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Preparation of 3,3-Di-*tert*-butylthiirane *trans*-1,2-Dioxide and Its Reaction with a Platinum(0) Complex To Give a (Disulfenato)platinum(II) Complex: Regioselectivity of the Oxidation of a Related (Sulfenato–thiolato)platinum(II) Complex

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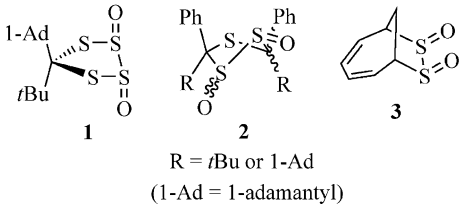
Dedicated to Professor Renji Okazaki on the occasion of his 70th birthday

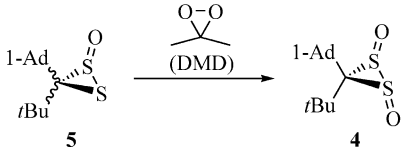
Keywords: Platinum / Dithiirane / *vic*-Disulfoxide / Oxidative addition / Oxidation

A three-membered *vic*-disulfoxide, 3,3-di-*tert*-butyldithiirane *trans*-1,2-dioxide (**8**), was synthesized by oxidation of the corresponding dithiirane 1-oxide **15** in high yield. Treatment of **8** and **15** with a platinum(0) complex, $[(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)]$, yielded the (disulfenato)Pt^{II} complex **18** and the (sulfenato–thiolato)Pt^{II} complex **14**, respectively, in high yields. Oxidation of the sulfenato–thiolato complex **14** with an acetone solution of dimethyldioxirane (DMD) took place at the sulfenato sulfur atom to yield the (sulfinato–thiolato)Pt^{II} complex **19**, while the oxidation with CF_3CO_3H occurred at the thiolato-sulfur atom leading to the disulfenato complex **18**. Oxidation of **14** with MCPBA formed both **18** and **19**. The position of oxidation on **14** with DMD was dependent on the acidity of a coexisting acid. Thus, oxidation of **14** with DMD/CF_3CO_2H provided **18** and that with DMD/$PhCO_2H$ gave **19**. Oxidation of **14** with an excess amount of DMD yielded the (disulfonato)Pt^{II} complex **20**.

Introduction

vic-Disulfoxides [RS(O)S(O)R] have long been recognized as unstable intermediates in the electrophilic oxidation of disulfides[1–3] until our success in 1999 with the isolation and unambiguous structure determination of tetrathiolane 2,3-dioxide **1**, which has a –S(O)–S(O)– bond.[4,5] Since then we have reported on isolable *vic*-disulfoxides **2**–**4**.[6–10] 3-(1-Adamantyl)-3-*tert*-butyldithiirane *trans*-1,2-dioxide (**4**) is the first three-membered *vic*-disulfoxide synthesized by the oxidation of the corresponding dithiirane 1-oxide **5** with an acetone solution of dimethyldioxirane (DMD) [Equation (1)].[9] An interesting reaction of **4** is its decomposition in refluxing chloroform as shown in Scheme 1 to give sulfine **6** and sulfur monoxide (SO) by the main path. SO was trapped with thioketone **7**, generated from a minor path, to provide dithiirane 1-oxide **5** (Scheme 1). The thermal decomposition was investigated in detail experimentally and theoretically, and, for the theoretical study, 3,3-di-*tert*-butyldithiirane *trans*-1,2-oxide (**8**) was employed as the model compound of **4**.[9]





(1)

In this paper we report on the synthesis and some reactions of *vic*-disulfoxide **8**, focusing, in particular, on the platinum complex of **8** and the related compounds. While the oxidative addition of several types of sulfur–sulfur bonds in cyclic sulfur compounds to platinum(0) complexes is a topic of recent research,[11–24] it has not been clarified whether *vic*-disulfoxides bring about a similar oxidative addition to platinum(0) complexes to provide (disulfenato)Pt^{II} complexes.[20] We have reported the reaction of dithiirane 1-oxides with $[(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)]$ to provide the corresponding (sulfenato–thiolato)Pt^{II} complexes **9** [Equa-

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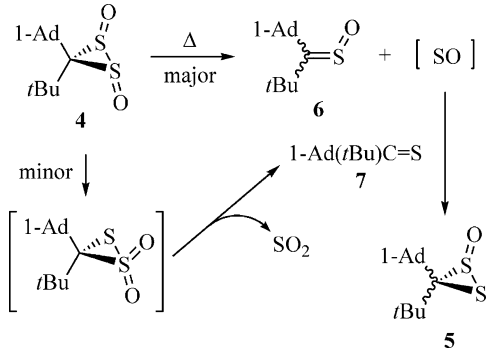
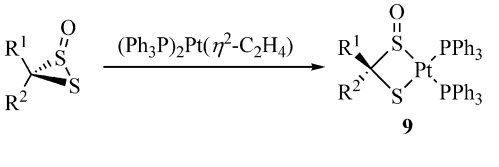


Scheme 1. Thermal decomposition of 3-(1-adamantyl)-3-*tert*-butyldithiirane *trans*-1,2-dioxide (**4**).

tion (2)].[18,19] The oxidation of (dithiolato)M^{II} (M = Ni, Pd, Pt) complexes with molecular oxygen or hydrogen peroxide was studied extensively in relation to their air sensitivity.[25–39] We recently reported the regioselective oxidation of (dithiolato)Pt^{II} complex **10** and its oxides with DMD under neutral conditions [Equation (3)].[24] We observed that the oxidation of the (sulfenato–thiolato)Pt^{II} complex **11** led to the (sulfinato–thiolato)Pt^{II} complex **12** and not the (disulfenato)Pt^{II} complex **13**. This regioselectivity was rationalized in terms of the fact that the sulfenato sulfur is more reactive than the thiolato sulfur because of the back-donation of the platinum atom as Schenk proposed for the reaction of $CpRuL_2[S(O)R]$ (L = phosphane ligands) with DMD [Equation (4)].[40] In order to verify whether this regioselectivity of oxidation is true for the present system and whether the regioselectivity is influenced by the presence or absence of acid, the related (sulfenato–thiolato)Pt^{II} complex **14** was prepared and subjected to an oxidation study.



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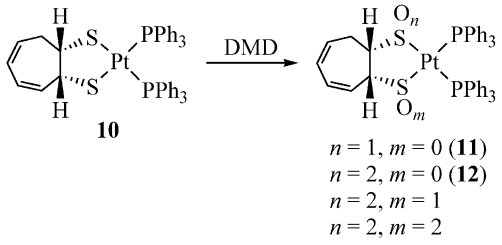

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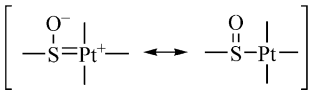

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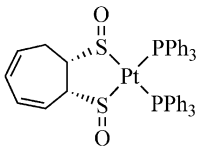
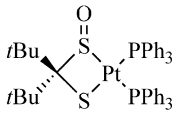


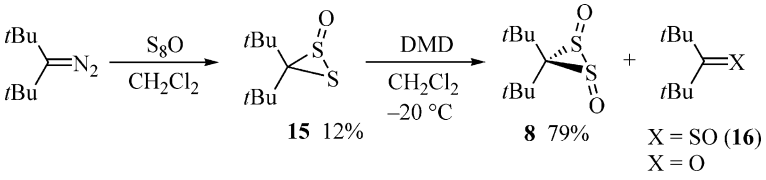


Results and Discussion

Di-*tert*-butyldithiirane 1-oxide (**15**) was prepared by the reaction of di-*tert*-butyldiazomethane with S_8O in 12% yield,[41] and was treated with DMD (5.9 molar equiv.) in dichloromethane at –20 °C. The ^1H NMR spectrum of the reaction mixture showed the formation of the desired 1,2-dioxide **8**, di-*tert*-butyl thioketone *S*-oxide (sulfine) (**16**), and di-*tert*-butyl ketone in a ratio of 89:10:1 (Scheme 2). The high yield of **8** indicated that the over-oxidation to give the trioxides and higher oxides hardly occurred under these conditions. The dioxide **8** was isolated by recrystallization at –20 °C in 79% yield as pale-yellow plates. The oxidation with *m*-chloroperbenzoic acid (MCPBA) (6 molar equiv.) at –20 °C proceeded slowly to give **8** in 31% yield together with sulfine **16** (6%) and the starting compound **15** (63%) (^1H NMR integral ratio). In the ^1H NMR and ^{13}C NMR spectra, the two *tert*-butyl groups of 1,2-dioxide **8** are equivalent, and in the ^{13}C NMR spectrum, the dithiirane carbon resonated at δ = 105.9 ppm, shifted to the lower field by 19.6 ppm than that of the 1-oxide **15** (δ = 86.3 ppm).

The structure of 1,2-dioxide **8** was determined by X-ray crystallography (Figure 1). In the crystal structure of **8** the *C*2 symmetry axis runs through the center of the S–S bond and the dithiirane carbon. The S–S bond length [2.2307(11) Å] is slightly longer than that of **4** [2.242(2) Å], and the dihedral angle O–S–S–O (149.0°) is very similar to that of **4** [149.6(3)°]. The angle between the two *tert*-butyl groups widens to 122.7(2)° as observed in **4** [123.6(5)°].[9]

1,2-Dioxide **8** was stable in the crystalline state at room temperature for a long time, but decomposed gradually in chloroform at room temperature to give sulfine **16** almost quantitatively after 9 d. Heating **8** in refluxing chloroform for 2 h yielded sulfine **16** (78%), dithiirane 1-oxide **15** (14%), and thioketone **17** (4%) [Equation (5)]. The reactions depicted in Scheme 1 can be applied to explain the



Scheme 2. Synthesis of 3,3-di-*tert*-butyldithiirane *trans*-1,2-oxide (**8**).

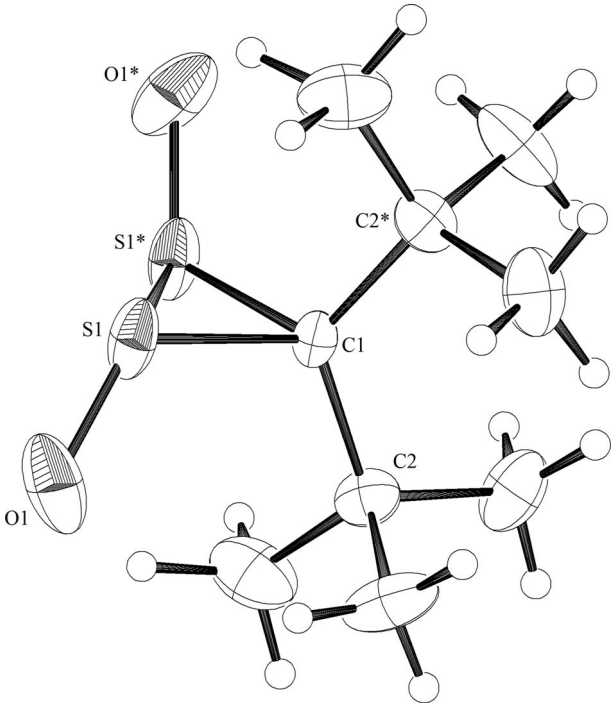
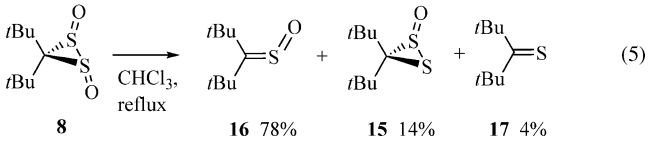


Figure 1. ORTEP drawing of 3,3-di-*tert*-butyldithiirane *trans*-1,2-dioxide (**8**) with 30% probability thermal ellipsoids. Relevant bond lengths [Å] and angles [°]: S1–O1 1.467(2), S1–C1 1.854(2), S1–S1* 2.2308(11), C1–C2 1.561(2), C1–S1 1.854(2), O1–S1–C1 115.79(10), O1–S1–S1* 113.48(9), C2–C1–C2* 122.7(2), C2–C1–S1* 110.44(10), C2–C1–S1 114.63(10), S1–C1–S1* 73.98(10).

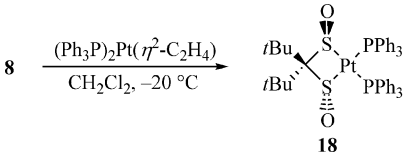
formation mechanism of **15**–**17**. No formation of **15** and **17** on the decomposition in chloroform at room temperature may indicate that the 1,2-oxygen shift of **8** to the dithiirane 1,1-dioxide requires a larger activation energy than the extrusion of SO to give **16**, which is consistent with the theoretical consideration.[9]



(5)

Platinum Complexes

1,2-Dioxide **8** was treated with [$(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$] in dichloromethane at 0 °C. The mixture containing the desired (disulfenato)Pt^{II} complex **18**, sulfine **16**, and **8** was recrystallized from a mixed solvent of hexane and dichloromethane at –20 °C to give **18** as a yellow powder in 56% yield [Equation (6)]. The structure of **18** was supported by the following spectroscopic data. In the ^{1}H NMR spectrum, the two *tert*-butyl groups are equivalent (δ = 1.41 ppm), indicating that the configuration of the two S=O groups in **18** is not *cis* but *trans*. In the ^{31}P NMR spectrum a singlet accompanying the satellite signals ($^1J_{Pt,P}$ = 2596 Hz) from the ^{195}Pt isotope is observed at δ = 15.2 ppm. This $^1J_{Pt,P}$ coupling constant value is comparable to those for phosphorus atoms *trans* to the S=O groups.[12–24] The absorption due to the S=O stretching vibration is observed at 1097 cm^{-1} in the IR spectrum, which is close to those of the reported (sulfenato)Pt^{II} complexes.[12–24] Recrystallization of **18** from benzene provided single crystals (yellow prisms) suitable for X-ray crystal analysis, and the structure was determined unambiguously (Figure 2).



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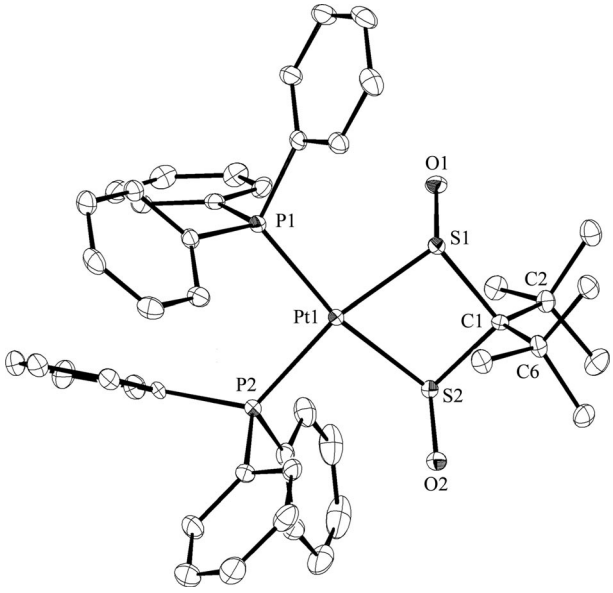
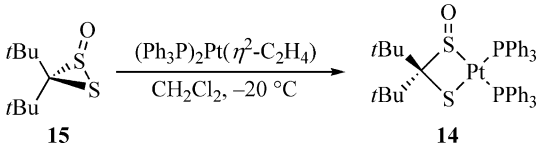


Figure 2. ORTEP drawing of (disulfenato)Pt^{II} complex **18** with 30% probability thermal ellipsoids. Hydrogen atoms and the solvated molecules (C_6H_6) were omitted for clarity.

The (sulfenato–thiolato)Pt^{II} complex **14** was prepared by the treatment of dithiirane 1-oxide **15** with [$(Ph_3P)_2Pt(\eta^2\text{-}C_2H_4)$] conducted in dichloromethane at –20 °C [Equation (7)]. The structure was determined by X-ray crystallography as depicted in Figure 3.



(7)

Oxidation of the sulfenato–thiolato complex **14** was investigated [Equation (8)] (Table 1). Oxidation with an equimolar amount of DMD in toluene at 0 °C yielded the (sulfinato–thiolato)Pt^{II} complex **19** as the main product together with the starting complex **14**, sulfine **16**, and [$Pt(PPh_3)_2$-(S_2O_2)][20,42] (Table 1, Entry 1). The (disulfenato)Pt^{II} complex **18** was not formed at all. The structure of **19** was deter-

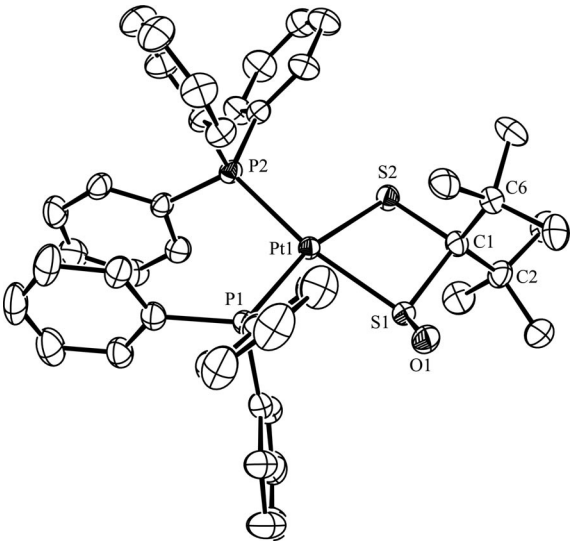


Figure 3. Molecular structure of the (sulfenato–thiolato)Pt^{II} complex **14** with 30% probability thermal ellipsoids. Hydrogen atoms and solvated molecules (CH_2Cl_2) are omitted for clarity.

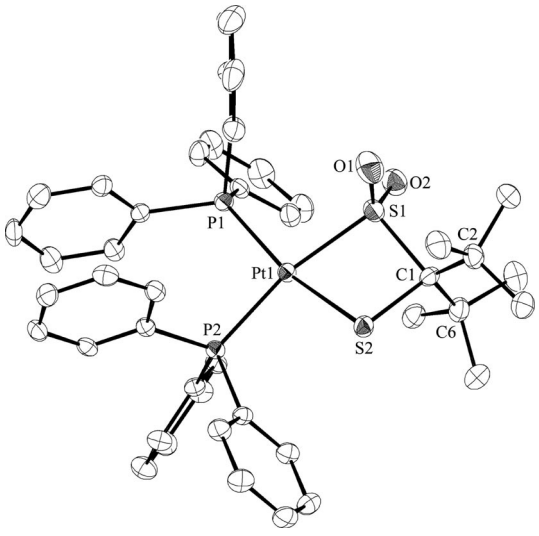
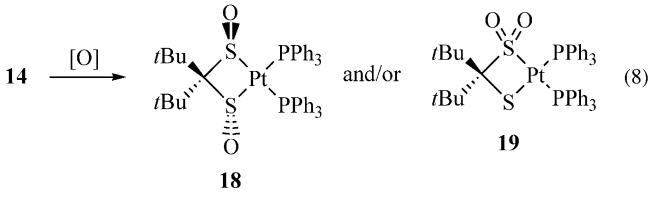


Figure 4. ORTEP drawing of (sulfinato–thiolato)Pt^{II} complex **19** with 30% probability thermal ellipsoids. Hydrogen atoms and solvated molecules (CH_2Cl_2) are omitted for clarity.

mined from spectroscopic data. In the ^{31}P NMR spectrum, two doublets accompanying satellite signals from the ^{195}Pt isotope are observed at δ = 11.6 (d, $^2J_{P,P}$ = 18.6 Hz, $^1J_{Pt,P}$ = 2310 Hz) and 18.7 (d, $^2J_{P,P}$ = 18.6 Hz, $^1J_{Pt,P}$ = 3053 Hz). In the infrared spectrum stretching vibrations from the SO_2 group appear at 1067 and 1197 cm^{-1}. The structure of **19** was finally determined by X-ray crystallography (Figure 4).



(8)

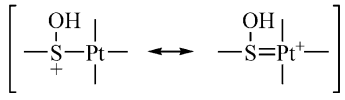
Table 1. Oxidation of (sulfenato–thiolato)Pt^{II} complex **14**.

Entry	[O]	**18**	**19**	**14**[a]	Others
1	DMD	0[b]	62[b]	32[b]	**16** {6[b], $[Pt(PPh_3)_2(S_2O_2)]$}
2	CF_3CO_3H	9[b]	0[b]	73[b]	**16** (18[b])
3	MCPBA	6[c]	9[c]	29[c]	$Ph_3P{=}O$ (56[c])
4	DMD/CF_3CO_2H	30[b]	0[b]	28[b]	**16** (42[b])
5	DMD/$PhCO_2H$	0	84[c]	0	$Ph_3P{=}O$ (16[b])

[a] Recovery. [b] ^1H NMR integral ratio. [c] ^{31}P NMR peak height ratio.

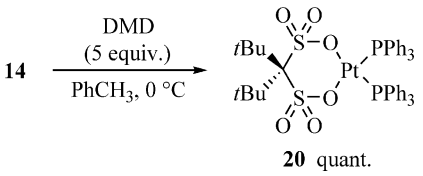
Thus, it was verified that the oxidation of the (sulfenato–thiolato)Pt^{II} complex **14** with DMD took place in the same regioselectivity as observed in the oxidation of **11** with DMD to give **12** [Equation (3)].

On the other hand, oxidation of **14** with CF_3CO_3H gave the (disulfenato)Pt^{II} complex **18** without **19** though this reaction was sluggish (a large portion of the starting complex **14** was recovered) and a substantial amount of sulfine **16** was formed as a decomposition product (^1H NMR integral ratio: **18/14/16** ≈ 9:73:18) (Table 1, Entry 2). When MCPBA was employed as the oxidant both **18** and **19** were formed albeit in low yields (**18/19/14**/$Ph_3P{=}O$ ≈ 6:9:29:56) (Entry 3). The oxidation of **14** with DMD in the presence of CF_3CO_2H yielded **18** together with **14** and **16** (**18/14/16** ≈ 30:28:42) (Entry 4), and that in the presence of benzoic acid gave **19** (**19**/$Ph_3P{=}O$ ≈ 81:16) (Entry 5). The change in regioselectivity as described above was explained by protonation on the sulfinyl oxygen atom with the coexisting carboxylic acid leading to a decrease in the electron density on the sulfinyl-sulfur atom [Equation (9)]. The extent of the decrease in the electron density is dependent on the strength of the acid.



(9)

Oxidation of (sulfenato–thiolato)Pt^{II} complex **14** with an excess amount of DMD (5 molar equiv.) provided the (disulfonato)Pt^{II} complex **20** quantitatively [Equation (10)], the structure of which was determined by X-ray crystallography (Figure 5). The PtO_2S_2C six-membered ring has a twist conformation in the crystalline state. While the two *tert*-butyl groups are equivalent in the ^{13}C NMR spectrum, they are nonequivalent in the ^1H NMR spectrum. In the ^{31}P NMR spectrum, a singlet with satellite signals from the ^{195}Pt isotope is observed at δ = 7.10 ppm ($^1J_{Pt-P}$ = 4157 Hz). Formation of a similar sulfonato complex was reported from the oxidation of the (dithiolato)Ni^{II} complex with hydrogen peroxide [Equation (11)].[43] ^{31}P NMR spectroscopic data of Pt^{II} complexes **14**, **18**–**20** are summarized in Table 2.



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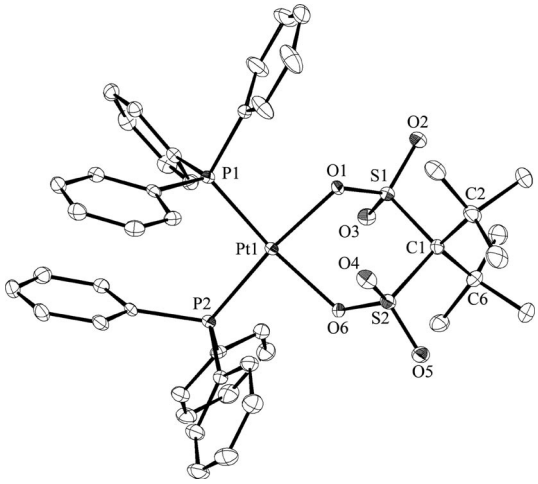
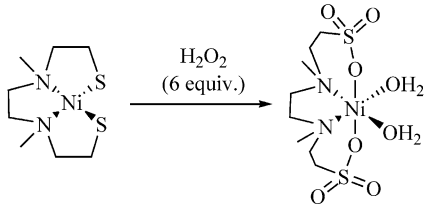


Figure 5. ORTEP drawing of (disulfonato)Pt^{II} complex **20** with 30% probability thermal ellipsoids. Relevant bond lengths [Å] and angles [°]: Pt1–O1 2.090(2), Pt1–O6 2.107(2), Pt1–P1 2.2224(9), Pt1–P2 2.2375(9), O1–S1 1.503(2), S1–O2 1.438(3), S1–O3 1.442(3), S1–C1 1.877(3), C1–C6 1.617(5), C1–C2 1.623(5), C1–S2 1.888(3), S2–O4 1.436(3), S2–O5 1.439(3), S2–O6 1.512(2), O1–Pt1–O6 85.47(9), O1–Pt1–P1 88.60(7), O6–Pt1–P1 173.97(6), O1–Pt1–P2 173.25(7), O6–Pt1–P2 87.92(6), P1–Pt1–P2 98.04(3), S1–O1–Pt1 115.52(13), O2–S1–O3 115.09(15), O2–S1–O1 109.79(14), O3–S1–O1 110.15(14), O2–S1–C1 106.74(15), O3–S1–C1 109.95(15), O1–S1–C1 104.55(14), C6–C1–C2 117.8(3), C6–C1–S1 108.3(2), C2–C1–S1 109.0(2), C6–C1–S2 109.0(2), C2–C1–S2 107.3(2), S1–C1–S2 104.76(16), O4–S2–O5 115.17(16), O4–S2–O6 110.18(14), O5–S2–O6 109.26(14), O4–S2–C1 109.91(16), O5–S2–C1 106.42(15), O6–S2–C1 105.39(14), S2–O6–Pt1 116.00(13).



(11)

Table 2. ^{31}P NMR spectroscopic data of Pt^{II} complexes **14** and **18**–**20**.

Compound	δ [ppm]	$^{2}J(^{31}P,^{31}P)$ [Hz]	$^{1}J(^{195}Pt,^{31}P)$ [Hz]
18	15.2	–	2596
14	16.8	24.4	3306
	17.9	24.4	2338
19	11.6	18.6	2310
	18.7	18.6	3053
20	7.10	–	4157

X-ray Crystallography of Platinum(II) Complexes 14 and 18–20

The selected bond lengths and angles of **14**, **18**, and **19** are summarized in Table 3. The sum of the four angles around the Pt atom in **14** and **18**–**20** is almost 360° and the platinum atoms keep the planarity in these complexes. The puckered angles of the four-membered rings of **18**, **14**, and **19** are 3.6°, 25.2°, and 13.0°, respectively. The S1–Pt1 and S2–Pt1 bond lengths in **18**, **14**, and **19** are not significantly influenced by the oxidation state of the sulfur atoms and lie in the narrow range 2.3065(14)–2.3421(6) Å. The P1–Pt1 and P2–Pt1 bond lengths in **18**, **14**, and **19** also fall into a narrow range [2.2943(14)–2.3347(19) Å], though the P1–Pt1 bonds *trans* to the thiolato ligands in **14** [2.2943(14) Å] and **19** [2.2956(15) Å] are slightly shorter than the others because of the weaker *trans* influence of the thiolato ligands compared with those of the sulfenato and sulfinato ligands. The P1–Pt1 [2.2224(9) Å] and P2–Pt1 [2.2375(9) Å] bond lengths in the disulfonato complex **20**, which are *trans* to the O atoms of the sulfonato ligands, are obviously shorter than the above Pt–P bond lengths.

Table 3. Selected bond lengths [Å] and bond angles [°] of **18**, **14**, and **19**.

	18	**14**	**19**
S1 S2	S1=SO S2=SO	S1=SO S2=S	S1=SO$_2$ S2=S
S1–Pt1	2.3134(10)	2.3421(6)	2.3221(16)
S2–Pt1	2.3251(10)	2.3065(14)	2.3163(15)
P1–Pt1 (*trans* to S2–Pt1)	2.3090(10)	2.2943(14)	2.2956(15)
P2–Pt1 (*trans* to S1–Pt1)	2.3347(10)	2.3130(15)	2.3012(14)
S1–O1, S1–O2	1.511(3)	1.506(5)	1.434(16) 1.464(5)
S2–O2	1.509(3)	–	–
S1–C1	1.917(3)	1.902(6)	1.936(6)
S2–C1	1.899(4)	1.860(7)	1.891(6)
C1–C2	1.577(5)	1.586(8)	1.571(9)
C1–C6	1.588(5)	1.591(8)	1.607(9)
S1–Pt1–P1	93.43(4)	93.53(5)	95.79(6)
P1–Pt1–P2	99.00(4)	99.30(5)	97.60(5)
P2–Pt1–S2	91.15(4)	94.02(5)	93.93(5)
S2–Pt1–S1	76.39(3) (359.97)[a]	72.94(5) (359.79)[a]	72.66(6) (359.98)[a]
S1–Pt1–P2	167.50(4)	166.78(5)	166.60(6)
S2–Pt1–P1	165.48(3)	165.89(6)	167.92(5)
Pt1–S1–C1	92.38(12)	92.2(2)	94.66(19)
S1–C1–S2	97.79(18)	94.5(3)	91.8(3)
C1–S2–Pt1	92.74(12)	94.40(18)	96.08(19)
C2–C1–C6	120.5(3) (3.6)[b]	118.5(5) (25.2)[b]	118.4(5) (13.0)[b]

[a] Sum of the above four angles around the Pt atom. [b] Puckered angle of the four-membered ring.

The S=O bond lengths of the SO$_2$ group in **19** and **20** [1.434(16)–1.464(5) Å] are shorter than those of the sulfenato ligands in **18** [1.509(3) and 1.511(3) Å] and **14** [1.506(5) Å]. This is in accordance with those for dialkyl

sulfones [R–S(O)$_2$–R′, S–O 1.436 Å[44]] and sulfoxides [R–S(O)–R′, S–O 1.497 Å[44]] (R, R′ = alkyl).

The S1–C1 bond [S(O)$_2$–C bond] in **19** is elongated to a length of 1.936(6) Å, which is much longer than those of a similar type in **20** [S1–C1 1.877(3) Å and S2–C1 1.888(3) Å]. This elongation in **19** is explained by a large steric repulsion between the two oxygen atoms and the two *tert*-butyl groups as well as the PPh_3 ligand at the *cis* position in the four-membered ring. While ordinary S–C bond lengths in organic sulfides, sulfoxides, and sulfones become shorter in this order (1.819, 1.809, and 1.779 Å, respectively[44]), this is not true for the present, sterically congested system.

Conclusions

We prepared a three-membered *vic*-disulfoxide, 3,3-di-*tert*-butyldithiirane *trans*-1,2-dioxide (**8**). Complexation of **8** with a platinum(0) complex yielded the (disulfenato)Pt^{II} complex **18** in high yield by oxidative addition. This is the only direct method for the synthesis of (disulfenato)Pt^{II} complexes. We showed that oxidation positions of (sulfenato–thiolato)Pt^{II} complexes, sulfenato sulfur or thiolato sulfur, can be controlled by the acidity of the reaction media.

Experimental Section

The melting points were determined with a Mel-Temp capillary tube apparatus and are uncorrected. ^{1}H, ^{13}C, and ^{31}P NMR spectra were determined with Bruker AM400 or DRX400 (400, 100.7, and 162 MHz, respectively) spectrometers using $CDCl_3$ as the solvent at 25 °C, unless otherwise noted. IR spectra were recorded with a Perkin–Elmer System 2000 FT-IR spectrometer. Elemental analyses were performed by the Molecular Analysis and Life Science Center of Saitama University, where those for platinum complexes were performed with WO_3 as the combustion improver. An acetone solution of dimethyldioxirane (DMD) was prepared by oxidation of acetone with Oxone® (Sigma–Aldrich).[45]

3,3-Di-*tert*-butyldithiirane 1-Oxide (15): A solution of di-*tert*-butyldiazomethane (727.9 mg, 4.719 mmol) in dichloromethane (20 mL) was added to a solution of S_8O (1.548 g, 5.691 mmol) in dichloromethane (250 mL) cooled to 0 °C. The mixture was stirred for 1 h at 0 °C and for 2 h at room temperature. Precipitates were filtered and washed with dichloromethane, and the filtrate and the washings were combined. The solvent was removed under reduced pressure, and the residue was subjected to column chromatography (silica gel: hexane/dichloromethane, 1:2) and then HPLC (hexane/dichloromethane, 3:2) to give dithiirane 1-oxide **15** as a pale-yellow oil (116.8 mg, 12%): ^{1}H NMR: δ = 1.08 (s, 9 H), 1.42 (s, 9 H) ppm. ^{13}C NMR: δ = 29.2 (CH_3), 31.9 (CH_3), 41.2 (C), 41.3 (C), 86.3 (C) ppm. IR (neat): $\tilde{\nu}$ = 1121 cm^{-1}. $C_9H_{18}OS_2$ (206.36): calcd. C 52.38, H 8.79; found C 52.63, H 8.82.

3,3-Di-*tert*-butyldithiirane *trans*-1,2-Dioxide (8): DMD (0.079 M, 17.0 mL, 1.343 mmol) was added to a solution of 3,3-di-*tert*-butyldithiirane 1-oxide (**15**) (46.8 mg, 0.227 mmol) in dichloromethane (1.5 mL) cooled to –20 °C under argon. The mixture was stirred at –20 °C for 2 h, and the solvent was removed under reduced pressure at 0 °C. The ^{1}H NMR spectrum of the residue showed the formation of 1,2-dioxide **8**, di-*tert*-butyl ketone (**17**), and di-*tert*-butyl thioketone *S*-oxide (**16**) in the ratio 89:1:10. The residue was recrystallized from a mixed solvent of hexane and dichloromethane at –20 °C to give 39.9 mg (79%) of 1,2-dioxide **8** as pale-yellow plates. M.p. 85 °C (decomp.). ^{1}H NMR: δ = 1.38 (s, 18 H) ppm. ^{13}C NMR: δ = 31.1 (CH_3), 41.6 (C), 105.9 (C) ppm. IR (KBr): $\tilde{\nu}$ = 1063 cm^{-1}. $C_9H_{18}O_2S_2$ (222.36): calcd. C 48.61, H 8.16; found C 48.87, H 8.22.

[2,2,4,4-Tetramethylpentane-3,3-dithiolato(2–)-κ*S*,κ*S*′]bis(triphenylphosphane)platinum *trans*-*S*,*S*′-Dioxide [(Disulfenato)Pt^{II} Complex 18]: A solution of [$(Ph_3P)_2Pt(\eta^2$-$C_2H_4)$] (92.9 mg, 0.124 mmol) in dichloromethane (2 mL) was added to a solution of 1,2-dioxide **8** (27.8 mg, 0.125 mmol) in dichloromethane (5 mL) cooled to 0 °C under argon. The mixture was stirred for 2 h at 0 °C, and the solvent was removed under reduced pressure. The residue was recrystallized twice from a mixed solvent of hexane and dichloromethane at –20 °C to give 66.3 mg (56%) of the (disulfenato)Pt^{II} complex **18**. M.p. 125 °C (decomp.). ^{1}H NMR: δ = 1.41 (s, 18 H), 7.18–7.22 (m, 12 H), 7.29–7.34 (m, 6 H), 7.38–7.43 (m, 12 H) ppm. ^{13}C NMR: δ = 31.22 (CH_3), 43.97 (C), 128.08 (t, $J_{P,C}$ = 5.3 Hz, CH), 130.20 (dd, $J_{P,C}$ = 57.2, 7.4 Hz, C), 130.27 (CH), 134.21 (t, $J_{P,C}$ = 5.6 Hz, CH) ppm. ^{31}P NMR: δ = 15.2 (s, $^1J_{Pt,P}$ = 2596 Hz for the satellite signals) ppm. IR (KBr): $\tilde{\nu}$ = 1097 cm^{-1}. $C_{45.5}H_{49}ClO_2P_2PtS_2$ ($C_{45}H_{48}O_2P_2PtS_2$·0.5CH_2Cl_2) (984.49): calcd. C 55.51, H 5.02; found C 56.17, H 5.03 (the ^{1}H NMR spectrum of the same sample subjected to the elemental analysis showed the presence of 0.50 molecules of CH_2Cl_2 and a molecule of **18**). Single crystals suitable for X-ray crystallography were obtained by recrystallization from benzene at room temperature.

[2,2,4,4-Tetramethylpentane-3,3-dithiolato(2–)-κ*S*,κ*S*′]bis(triphenylphosphane)platinum *S*-Oxide [(Sulfenato–thiolato)Pt^{II} Complex 14]: A solution of [$(Ph_3P)_2Pt(\eta^2$-$C_2H_4)$] (202.1 mg, 0.218 mmol) in dichloromethane (8 mL) was added to a solution of dithiirane 1-oxide **15** (45.0 mg, 0.218 mmol) in dichloromethane (3 mL) cooled to 0 °C under argon. The mixture was stirred for 2 h at 0 °C, and the solvent was removed under reduced pressure. The residue was recrystallized from a mixed solvent of hexane and dichloromethane at –20 °C to give 152.5 mg (76%) of the (sulfenato–thiolato)Pt^{II} complex **14** as yellow prisms. M.p. 207 °C (decomp.). ^{1}H NMR: δ = 1.12 (s, 9 H), 1.45 (br. s, 6 H), 1.62 (s, 3 H), 7.14–7.20 (m, 12 H), 7.24–7.30 (m, 6 H), 7.38–7.45 (m, 12 H) ppm. ^{13}C NMR: δ = 29.30 (CH_3), 32.98 (br. s, CH_3), 42.60 (C), 46.30 (C), 127. 72 (t, $J_{P,C}$ = 9.9 Hz, CH), 130.01 (CH), 134.3 (m, CH) ppm (signals for aromatic quaternary carbons appear at δ = 130.425, 130.794, 130.892, and 131.297 ppm, which are not assigned). ^{31}P NMR: δ = 16.8 (d, $^2J_{P,P}$ = 24.4 Hz and $^1J_{Pt,P}$ = 3306 Hz for the satellite signals), 17.9 (d, $^2J_{P,P}$ = 24.4 Hz and $^1J_{Pt,P}$ = 2338 Hz for the satellite signals) ppm. $C_{47}H_{52}Cl_4OP_2PtS_2$ ($C_{45}H_{48}OP_2PtS_2$·2CH_2Cl_2) (1095.89): calcd. C 51.51, H 4.78; found C 51.24, H 4.66.

[2,2,4,4-Tetramethylpentane-3,3-dithiolato(2–)-κ*S*,κ*S*′]bis(triphenylphosphane)platinum *S*,*S*-Dioxide [(Sulfinato–thiolato)Pt^{II} Complex 19]: A solution of DMD (0.085 M, 0.34 mL, 0.029 mmol) was added to a solution of the (sulfenato–thiolato)Pt^{II} complex **14** (27.1 mg, 0.0292 mmol) in toluene (3 mL) cooled to 0 °C under argon. The mixture was stirred for 2 h at 0 °C, and the solvent was removed under reduced pressure at 0 °C. The ^{1}H NMR spectrum of the residue (28.7 mg) indicated the presence of **19**, **14**, and sulfine **16** in the ratio 62:32:6, while the ^{31}P NMR spectrum showed signals from **19** (δ = 11.6 and 18.7 ppm) and **14** (δ = 16.8 and 18.9 ppm) together with a small amount of [$Pt(PPh_3)_2(S_2O_2)$] (δ = 6.3 ppm). The residue was recrystallized from a mixed solvent of hexane and dichloromethane at –20 °C to give 5.1 mg of an ca. 2:1 mixture of **19** and **14**. As we could not obtain **19** in the pure form, even by

repeated recrystallization, elemental analysis of **19** was not done. However, a single, yellow crystal suitable for X-ray analysis was obtained. ^{1}H NMR: δ = 1.50 (br. s, 18 H), 7.14–7.21 (m, 12 H), 7.28–7.32 (m, 6 H), 7.38–7.44 (m, 6 H), 7.50–7.55 (m, 6 H) ppm. ^{31}P NMR: δ = 11.6 (d, $^2J_{P,P}$ = 18.6, $^1J_{Pt,P}$ = 2310 Hz), 18.7 (d, $^2J_{P,P}$ = 18.6, $^1J_{Pt,P}$ = 3053 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 1067, 1197 (SO_2) cm^{-1}.

[2,2,4,4-Tetramethylpentane-3,3-disulfonato(2–)-κ*O*,κ*O*′]bis(triphenylphosphane)platinum [(Disulfonato)Pt^{II} Complex 20]: DMD (0.083 M, 1.25 mL, 0.10 mmol) was added dropwise to a solution of the (sulfenato–thiolato)Pt^{II} complex **14** (19.3 mg, 0.021 mmol) in toluene (7 mL) at 0 °C under argon. The mixture was stirred for 2 h at 0 °C, and the solvent was removed under reduced pressure at 0 °C to give an almost pure **20** as a yellow-white solid (20.9 mg). The crude material was recrystallized from a mixed solvent of hexane and dichloromethane at –20 °C to give 7.1 mg (34%) of **20** as colorless prisms. M.p. 280 °C (decomp.). ^{1}H NMR: δ = 1.52 (br. s, 9 H), 1.58 (s, 9 H), 7.20–7.26 (m, 12 H), 7.36–7.40 (m, 6 H), 7.53–7.59 (m, 12 H) ppm. ^{13}C NMR: δ = 32.91 (CH_3), 42.32 (C), 126.10 (d, $J_{P,C}$ = 68.3 Hz, C), 128.47 (t, $J_{P,C}$ = 5.9 Hz, CH), 131.60 (CH), 134.58 (t, $J_{P,C}$ = 5.4 Hz, CH_3) ppm. ^{31}P NMR: δ = 7.10 (s, $^1J_{Pt,P}$ = 4157 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 1139, 1284 (SO_2) cm^{-1}. $C_{45}H_{48}O_6P_2PtS_2$ (1006.02): calcd. C 53.73, H 4.81; found C 54.01, H 5.04.

X-ray Crystallography: X-ray crystallographic analyses were performed with a Mac Science DIP3000 diffractometer (for **14**) or a Bruker AXS SMART diffractometer (for others) with a graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The structures were solved by direct methods and refined with full-matrix least-squares (SHELXL-97[46]) using all independent reflections.

Crystal Data for 8: $C_9H_{18}O_2S_2$, M_r = 222.35 g mol^{-1}, yellow prism, crystal size = 0.40 × 0.40 × 0.40 mm, monoclinic, *C*2/*c*, *a* = 14.9253(13), *b* = 7.0524(6), *c* = 11.4484(9) Å, β = 105.485(2)°, *V* = 1161.31(17) Å^3, $\rho_{calcd.}$ = 1.272 g cm^{-3}, *Z* = 4, μ(Mo-K_α) = 0.428 cm^{-1}. Intensity data of 1069 unique reflections were collected over the range –18 ≤ *h* ≤ 17, –8 ≤ *k* ≤ 8, –13 ≤ *l* ≤ 13 at 223 K. R_1 = 0.0412 [$I \geq 2\sigma(I)$, 956 reflections], wR_2 = 0.1062 (for all), and Gof = 1.093, 96 parameters; max./min. residual electron density: 0.253/–0.176 e Å^{-3}.

Crystal Data for 18: $C_{57}H_{60}O_2P_2PtS_2$ ($C_{45}H_{48}O_2P_2PtS_2$·2C_6H_6), M_r = 1098.20 g mol^{-1}, yellow prism, crystal size = 0.25 × 0.20 × 0.12 mm, triclinic, $P\bar{1}$, *a* = 10.8885(8), *b* = 13.1343(10), *c* = 17.7604(13) Å, α = 81.859(2), β = 88.115(2), γ = 82.946(2)°, *V* = 2495.0(3) Å^3, $\rho_{calcd.}$ = 1.462 g cm^{-3}, *Z* = 2, μ(Mo-K_α) = 3.001 cm^{-1}. Intensity data of 9229 unique reflections were collected over the range –12 ≤ *h* ≤ 13, –15 ≤ *k* ≤ 15, –21 ≤ *l* ≤ 20 at 123 K. R_1 = 0.0341 [$I \geq 2\sigma(I)$, 8355 reflections], wR_2 = 0.0798 (for all), and Gof = 1.037, 584 parameters; max./min. residual electron density: 1.370/–0.423 e Å^{-3}.

Crystal Data for 14: $C_{47}H_{52}Cl_4OP_2PtS_2$ ($C_{45}H_{48}OP_2PtS_2$·2CH_2Cl_2), M_r = 1095.910 g mol^{-1}, yellow prism, crystal size = 0.24 × 0.12 × 0.12 mm, triclinic, $P\bar{1}$, *a* = 11.6740(4), *b* = 14.6560(4), *c* = 15.3800(4) Å, α = 113.041(2), β = 94.326(2), γ = 91.289(2)°, *V* = 2410.72(12) Å^3, $\rho_{calcd.}$ = 1.510 g cm^{-3}, *Z* = 2, μ(Mo-K_α) = 3.319 cm^{-1}. Intensity data of 8622 unique reflections were collected over the range –14 ≤ *h* ≤ 14, –18 ≤ *k* ≤ 18, –19 ≤ *l* ≤ 18 at 298 K. R_1 = 0.0422 [$I \geq 2\sigma(I)$, 7676 reflections], wR_2 = 0.1179 (for all), and Gof = 1.037, 523 parameters; max./min. residual electron density: 0.958/–1.616 e Å^{-3}.

Crystal Data for 19: $C_{47}H_{52}Cl_4O_2P_2PtS_2$ ($C_{45}H_{48}O_2P_2PtS_2$·2CH_2Cl_2), M_r = 1111.84 g mol^{-1}, yellow prism, 0.25 × 0.20 × 0.10 mm, triclinic, $P\bar{1}$, *a* = 11.6339(6), *b* = 14.6630(7), *c* = 15.1190(8) Å, α = 113.4220(10), β = 94.0080(10), γ = 93.0900(10)°, *V* = 2351.4(2) Å^3, $\rho_{calcd.}$ = 1.570 g cm^{-3}, *Z* = 2, μ(Mo-K_α) = 3.405 cm^{-1}. Intensity data of 8731 unique reflections were collected over the range –12 ≤ *h* ≤ 14, –17 ≤ *k* ≤ 16, –13 ≤ *l* ≤ 18 at 153 K. R_1 = 0.0438 [$I \geq 2\sigma(I)$, 7944 reflections], wR_2 = 0.1144 (for all), and Gof = 1.037, 523 parameters; max./min. residual electron density: 2.599/–1.047 e Å^{-3}.

Crystal Data for 20: $C_{47}H_{52}Cl_4O_6P_2PtS_2$ ($C_{45}H_{48}O_6P_2PtS_2$·2CH_2Cl_2), M_r = 1175.84 g mol^{-1}, colorless prism, crystal size = 0.30 × 0.22 × 0.20 mm, monoclinic, $P2_1/c$, *a* = 11.9094(5), *b* = 24.2783(11), *c* = 16.9933(7) Å, β = 98.3500(10)°, *V* = 4861.4(4) Å^3, $\rho_{calcd.}$ = 1.607 g cm^{-3}, *Z* = 4, μ(Mo-K_α) = 3.305 cm^{-1}. Intensity data of 9053 unique reflections were collected over the range –14 ≤ *h* ≤ 14, –28 ≤ *k* ≤ 29, –20 ≤ *l* ≤ 17 at 123 K. R_1 = 0.0294 ($I \geq 2\sigma(I)$, 8018 reflections), wR_2 = 0.0716 (for all), and Gof = 1.047, 565 parameters; max./min. residual electron density: 1.444/–0.844 e Å^{-3}.

CCDC-655818 (for **8**), -655819 (for **18**), -655820 (for **14**), -655821 (for **19**), and -655822 (for **20**) contain the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see also the footnote on the first page of this article): ^{13}C NMR spectra of **14**, **18**, and **20**, and ^{1}H and ^{31}P NMR spectra of **19** as a mixture with **14**.

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