.81×10^{-2}	1.42×10^{-2}	1.68×10^{-3}	1.72×10^{-3}
2	**5a**	2.80×10^{-2}	2.80×10^{-2}	3.26×10^{-3}	1.34×10^{-3}
3	**5a**	2.81×10^{-2}	5.59×10^{-2}	6.97×10^{-3}	1.27×10^{-3}
4	**5b**	2.80×10^{-2}	1.40×10^{-2}	2.05×10^{-3}	2.01×10^{-3}
5	**5c**	2.80×10^{-2}	1.43×10^{-2}	1.63×10^{-3}	1.61×10^{-3}

[a] Initial concentrations are given in mol L^{-1}. [b] Rate constants [s^{-1}] based on the consumption of **5a**–**c** were calculated by using the concentration of **5a**–**c** obtained by $^{31}P\{^1H\}$ NMR spectroscopy. [c] Rate constants [s^{-1}] based on the consumption of **1** were determined by using the concentration of **1** calculated with Equation (1).

In order to ensure a good signal-to-noise ratio and a maintainable accumulation recording time of the $^{31}P\{^1H\}$ NMR spectra, the concentration of **5a**–**c** had approximately the same value for each run.

The obtained results showed that the rate of consumption of **5a** is linearly dependent on the concentration of **1** when using the same initial concentration of **5a** in each

case. No other signals than that due to **5a**, **6a**, and **7a** were detected in the $^{31}P\{^{1}H\}$ NMR spectra; **6a** and **7a** were found to be formed side by side in a constant ratio of 1:1 during the course of the experiment. An appropriate plot of the natural logarithm of the relative concentration of **1**, calculated on the basis of the concentration of **5a** [Equation (1)], over time gave nearly linear slopes (Figure 5) and comparable rate constants.

$$[\mathbf{1}]_t = [\mathbf{1}]_0 - 1/2\cdot([\mathbf{5}]_0 - [\mathbf{5}]_t) \quad (1)$$

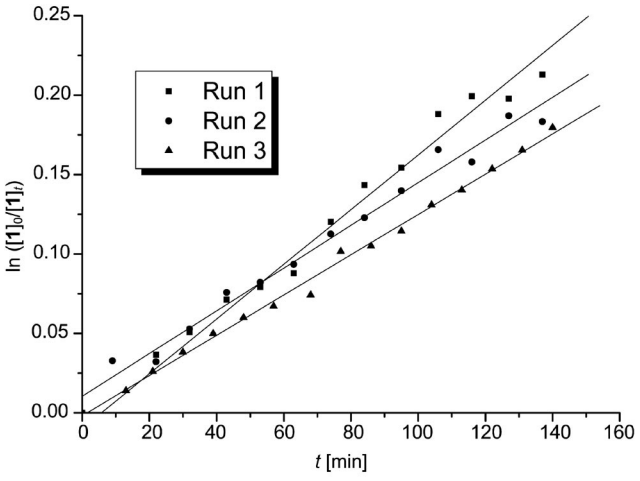


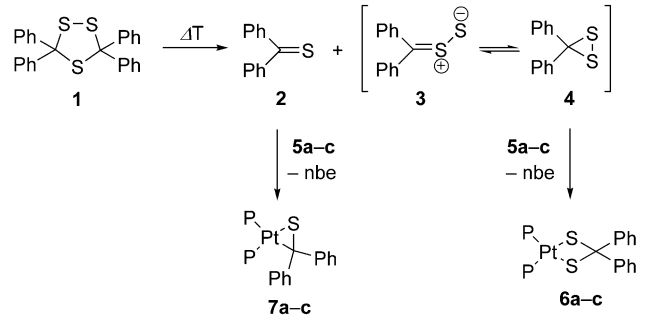
Figure 5. Plot of the natural logarithm of the relative concentration of **1** vs. the time followed by a linear regression of each data set in order to calculate the rate constants based on the concentration of **1**.

These data agree well with first-order kinetics in **1**; hence, the cycloreversion of **1** is the initial and rate-determining step of the overall reaction. As a consequence, the reaction rate should be independent of the nature of the Pt^0 complex **5** as well as its concentration, because **5** only serves as trapping agent and is not involved in the rate-determining step. Indeed, reaction rate constants determined for the reactions of **1** with **5b** and **5c** are approximately the same with respect to the rather rough method with relatively large error (Table 1, Runs 4 and 5).

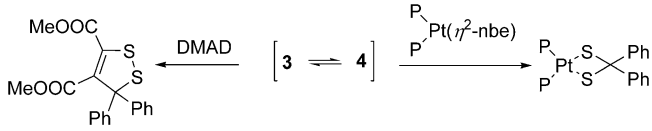
These results allow one to formulate a new reaction mechanism (Scheme 5) in which the first step is the cycloreversion of 1,2,4-trithiolane (**1**) into thiobenzophenone (**2**) and diphenylthiosulfine (**3**). The latter rearranges to diphenyldithiirane (**4**), which reacts with **5** by insertion into the sulfur–sulfur bond.

Taking into account that **3** was successfully trapped by Huisgen and Rapp in a similar reaction with DMAD (dimethyl acetylenedicarboxylate),[2] it is very likely that **3** exists in an equilibrium with **4** (Scheme 6).

As **4** is more stable then **3**, **4** is probably the major component of that equilibrium system. However, diphenyldithiirane (**4**) is unreactive towards DMAD, and for this reason diphenylthiosulfine (**3**) is selectively trapped with DMAD.



Scheme 5. Postulated mechanism of the formation of dithiolato complexes **6** and η^2-thioketone complexes **7** in the reaction of **1** with **5a**–**c** [a: P = 1/2 dppn; b: P = 1/2 dppbe; c: P = 1/2 dpp-(o-xyl)].



Scheme 6. Comparison of the trapping reactions of diphenylthiosulfine (**3**) and diphenyldithiirane (**4**) with DMAD and a (bisphosphane)Pt^0 complex fragment, respectively.

Conclusions

In summary, the current study shows that 3,3,5,5-tetraphenyl-1,2,4-trithiolane (**1**) is reactive towards Pt^0 complex fragments containing bridged bisphosphane ligands at elevated temperatures, yielding equimolar amounts of dithiolato complexes of type **6** and η^2-thioketone complexes of type **7**. The appropriate Pt^0(bisphosphane)(η^2-nbe) complexes turned out to be a very efficient source of the requested Pt^0 moiety. By means of kinetic measurements based on $^{31}P\{^{1}H\}$ NMR spectroscopy, the initial step of these reactions was determined to be the thermal cycloreversion of **1**. Thus, a convincing reaction mechanism could be formulated (Scheme 5). This, as well as the isolation of the corresponding interception products, should verify the pathway of the cleavage of **1** into a thioketone and the corresponding thiosulfine. Furthermore the formation of dithiolato complexes **6** confirms the proposed rearrangement of the in situ generated thiosulfine into the appropriate dithiirane and gives unambiguous evidence for an equilibrium between thiosulfine **3** and dithiirane **4** in solutions at room temperature.

Experimental Section

General Procedures: Unless otherwise stated, all reactions were carried out under an atmosphere of argon by using standard Schlenk techniques. Used solvents were distilled from sodium and benzophenone prior use. Thiobenzophenone (**2**),[13] 3,3,5,5-tetraphenyl-1,2,4-trithiolane (**1**),[2b] and **5a**–**c**[9] were prepared according to literature procedures. ^{1}H, $^{13}C\{^{1}H\}$, and $^{31}P\{^{1}H\}$ NMR spectra were recorded with Bruker Avance 400 or Bruker Avance 200 spectrometers at 27 °C. ^{1}H NMR spectra were calibrated by using the signal of the residual non-deuterated solvent, whereas $^{13}C\{^{1}H\}$ NMR

spectra were measured by using the signal of the solvent as internal standard. $^{31}P\{^1H\}$ NMR spectra were determined by using 85% H_3PO_4 as external standard. Assignments of the ^1H and $^{13}C\{^1H\}$ NMR signals were confirmed by two-dimensional NMR methods (^1H–^1H COSY, ^1H–^{13}C HSQC, and ^1H–^{13}C HMBC NMR). Infrared spectra were taken with a Perkin–Elmer System 2000 FTIR spectrometer. Mass spectra were obtained by using a Finnigan Mat SSQ 710 mass spectrometer. Elemental analyses were performed with a Vario EL III CHNS (Elementaranalysen GmbH Hanau) as single determinations. Melting points were determined with an Axiolab microscope with a TMHS 600 heating plate and are uncorrected.

General Procedure for the Syntheses of Pt^0(bisphosphane)(η^2-thiobenzophenone) Complexes (7a–c): The appropriate Pt^0(bisphosphane)(η^2-nbe) complex **5** (1 equiv.) was dissolved in toluene (15 mL) and **2** (1.1 equiv.) dissolved in toluene (5 mL) was added dropwise with stirring. The color of the red (**5a**) or yellow (**5b**, **5c**) solution rapidly turned light green. The resulting solution was stirred for an additional 3 h. The solvent was removed in vacuo, and the residue was washed several times with diethyl ether to give the thioketone complexes in satisfying purity.

7a: Compound **5a** (109 mg, 0.139 mmol) was treated with **2** (31 mg, 0.156 mmol) to give **7a** (80 mg, 0.090 mmol, 65%) as a yellow solid. M.p. 280 °C (decomp.). ^1H NMR (400 MHz, CD_2Cl_2, 27 °C): δ = 8.12 (m, 2 H, 4-H and 5-H of dppn), 7.50–7.40 (m, 4 H, 2-H, 3-H, 6-H, and 7-H of dppn), 7.24–7.12 [m, 14 H, *o*-C_6H_5, *m*-C_6H_5, and *p*-C_6H_5 of dppn and *m*-C_6H_5 of S=C(Ph)$_2$], 7.08 (m, 2 H, *p*-C_6H_5 of dppn), 7.00 [t, $^3J_{H,H}$ = 7.6 Hz, 4 H, *o*-C_6H_5 of S=C(Ph)$_2$], 6.93 [m, 4 H, *p*-C_6H_5 of S=C(Ph)$_2$], 6.81 (m, 4 H, *m*-C_6H_5 of dppn), 6.50 (m, 4 H, *o*-C_6H_5 of dppn) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2, 27 °C): δ = 150.7 [m, *ipso*-C_6H_5 of S=C(Ph)$_2$], 137.5 (m, *C*-1 and *C*-8 of dppn), 134.5–134.0 (m, *C*-8a and *o*-C_6H_5 of dppn), 133.7–133.4 (m, *C*-4, *C*-5, and *o*-C_6H_5 of dppn), 130.3 (s, *p*-C_6H_5 of dppn), 133.0 (m, *ipso*-C_6H_5 of dppn), 130.0–129.8 [m, *p*-C_6H_5 of dppn and *m*-C_6H_5 of S=C(Ph)$_2$], 128.5 (m, *m*-C_6H_5 of dppn), 127.8 (m, *m*-C_6H_5 of dppn), 127.0 [s, *o*-C_6H_5 of S=C(Ph)$_2$], 125.7 (m, *C*-2, *C*-3, *C*-6, *C*-7, and *C*-4a of dppn), 124.0 [s, *p*-C_6H_5 of S=C(Ph)$_2$], 82.8 [s, S=*C*(Ph)$_2$] ppm. $^{31}P\{^1H\}$ NMR (81 MHz, C_6D_6, 27 °C): δ = 12.7 (d with ^{195}Pt satellites, $^1J_{P,Pt}$ = 2739 Hz, $^2J_{P,P}$ = 22.4 Hz), 10.3 (d with ^{195}Pt satellites, $^1J_{P,Pt}$ = 3900 Hz, $^2J_{P,P}$ = 22.4 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 3052 (m), 1625 (m), 1588 (m), 1482 (s), 1435 (vs), 1095 (s), 770 (s), 745 (s), 694 (vs), 590 (vs), 523 (vs), 499 (vs) cm^{-1}. MS (DEI): *m*/*z* = 890 [M]$^+$, 692 [(dppn)Pt]$^+$. $C_{47}H_{36}P_2PtS$ (889.88): calcd. C 63.44, H 4.08, S 3.60; found C 64.17, H 3.55, S 3.57.

7b: Compound **5b** (140 mg, 0.190 mmol) was treated with **2** (41 mg, 0.207 mmol) to give **7b** (110 mg, 0.131 mmol, 69%) as yellow solid. M.p. 160 °C (decomp.). ^1H NMR (400 MHz, CD_2Cl_2, 27 °C): δ = 7.75 (m, 2 H, *o*-C_6H_4 of dppbe), 7.64 (m, 4 H, *o*-C_6H_5 of dppbe), 7.48 (m, 2 H, *m*-C_6H_4 of dppbe), 7.41 (m, 6 H, *m*-C_6H_5 and *p*-C_6H_5 of dppbe), 7.29–7.12 [m, 14 H, *m*-C_6H_5 and *o*-C_6H_5 of dppbe and *m*-C_6H_5 of S=C(Ph)$_2$], 6.86 [m, 6 H, *o*-C_6H_5 and *p*-C_6H_5 of S=C(Ph)$_2$] ppm. $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2, 27 °C): δ = 151.0 [m, *ipso*-C_6H_5 of S=C(Ph)$_2$], 146.5 (m, *ipso*-C_6H_4 of dppbe), 133.6–133.1 (m, *m*-C_6H_4, *o*-C_6H_5 and *ipso*-C_6H_5 of dppbe), 131.9–131.5 (m, *o*-C_6H_4 of dppbe), 130.8 (s, *p*-C_6H_5 of dppbe), 130.2 (m, *m*-C_6H_5 of dppbe), 129.0 (m, *m*-C_6H_5 of dppbe), 128.6 [m, *o*-C_6H_5 or *m*-C_6H_5 of S=C(Ph)$_2$], 127.7 [s, *o*-C_6H_5 or *m*-C_6H_5 of S=C(Ph)$_2$], 124.1 [s, *p*-C_6H_5 of S=C(Ph)$_2$], 80.8 [s, S=*C*(Ph)$_2$] ppm. $^{31}P\{^1H\}$ NMR (81 MHz, C_6D_6, 27 °C): δ = 49.7 (d with ^{195}Pt satellites, $^1J_{P,Pt}$ = 2909 Hz, $^2J_{P,P}$ = 27.6 Hz), 42.4 (d with ^{195}Pt satellites, $^1J_{P,Pt}$ = 4070 Hz, $^2J_{P,P}$ = 27.6 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 3052 (m), 1637 (m), 1587 (m), 1483 (s), 1435 (s), 1099 (s), 746 (m), 694 (vs), 553 (vs), 529 (vs), 506 (s) cm^{-1}. MS (DEI): *m*/*z* = 839 [M]$^+$, 641 [(dppbe)Pt]$^+$, 563 [(dppbe)Pt – Ph]$^+$, 485 [(dppbe)Pt – 2Ph]$^+$. $C_{43}H_{34}P_2PtS$·0.33toluene (870.54): calcd. C 62.55, H 4.25, S 3.68; found C 62.27, H 3.95, S 3.69.

7c: Compound **5c** (121 mg, 0.158 mmol) was treated with **2** (34 mg, 0.171 mmol) to give **7c** (65 mg, 0.075 mmol, 47%) as a pale yellow solid. M.p. 145 °C. ^1H NMR (400 MHz, CD_2Cl_2, 27 °C): δ = 7.78 [m, 4 H, *o*-C_6H_5 of dpp(o-xyl)], 7.44 [m, 6 H, *m*-C_6H_5 and *p*-C_6H_5 of dpp(o-xyl)], 7.24 [m, 2 H, *p*-C_6H_5 of dpp(o-xyl)], 7.16 [m, 4 H, *o*-C_6H_5 of dpp(o-xyl)], 7.06 [m, 4 H, *m*-C_6H_5 of dpp(o-xyl)], 6.97 [m, 4 H, *m*-C_6H_5 of S=C(Ph)$_2$], 6.82 [m, 2 H, *m*-C_6H_4 of dpp-(o-xyl)], 6.77 [m, 6 H, *o*-C_6H_5 and *p*-C_6H_5 of S=C(Ph)$_2$], 6.34 [m, 1 H, *o*-C_6H_4 of dpp(o-xyl)], 6.26 [m, 1 H, *o*-C_6H_4 of dpp(o-xyl)], 4.02 (m, 4 H, PC*H*$_2$) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2, 27 °C): δ = 149.7 [m, *ipso*-C_6H_5 of S=C(Ph)$_2$], 135.3 [m, *ipso*-C_6H_5 of dpp(o-xyl)] 133.9–133.0 [m, *ipso*-C_6H_5, *o*-C_6H_5 and *ipso*-C_6H_4 of dpp(o-xyl)], 131.2 [m, *o*-C_6H_4 of dpp(o-xyl)], 130.6 [s, *p*-C_6H_5 of dpp(o-xyl)], 129.9 [m, *p*-C_6H_5 of dpp(o-xyl) and *m*-C_6H_5 of S=C(Ph)$_2$], 128.7–128.1 [m, *m*-C_6H_5 of dpp(o-xyl)], 126.8 [m, *m*-C_6H_4 of dpp(o-xyl) and *o*-C_6H_5 of S=C(Ph)$_2$], 124.1 [s, *p*-C_6H_5 of S=C(Ph)$_2$], 85.7 [s, S=*C*(Ph)$_2$], 40.1–36.9 (m, P*C*H$_2$) ppm. $^{31}P\{^1H\}$ NMR (81 MHz, C_6D_6, 27 °C): δ = 10.4 (d with ^{195}Pt satellites, $^1J_{P,Pt}$ = 4333 Hz, $^2J_{P,P}$ = 4.3 Hz), 8.7 (d with ^{195}Pt satellites, $^1J_{P,Pt}$ = 3062 Hz, $^2J_{P,P}$ = 4.3 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 3052 (m), 1625 (m), 1588 (m), 1483 (s), 1435 (vs), 1099 (s), 769 (s), 742 (s), 695 (vs), 505 (vs) cm^{-1}. MS (DEI): *m*/*z* = 867 [M]$^+$, 669 [{dpp(o-xyl)}Pt]$^+$, 588 [{dpp(o-xyl)}Pt – Ph]$^+$, 512 [{dpp(o-xyl)}Pt – 2Ph]$^+$, 434 [{dpp(o-xyl)}Pt – 3Ph]$^+$. $C_{45}H_{38}P_2PtS$ (867.87): calcd. C 62.28, H 4.41, S 3.69; found C 62.41, H 3.98, S 3.38.

General Procedure for the Syntheses of Pt^{II}(bisphosphane)(diphenylmethanedithiolato) Complexes (6a–c): The appropriate Pt^0(bisphosphane)(η^2-nbe) complex **5** (1 equiv.) was dissolved in toluene (30 mL) and **1** was added stoichiometrically. The solution was stirred for 3 h at 50 °C. After cooling, the solvent was removed in vacuo and a green-blue mixture consisting of thioketone complex, dithiolato complex, and **2** was obtained. After several washings with diethyl ether the yellow solid was dissolved in a small amount of thf. Pentane was allowed to diffuse into the solution to give yellow crystals. After two additional crystallization steps pure dithiolato complexes were obtained.

6a: Compound **5a** (147 mg, 0.187 mmol) was treated with **1** (80 mg, 0.187 mmol) to give **6a** (30 mg, 0.033 mmol, 18%) as pale yellow needles. M.p. 280 °C (decomp.). ^1H NMR (400 MHz, CD_2Cl_2, 27 °C): δ = 8.18 (m, 2 H, 4-H and 5-H of dppn), 7.62 [m, 4 H, *o*-C_6H_5 of $S_2C(Ph)_2$], 7.49 (m, 2 H, 3-H and 6-H of dppn), 7.43 (m, 2 H, 2-H and 7-H of dppn), 7.32–7.16 [*m*, 24 H, *o*-C_6H_5, *m*-C_6H_5, and *p*-C_6H_5 of dppn and *m*-C_6H_5 of $S_2C(Ph)_2$], 7.09 [m, 2 H, *p*-C_6H_5 of $S_2C(Ph)_2$] ppm. $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2, 27 °C): δ = 155.6 [m, *ipso*-C_6H_5 of $S_2C(Ph)_2$], 138.9 (m, *C*-8a of dppn), 137.6 (m, *C*-2 and *C*-7 of dppn), 135.8 (m, *C*-1 and *C*-8 of dppn), 134.3 (m, *C*-4 and *C*-5 of dppn), 134.1 (t, $^2J_{C,P}$ = 5.7 Hz, *o*-C_6H_5 of dppn), 130.9 (s, *p*-C_6H_5 of dppn), 129.9 (m, *ipso*-C_6H_5 of dppn), 128.4 (t, $^3J_{C,P}$ = 5.6 Hz, *m*-C_6H_5 of dppn), 127.3 [s, *m*-C_6H_5 of $S_2C(Ph)_2$], 126.8 [s, *o*-C_6H_5 of $S_2C(Ph)_2$], 125.8 (m, *C*-3 and *C*-6 of dppn), 125.5 [s, *p*-C_6H_5 of $S_2C(Ph)_2$], 121.7 (m, *C*-4a of dppn), 73.8 [m, $S_2C(Ph)_2$] ppm. $^{31}P\{^1H\}$ NMR (81 MHz, C_6D_6, 27 °C): δ = 13.4 (s with ^{195}Pt satellites, $^1J_{P,Pt}$ = 2666 Hz, P_2PtS_2) ppm. IR (KBr): $\tilde{\nu}$ = 3053 (m), 1625 (m), 1482 (m), 1436 (s), 1096 (s), 771 (m), 744 (m), 693 (vs), 592 (vs), 527 (vs), 503 (vs) cm^{-1}. MS (DEI): *m*/*z* = 922 [M]$^+$, 755 [(dppn)PtS_2]$^+$, 723 [(dppn)PtS]$^+$, 645 [(dppn)PtS – Ph]$^+$, 535 [(dppn)Pt – 2Ph]$^+$, 459 [(dppn)Pt – 3Ph]$^+$, 427 [M –

(dppn)]$^+$. $C_{47}H_{36}P_2PtS_2$ (921.94): calcd. C 61.23, H 3.94, S 6.96; found C 61.05, H 3.81, S 6.75.

6b: Compound **5b** (140 mg, 0.190 mmol) was treated with **1** (80 mg, 0.187 mmol) to give **6b** (30 mg, 0.035 mmol, 18%) as yellow crystals. M.p. 238 °C (decomp.). ^{1}H NMR (400 MHz, CD_2Cl_2, 27 °C): δ = 7.71 (m, 2 H, *o*-C_6H_4 of dppbe), 7.68–7.63 [m, 12 H, *o*-C_6H_5 of dppbe and *o*-C_6H_5 of $S_2C(Ph)_2$], 7.56 (m, 2 H, *m*-C_6H_4 of dppbe), 7.48–7.39 (m, 12 H, *m*-C_6H_5 and *p*-C_6H_5 of dppbe), 7.17 [m, 4 H, *m*-C_6H_5 of $S_2C(Ph)_2$], 7.07 [m, 2 H, *p*-C_6H_5 of $S_2C(Ph)_2$] ppm. ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2, 27 °C): δ = 155.5 [s, *ipso*-C_6H_5 of $S_2C(Ph)_2$], 142.5 (m, *ipso*-C_6H_4 of dppbe), 134.0 (m, *o*-C_6H_4 of dppbe), 133.6 (t, $^2J_{C,P}$ = 6.0 Hz, *o*-C_6H_5 of dppbe), 132.4 (m, *m*-C_6H_4 of dppbe), 131.5 (s, *p*-C_6H_5 of dppbe), 130.5 (m, *ipso*-C_6H_5 of dppbe), 129.0 (t, $^3J_{C,P}$ = 5.6 Hz, *m*-C_6H_5 of dppbe), 127.3 [s, *m*-C_6H_5 of $S_2C(Ph)_2$], 126.5 [s, *o*-C_6H_5 of $S_2C(Ph)_2$], 125.6 [s, *p*-C_6H_5 of $S_2C(Ph)_2$], 77.8 [s, $S_2C(Ph)_2$] ppm. ^{31}P{^{1}H} NMR (81 MHz, C_6D_6, 27 °C): δ = 44.1 (s with ^{195}Pt satellites, $^1J_{P,Pt}$ = 2847 Hz, P_2PtS_2) ppm. IR (KBr): $\tilde{\nu}$ = 3052 (m), 1636 (m), 1482 (m), 1435 (s), 1099 (s), 748 (m), 694 (vs), 672 (m), 559 (vs), 533 (vs), 505 (s) cm^{-1}. MS (DEI): *m*/*z* = 871 [M]$^+$, 838 [M – S]$^+$, 705 [(dppbe)PtS_2]$^+$, 673 [(dppbe)PtS]$^+$, 563 [(dppbe)Pt – Ph]$^+$, 486 [(dppbe)Pt – 2Ph]$^+$. $C_{43}H_{34}P_2PtS_2$ (871.90): calcd. C 59.23, H 3.93, S 7.36; found C 59.12, H 4.43, S 6.83.

6c: Compound **5c** (146 mg, 0.191 mmol) was treated with **1** (84 mg, 0.196 mmol) to give **6c** (45 mg, 0.050 mmol, 26%) as yellow crystals. M.p. 271 °C. ^{1}H NMR (400 MHz, CD_2Cl_2, 27 °C): δ = 7.72 [m, 8 H, *o*-C_6H_5 of dpp(o-xyl)], 7.49–7.38 [m, 16 H, *m*-C_6H_5 and *p*-C_6H_5 of dpp(o-xyl) and *o*-C_6H_5 of $S_2C(Ph)_2$], 7.11 [m, 4 H, *m*-C_6H_5 of $S_2C(Ph)_2$], 7.06 [m, 4 H, *m*-C_6H_4 of dpp(o-xyl) and *p*-C_6H_5 of $S_2C(Ph)_2$], 6.57 [m, 2 H, *o*-C_6H_4 of dpp(o-xyl)], 3.94 (m, 4 H, PCH_2) ppm. ^{13}C{^{1}H} NMR (50 MHz, CD_2Cl_2, 27 °C): δ = 155.4 [s, *ipso*-C_6H_5 of $S_2C(Ph)_2$], 134.1 [t, $^2J_{C,P}$ = 5.3 Hz, *o*-C_6H_5 of dpp(o-xyl)], 133.5 [s, *ipso*-C_6H_4 of dpp(o-xyl)], 132.0 [m, *ipso*-C_6H_5 of dpp(o-xyl)], 131.5 (s, *o*-C_6H_4 of dppbe), 131.2 [s, *p*-C_6H_5 of dpp(o-xyl)], 128.4 [t, $^3J_{C,P}$ = 5.2 Hz, *m*-C_6H_5 of dpp(o-xyl)], 127.6 [s, *m*-C_6H_4 of dpp(o-xyl)], 127.3 [s, *m*-C_6H_5 of $S_2C(Ph)_2$], 126.6 [s, *o*-C_6H_5 of $S_2C(Ph)_2$], 125.5 [s, *p*-C_6H_5 of $S_2C(Ph)_2$], 75.5 [m, $S_2C(Ph)_2$], 36.6 (m, PCH_2) ppm. ^{31}P{^{1}H} NMR (81 MHz, C_6D_6, 27 °C): δ = 5.1 (s with ^{195}Pt satellites, $^1J_{P,Pt}$ = 2931 Hz, P_2PtS_2) ppm. IR (KBr): $\tilde{\nu}$ = 3053 (m), 1618 (w), 1591 (w), 1483 (s), 1435 (vs), 1310 (w), 1184 (w), 1099 (s), 1073 (w), 1029 (w), 865 (m), 836 (m), 771 (m), 743 (s), 693 (vs), 505 (vs) cm^{-1}. MS (DEI): *m*/*z* = 899 [M]$^+$, 733 [{dpp(o-xyl)}PtS_2]$^+$, 700 [{dpp(o-xyl)}PtS]$^+$, 591 [{dpp(o-xyl)}Pt – Ph]$^+$. $C_{45}H_{38}P_2PtS_2$ (921.94): calcd. C 60.06, H 4.26, S 7.13; found C 59.79, H 4.10, S 7.34.

Kinetic Measurements: The kinetics of the reactions of **1** with the Pt^0(bisphosphane)(η^2-nbe) complexes **5** were investigated by ^{31}P{^{1}H} NMR spectroscopy. The appropriate Pt^0(bisphosphane)(η^2-nbe) complex **5a**–**c** (ca. 0.021 mmol) and triphenylphosphane oxide (internal standard, 0.021 mmol) were dissolved in [D_6]-benzene (0.75 mL) and **1** was added in the described amounts (Table 1). The solution was transferred into a NMR tube and a ^{31}P{^{1}H} NMR spectrum was measured every 9 min with an overall accumulation time of 5.5 min to monitor the reaction progress. To determine the reaction rate constant, the signals of the Pt^0 starting material and those of triphenylphosphane oxide were integrated by using the program "MesTreC 4.7.0". The integrals of the Pt^0(bisphosphane)(η^2-nbe) complexes were divided by the ones of the internal standard to obtain a term for the concentration of **5** at every measuring point. These values were transferred into the term ln([**5**]$_0$/[**5**]$_t$), where [**5**]$_0$ is the initial concentration of **5**. Plotting ln([**5**]$_0$/[**5**]$_t$) vs. time, followed by a linear fit of each data set, gave the appropriate reaction rate constant for a reaction of first-order kinetics based on the concentration of **5**. The rate constants based on the concentration of **1** were determined by using the concentrations of **1**, calculated with Equation (1). Plotting ln([**1**]$_0$/[**1**]$_t$) vs. time and a subsequent linear regression revealed the requested rate constants.

X-ray Crystal Structure Determinations: The intensity data for the compounds were collected with a Nonius KappaCCD dif-

Table 2. Crystal data and refinement details for the X-ray structure determinations.

	6b	**6c**	**7b**	**7c**
Formula	$C_{43}H_{34}P_2PtS_2{\cdot}0.5C_6H_6$	$C_{45}H_{38}P_2PtS_2{\cdot}0.75C_4H_8O$	$C_{43}H_{34}P_2PtS{\cdot}C_4H_8O$	$C_{45}H_{38}P_2PtS{\cdot}0.5C_5H_{12}$
Mol. mass [g mol^{-1}]	910.91	953.98	911.90	903.92
T [°C]	–90(2)	–90(2)	–90(2)	–90(2)
Crystal system	monoclinic	triclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$P2_1$	$P2_1/n$
a [Å]	10.0310(4)	12.3635(4)	9.7461(4)	12.1270(3)
b [Å]	24.5801(12)	14.2706(3)	16.5291(6)	13.3260(4)
c [Å]	15.1680(5)	15.2932(5)	12.0115(5)	26.8843(6)
α [°]	90	91.670(2)	90	90
β [°]	93.864(3)	110.584(1)	94.828(2)	93.836(2)
γ [°]	90	110.402(2)	90	90
V [Å^3]	3731.4(3)	2331.9(1)	1928.12(13)	4334.89(19)
Z	4	2	2	4
ρ [g cm^{-3}]	1.621	1.359	1.571	1.385
μ [cm^{-1}]	39.92	31.98	38.12	33.89
Measured data	24191	17022	13040	22328
Data with $I > 2\sigma(I)$	5528	8523	6845	7882
Unique data/R_{int}	8455/0.0867	10608/0.0353	8027/0.0524	9469/0.0428
wR_2 (all data, on F^2)[a]	0.1445	0.1115	0.0955	0.1047
R_1 [$I > 2\sigma(I)$][a]	0.0564	0.0444	0.0413	0.0399
s[b]	1.023	1.034	0.971	1.064
Res. dens. [e Å^{-3}]	1.526/–3.182	1.265/–1.015	1.580/–1.352	1.547/–1.553
Flack parameter			0.009(8)	

[a] Definition of the *R* indices: $R_1 = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$, $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ with $w^{-1} = \sigma^2(F_o^2) + (aP)^2$. [b] $s = \{\Sigma[w(F_o^2 - F_c^2)^2]/(N_o - N_p)\}^{1/2}$.

fractometer by using graphite-monochromated Mo-K_α radiation. Data were corrected for Lorentz and polarization effects but not for absorption effects[14,15] The structures were solved by direct methods (SHELXS)[16] and refined by full-matrix least-squares techniques against F_o^2 (SHELXL-97) (Table 2).[17] All hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-disordered non-hydrogen atoms were refined anisotropically.[17] Diamond 3.0b as well as POV-Ray 3.6.1c were used for structure representations. CCDC-713946 (for **6b**), -713947 (for **6c**), -713948 (for **7b**), and -713949 (for **7c**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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