Registry No. $Cr(CO)_6$, 13007-92-6; $Mo(CO)_6$, 13939-06-5; $W(CO)_6$, 14040-11-0; SiO_2, 7631-86-9.

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A Versatile Starting Material: Substitution Reactions of Bis(acetato)bis(diethyl sulfide)platinum with Phosphines, Thiols, *o*-Hydroquinones and Dihydroxybenzoquinones

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The new compound *cis*-$Pt(OAc)_2(Et_2S)_2$ has been prepared, and its use as a starting material in the synthesis of new complexes of platinum has been investigated. Substitution reactions with HO–OH or HO_2–O_2H (HO–OH = substituted catechol, HO_2–O_2H = substituted 2,5-dihydroxy-1,4-benzoquinone) gave the corresponding *cis*-$Pt(O–O)(Et_2S)_2$ and *cis*-$Pt(O_2–O_2)(Et_2S)_2$ compounds. In the case of O_2–O_2 = 2,5-dioxy-1,4-benzoquinone, a slow conversion to a yellow isomer formulated as *trans*-$Pt_2(\mu\text{-}(O_2–O_2))_2(Et_2S)_4$ was observed. Reaction of $K_4[Pt_2(\mu\text{-}(O_2–O_2))_2Cl_4]$ (O_2–O_2 = 3,6-dichloro-2,5-dioxy-1,4-benzoquinone) with Et_2S also gave *trans*-$Pt_2(\mu\text{-}(O_2–O_2))_2(Et_2S)_4$. Reactions with ArSH (Ar = 4-MePh, 4-ClPh) first gave $Pt(SAr)_2(Et_2S)_2$, which then slowly reacted further to form $[Pt(SAr)_2]_n$. Reactions with phosphines (PPh_3, $PPhMe_2$) led to displacement of the diethyl sulfide group(s) giving mono- and bis-substituted phosphine compounds. Iodine oxidation of the 1,2-quinone complexes $Pt(O–O)(Et_2S)_2$ resulted in the rapid formation of the free 1,2-quinone, whereas $Pt(SPhMe\text{-}4)_2(Et_2S)_2$ gave with iodine the free disulfide $(4\text{-}MePhS–)_2$. In both cases $PtI_2(Et_2S)_2$ was also formed. The configurations of the compounds described were derived from ^1H NMR and IR data.

Introduction

The preparation of many transition-metal compounds is often achieved by ligand-substitution reactions in which a weaker coordinating ligand is replaced by a stronger one. Therefore, compounds which can act as useful and versatile starting materials in the preparation of a variety of other compounds are of great interest, particularly when they are readily synthesized from commercially available starting materials and are stable on handling and storing over prolonged periods. In addition, such compounds should undergo selective substitutions with other ligands.

Our interest in platinum chemistry led us to investigate which starting materials met these criteria. This study resulted in the preparation of $Pt(OAc)_2(Et_2S)_2$, a compound which has all the properties mentioned above. Both the acetato or sulfide groups can be readily substituted simultaneously or separately in high yield. To demonstrate the important role that such a compound can play in the preparation of interesting new complexes, we studied several reactions with $Pt(OAc)_2(Et_2S)_2$. Substitutions with *o*-hydroquinones (catechols) were chosen because of the recent interest in the transition-metal chemistry of these ligands,[1,2] which play an important role in biochemistry.[3,4]

Compounds of dioxybenzoquinones with transition metals are mostly polymers.[5-7] They have been of considerable interest, as it was expected that due to the easily polarizable dioxybenzoquinone ligands, the compounds could have unusual magnetic and electrical properties.[6,7] Nonpolymeric transition-metal compounds, however, are not very common,[8] and therefore substitution reactions of 2,5-dihydroxybenzoquinone with, e.g., $Pt(OAc)_2(Et_2S)_2$ were studied.

Many thiol complexes of the nickel triad were prepared by fission of the sulfur bridges of the polymeric metal thiolates.[9] In this paper it is shown that platinum thiolates can easily be prepared by substitution of acetato groups.

Experimental Section

The substituted catechols, 3,6-dichloro-2,5-dihydroxy-1,4-benzoquinone, K_2PtCl_4, (4-methylphenyl)thiol, and (4-chloro-

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Table I. Analytical Data

compd[a]	% C		% H		% S		% others	
	found	calcd	found	calcd	found	calcd	found	calcd
cis-$Pt(OAc)_2(Et_2S)_2$	28.83	29.20	5.29	5.31	13.94	12.99	40.1(Pt)	39.5(Pt)
cis-$Pt(O_2CCF_3)_2(Et_2S)_2$	23.96	23.96	3.43	3.35	11.76	10.66		
trans-$Pt(O_2CCF_3)_2$(*i*-$Pr_2S)_2$	28.75	29.22	4.37	4.29	10.29	9.75		
cis-$Pt(O–O)(Et_2S)_2$	34.61	34.77	4.96	5.00	13.20	13.26	40.6(Pt)	40.4(Pt)
cis-Pt(*t*-$Bu_2O–O)(Et_2S)_2$	44.08	44.50	6.81	6.79	11.28	10.46	34.0(Pt)	32.9(Pt)
cis-$Pt(NaphthO–O)(Et_2S)_2$	40.89	40.51	4.86	4.91	11.56	12.02	36.7(Pt)	36.6(Pt)
cis-$Pt(O_2–O_2)(Et_2S)_2\cdot H_2O$	31.60	31.63	4.47	4.55	12.32	12.06		
trans-$Pt_2(\mu\text{-}(O_2–O_2))_2(Et_2S)_4$	32.94	32.74	4.35	4.32	13.04	12.49		
cis-$Pt(Cl_2O_2–O_2)(Et_2S)_2$	28.66	28.87	3.43	3.46	10.84	11.01	12.2(Cl)	12.2(Cl)
trans-$Pt_2(\mu\text{-}(Cl_2O_2–O_2))_2(Et_2S)_4$[b]	28.87	28.87	3.53	3.46	11.79	11.01	12.6(Cl)	12.2(Cl)
cis-$Pt(Ph_2O_2–O_2)(Et_2S)_2\cdot 2CHCl_3$	37.38	37.18	3.50	3.34	7.04	7.09	22.2(Pt)	21.6(Pt)
$Pt(SPhMe\text{-}4)_2(Et_2S)_2$	41.87	42.49	5.20	5.51	19.78	20.63	33.0(Pt)	31.4(Pt)
cis-$Pt(OAc)_2(PPh_3)(Et_2S)$	47.30	46.91	4.72	4.69	4.39	4.82		
cis-$Pt(OAc)_2(PPh_3)_2$	57.09	57.33	4.44	4.33				
cis-$Pt(OAc)_2(PPhMe_2)_2$	40.24	40.75	5.00	4.79				
cis-Pt(*t*-$Bu_2O–O)(PPhMe_2)_2$	52.11	52.09	6.22	6.12				
cis-$Pt(NaphthO–O)(PPh_3)_2\cdot CH_2Cl_2$	59.15	56.65	4.09	3.92				
cis-$Pt(O_2–O_2)(PPh_3)_2\cdot CH_2Cl_2$	53.78	54.78	3.71	3.53				
cis-$Pt(O_2–O_2)(PPhMe_2)_2\cdot 1.5CHCl_3$	35.22	35.79	3.19	3.25			21.8(Cl)	20.3(Cl)
trans-$Pt(SPhMe\text{-}4)_2(PPhMe_2)_2$	49.54	50.20	5.11	5.06	8.82	8.93		
$K_4[Pt_2(\mu\text{-}(Cl_2O_2–O_2))_2Cl_4]\cdot 6H_2O$[c]	11.65	11.90	0.87	0.99			22.6(Cl)	23.4(Cl)
$(NH_4)_4[Pt_2(\mu\text{-}(Cl_2O_2–O_2))_2Cl_4]\cdot 2H_2O$[d]	13.50	13.67	1.75	1.91			24.6(Cl)	26.9(Cl)

[a] OAc = O_2CCH_3, O–O = catechol (1,2-benzoquinone(2−)), *t*-$Bu_2O–O$ = 3,5-di-*tert*-butylcatechol, NaphthO–O = 2,3-dihydroxynaphthalene, $O_2–O_2$ = 2,5-dioxy-1,4-benzoquinone, $Cl_2O_2–O_2$ = 3,6-dichloro-2,5-dioxy-1,4-benzoquinone, $Ph_2O_2–O_2$ = 3,6-diphenyl-2,5-dioxy-1,4-benzoquinone. [b] % Pt: found, 33.0; calcd, 33.5. [c] % K: found, 13.5; calcd, 12.9. [d] % Pt: found, 39.0; calcd, 37.0. N: found, 4.92; calcd, 5.31.

phenyl)thiol were commercially available. The compounds 2,5-dihydroxy-1,4-benzoquinone[10] and 3,6-diphenyl-2,5-dihydroxy-1,4-benzoquinone[11] were prepared according to the literature. Crude $PtCl_2(Et_2S)_2$, obtained from $K_2PtCl_4 + 4Et_2S$ in H_2O,[12] was dissolved in warm benzene, and the solution was slowly evaporated in air. The pale yellow plates of *cis*-$PtCl_2(Et_2S)_2$ were collected in portions and washed with benzene (the washings were added to the evaporating solution). This resulted in yields of typically over 90%. Only in the last fraction (<6%) was trans product present. *trans*-$PtCl_2$(*i*-$Pr_2S)_2$ was obtained in 90% yield by using an excess of *i*-Pr_2S. No cis product could be obtained.

^1H NMR spectra were recorded on a Varian HA 100 spectrometer and IR spectra (Nujol or KBr) on a Perkin-Elmer Model 283 IR spectrometer. Elemental analyses were performed by Childers Laboratories, Milstead, NJ, and Chemical Analytical Services, University of California, Berkeley, CA, and are summarized in Table I.

Preparation of *cis*-$Pt(OAc)_2(Et_2S)_2$. Silver acetate (25 mmol) was added to a suspension of $PtCl_2(Et_2S)_2$ (10 mmol) in dry benzene (50 mL), and the mixture was stirred at 55–65 °C for 1 h. After the mixture was cooled, AgCl was removed by filtration, and subsequently the solution was evaporated under vacuum until no more benzene came off. The oily residue was then stirred with 25 mL of dry ether for 30 min. The white crystalline precipitate of *cis*-$Pt(OAc)_2(Et_2S)_2$ was isolated on a filter and dried for 2 h under vacuum. The yield of this fraction was typically 70–80%. A second fraction of white needles (5–10% yield) was obtained from the ether solution at −20 °C. Both fractions were slowly attacked by moisture, but the needles reacted more rapidly, liquefying in moist air. Dehydration of the hydrated compound can be achieved by dissolution in warm benzene, subsequent evaporation of the benzene under slightly reduced pressure at 50–60 °C, and working up the oily residue as described earlier. Over prolonged periods the compound has to be stored below 5 °C and protected from light. In the following preparations, the amounts of $Pt(OAc)_2(Et_2S)_2$ were weighed quickly in air and then added to the reaction flask. Small amounts of moisture did not influence these reactions.

Other carboxylato compounds of platinum, *cis*-$Pt(O_2CR)_2(Et_2S)_2$ (R = $CH(CH_3)_2$, CH_2Cl, CF_3) and *trans*-$Pt(O_2CCF_3)_2$(*i*-$Pr_2S)_2$, were prepared similarly and when necessary recrystallized from CH_2Cl_2/hexane under cold conditions.

Preparation of *cis*-Pt(*t*-$Bu_2O–O)(Et_2S)_2$ (*t*-$Bu_2O–O$ = 3,5-Di-*tert*-butylcatechol). Di-*tert*-butylcatechol (1 mmol) was added to a solution of $Pt(OAc)_2(Et_2S)_2$ (1 mmol) in CH_2Cl_2. After 5 min, the solvent was removed under vacuum and the residue recrystallized from hexane at −30 °C. Cream colored crystals of Pt(*t*-$Bu_2O–O)(Et_2S)_2$ were obtained in 90% yield. Compounds with catechol and 3-methyl- and 3-nitrocatechol were prepared in an analogous manner. In the case of unsubstituted catechol (1,2-dihydroxybenzene) a small amount of a dark green oil was discarded. Yellow crystals of *cis*-$Pt(NaphthO–O)(Et_2S)_2$ (NaphthO–O = 2,3-dioxynaphthalene) were obtained in 90% yield in an analogous manner with 2,3-dihydroxynaphthalene. The crystals were recrystallized from CH_2Cl_2/hexane.

Preparation of *cis*-$Pt(Cl_2O_2–O_2)(Et_2S)_2$ ($Cl_2O_2–O_2$ = 3,6-Dichloro-2,5-dioxy-1,4-benzoquinone). $Pt(OAc)_2(Et_2S)_2$ (1 mmol) was dissolved in CH_2Cl_2 (5 mL) and an excess of 3,6-dichloro-2,5-dihydroxy-1,4-benzoquinone (3 mmol) was added. After 2 h of stirring the excess 3,6-dichloro-2,5-dihydroxy-1,4-benzoquinone was removed by filtration and the solution evaporated to dryness under vacuum. The dark purple residue was recrystallized from a minimum amount of $CHCl_3$. Dark purple plates of *cis*-$Pt(Cl_2O_2–O_2)(Et_2S)_2$ were obtained in 80% yield. Dark purple crystals of *cis*-$Pt(Ph_2O_2–O_2)(Et_2S)_2\cdot 2CHCl_3$ ($Ph_2O_2–O_2$ = 3,6-diphenyl-2,5-dioxy-1,4-benzoquinone) were prepared with 3,6-diphenyl-2,5-dihydroxy-1,4-benzoquinone in an analogous manner. Both compounds were only slightly soluble in cold CH_2Cl_2 or $CHCl_3$ but dissolved readily upon heating.

Preparation of *cis*-$Pt(O_2–O_2)(Et_2S)_2\cdot H_2O$ ($O_2–O_2$ = 2,5-Dioxy-1,4-benzoquinone). 2,5-Dihydroxy-1,4-benzoquinone (2 mmol) and $Pt(OAc)_2(Et_2S)_2$ (1 mmol) were stirred in CH_2Cl_2 (5 mL) for 30 min. Hexane (5 mL) was added, and subsequently the solution was filtered. Slow evaporation in air at low temperatures (−10–0 °C) gave dark red crystals of *cis*-$Pt(O_2–O_2)(Et_2S)_2\cdot H_2O$ in 30–50% yield. The product was often contaminated with small yellow crystals of *trans*-$Pt_2(\mu\text{-}(O_2–O_2))_2(Et_2S)_4$. This trans isomer was formed by a slow conversion of the cis isomer, which was evidenced by ^1H NMR (in $CDCl_3$ solutions). Reaction of $PtCl_2(Et_2S)_2$ with $Ag_2(O_2–O_2)$ gave the same products.

Preparation of *trans*-$Pt_2(\mu\text{-}(O_2–O_2))_2(Et_2S)_4$ ($O_2–O_2$ = 2,5-Dioxy-1,4-benzoquinone). On standing at room temperature, the dark red solution of *cis*-$Pt(O_2–O_2)(Et_2S)_2$ slowly turned lighter in color. After several days, the solution was concentrated until crystallization was observed. Further crystallization at −20 °C gave yellow crystals of *trans*-$Pt_2(\mu\text{-}(O_2–O_2))_2(Et_2S)_4$ in 60% yield. The compound was recrystallized from hot $CHCl_3$ in which it is moderately soluble.

Preparation of *trans*-$K_4[Pt_2(\mu\text{-}(Cl_2O_2))_2Cl_4]\cdot 6H_2O$. The silver salt of 3,6-dichloro-2,5-dihydroxy-1,4-benzoquinone (2 mmol) was added to a solution of K_2PtCl_4 (2 mmol) in water (20 mL). A dark red solution and a pink precipitate were obtained. When the precipitate was collected on a filter and vacuum dried, the weight corresponded with the expected weight of a quantitative conversion to AgCl and $[Pt(\mu\text{-}(Cl_2O_2–O_2))]_n$. Evaporation of the solution in a vacuum de-

Table II. ^{1}H NMR Data[a]

compd[b]	O_2CR, O–O O_2–O_2, SAr	Et_2S,[c] PR_3
cis-$Pt(OAc)_2(Et_2S)_2$	2.01 (5 Hz)	2.92, 2.65; 1.45
cis-$Pt(O_2CCH_2Cl)_2(Et_2S)_2$	4.00	2.93,[d] 2.66;[d] 1.46
cis-$Pt(O_2CCH(CH_3)_2)_2(Et_2S)_2$	2.49; 1.08	2.91, 2.64; 1.44
cis-$Pt(O_2CCF_3)_2(Et_2S)_2$		2.87,[e] 2.66;[e] 1.48
trans-$Pt(O_2CCF_3)_2$(i-$Pr_2S)_2$		3.16; 1.55
trans-$PtI_2(Et_2S)_2$		3.17 (42 Hz); 1.40
2,5-*t*-Bu_2-1,2-benzoquinone	6.94, 6.21; 1.26, 1.22	
1,2-benzoquinone	7.05, 6.39	
cis-Pt(O–O)$(Et_2S)_2$	6.66, 6.42	3.14, 2.85; 1.41
cis-Pt(*t*-Bu_2O–O)$(Et_2S)_2$	6.62; 1.40, 1.27	~3.19, ~2.77; 1.40, 1.39
cis-Pt(NaphthO–O)$(Et_2S)_2$	7.50, 7.04, 6.93 (5.5 Hz)	3.10, 2.79; 1.40
cis-$Pt(O_2$–$O_2)(Et_2S)_2 \cdot H_2O$	5.44 (5.5 Hz)	3.03, 2.82; 1.44
trans-$Pt_2(\mu$-$(O_2$–$O_2))_2(Et_2S)_4$	5.10 (5 Hz)	3.01 (38 Hz); 1.32
cis-$Pt(Cl_2O_2$–$O_2)(Et_2S)_2$		3.10, 2.87; 1.48
trans-$Pt_2(\mu$-$(Cl_2O_2$–$O_2))_2(Et_2S)_4$		3.02 (37 Hz); 1.29
cis-$Pt(Ph_2O_2$–$O_2)(Et_2S)_2 \cdot 2CHCl_3$	7.42, 7.19	2.87, 2.67; 1.35
trans-Pt(SPhMe-4)$_2(Et_2S)_2$	7.36, 6.78; 2.19	2.91 (34 Hz), 1.30
cis-$Pt(OAc)_2(PPh_3)(Et_2S)$	2.02 (2.5 Hz); 1.45 (6 Hz)	~2.70, ~2.54; 1.09; 7.84, 7.44
cis-$Pt(OAc)_2(PPh_3)_2$	1.36 (4 Hz)	7.57, ~7.20
cis-$Pt(OAc)_2(PPhMe_2)_2$	2.02 (3.5 Hz)	~7.56, 7.38; 1.45 (33.4 Hz, 11.5 Hz[f])
cis-Pt(*t*-Bu_2O–O)$(PPhMe_2)_2$	6.74, 6.51; 1.46, 1.28	7.48, 7.31; 1.67 (29.5 Hz, 11.5 Hz[f])
cis-$Pt(O_2$–$O_2)(PPhMe_2)_2 \cdot 1.5CHCl_3$	5.50 (4 Hz)	~7.39, 1.66 (32 Hz, 11.5 Hz[f])
cis-$Pt(O_2$–$O_2)(PPh_3)_2 \cdot CH_2Cl_2$	5.11 (3.5 Hz)	~7.33
cis-Pt(NaphthO–O)$(PPh_3)_2 \cdot CH_2Cl_2$	...; 6.98, 6.69	7.53, 7.25
trans-Pt(SPhCl-4)$_2(PPhMe_2)_2$	7.22, 6.84	7.45, 7.27; 1.71 (27.5 Hz, 7.2 Hz[g])
trans-Pt(SPhMe-4)$_2(PPhMe_2)_2$	7.27, 6.75; 2.21	7.51, 7.27; 1.68 (27.5 Hz, 7.2 Hz[g])
4-MePhSSPhMe-4	7.37, 7.08; 2.30	

[a] Phenyl protons were in general observed as multiplets, depending upon the nature of the phenyl group. $J(^{195}Pt$–H) is given in parentheses. [b] See note *a* of Table I. Lattice solvent was confirmed with ^{1}H NMR or IR. [c] The α-protons of Et_2S were inequivalent and broadened for the cis compounds. [d] Only a slightly broadened. [e] Not broadened. [f] $J(^{31}P$–H), doublet structure. [g] $J(^{31}P$–H), triplet structure.

siccator gave red crystals of unreacted K_2PtCl_4 and dark red crystals of $K_2(Cl_2O_2$–$O_2)\cdot 2H_2O$ for which excellent analytical data were obtained. When 4 mmol of $Ag_2(Cl_2O_2$–$O_2)$ was used, $K_2(Cl_2O_2$–$O_2)\cdot 2H_2O$ was isolated in 100% yield as the only product from the solution. Again the precipitate corresponded with a quantitative formation of AgCl and $[Pt(Cl_2O_2$–$O_2)]_n$. However, on prolonged stirring, the reaction mixture resulting from $Ag_2(Cl_2O_2$–$O_2)$ (2 mmol) and K_2PtCl_4 (2 mmol) at 80 °C slowly lightened in color, and after 1 day the color had turned more yellow. The precipitate was removed by filtration of the warm solution and was washed with hot water. The filtrate was set aside in a beaker to evaporate slowly in air. Yellow needles of $K_4[Pt_2(\mu$-$(Cl_2O_2$–$O_2))_2Cl_4]\cdot 6H_2O$ were obtained in 50% yield. Addition of NH_4NO_3 (tenfold excess) to the water solution gave yellow crystals of $(NH_4)_4[Pt_2(\mu$-$(Cl_2O_2$–$O_2))Cl_4]\cdot 2H_2O$.

Preparation of *trans*-$Pt_2(\mu$-$(Cl_2O_2$–$O_2))_2(Et_2S)_4$. Excess Et_2S (3 mmol) was added to a well-stirred solution of $K_4[Pt_2(\mu$-$(Cl_2O_2$–$O_2))_2Cl_4]\cdot 3H_2O$ (1 mmol) in water (20 mL). After 20 min, the light yellow precipitate was dissolved in CH_2Cl_2, and the organic layer was separated from the water layer. Evaporation of the CH_2Cl_2 solution gave the crude product. Recrystallization from CH_2Cl_2/hexane at −20 °C gave an 85% yield of yellow needles of $Pt_2(\mu$-$(Cl_2O_2$–$O_2))_2(Et_2S)_4$ which were moderately soluble in hot $CHCl_3$ or warm CH_2Cl_2.

Preparation of *cis*-$Pt(OAc)_2(PPh_3)(Et_2S)$. Triphenylphosphine (1 mmol) was added to a CH_2Cl_2 solution (5 mL) of $Pt(OAc)_2(Et_2S)_2$ (1 mmol). After 30 min, pentane (25 mL) was added to the solution and the mixture set aside at −20 °C. Fine white crystals of *cis*-$Pt(OAc)_2(PPh_3)(Et_2S)$ were obtained in 85% yield. Recrystallization from CH_2Cl_2/pentane gave colorless needles.

Preparation of *cis*-$Pt(OAc)_2(PPh_3)_2$. With 2 mmol of PPh_3, white crystals of *cis*-$Pt(OAc_2)(PPh_3)_2$ were obtained in 90% yield by an analogous reaction over a period of 3 h. With $PPhMe_2$ the corresponding cis product of dimethylphenylphosphine was obtained in a similar yield.

Preparation of *cis*-Pt(NaphthO–O)$(PPh_3)_2$. Triphenylphosphine (1 mmol) was added to a saturated solution of *cis*-Pt(NaphthO–O)$(Et_2S)_2$ (0.5 mmol) in CH_2Cl_2. After 24 h, the yellow needles of *cis*-Pt(NaphthO–O)$(PPh_3)_2$ (NaphthO–O = 2,3-dioxynaphthalene) were collected on a filter with a yield of 80%. Dark red crystals of *cis*-$Pt(O_2$–$O_2)(PPh_3)_2\cdot CH_2Cl_2$ and *cis*-$Pt(O_2$–$O_2)(PPhMe_2)_2\cdot 1.5CHCl_3$ (O_2–O_2 = 2,5-dioxybenzoquinone) were prepared similarly in CH_2Cl_2 and $CHCl_3$, respectively. Yellow crystals of *cis*-Pt(*t*-Bu_2O_2–O_2)$(PPhMe_2)_2$ were obtained from $CHCl_3$/hexane. The yields ranged from 80 to 95%.

Preparation of Pt(SPhMe-4)$_2(Et_2S)_2$. MePhSH (2 mmol) was added to a solution of $Pt(OAc)_2(Et_2S)_2$ (1 mmol) in CH_2Cl_2 (3 mL). After 30 s, hexane (10 mL) was added, and the solution was immediately concentrated under vacuum without heating. When a yellow precipitate formed, more hexane was quickly added, and the precipitate was collected on a filter. Pt(SPhMe-4)$_2(Et_2S)_2$ was vacuum dried and stored in a refrigerator. The yield was 75%. The 4-ClPh compound was obtained in an analogous manner.

Preparation of [Pt(SPhCl-4)$_2]_n$. Addition of 4-ClPhSH (2 mmol) to a CH_2Cl_2 (10 mL) solution of $Pt(OAc)_2(Et_2S)_2$ gave the slow formation of a yellow precipitate. This was collected on a filter after 1 day and vacuum dried. The resulting compound, which analyzed as [Pt(SPhCl-4)$_2(Et_2S)_{0.25}$] was formed in 70% yield. It was almost insoluble in CH_2Cl_2 or $CHCl_3$. Refluxing in $CHCl_3$ lowered the content of Et_2S although a small amount remained which was liberated by the addition of $PPhMe_2$ (^{1}H NMR).

Preparation of *trans*-$Pt(SAr)_2(PPhMe_2)_2$. Addition of 2 equiv of $PPhMe_2$ to a CH_2Cl_2 solution or suspension of $Pt(SAr)_2(Et_2S)_2$ or $[Pt(SAr)_2]_n$ gave a yellow solution. After addition of hexane, yellow needles of *trans*-$Pt(SAr)_2(PPhMe_2)_2$ (Ar = 4-MePh, 4-ClPh) formed in 80–90% yield at −20 °C. Similar compounds were obtained with PPh_3 although the reaction was much slower.

All phosphine compounds of the type Pt(O–O)$(PR_3)_2$, $Pt(O_2$–$O_2)(PR_3)_2$, and $Pt(SAr)_2(PR_3)_2$ described previously could equally well be prepared from $Pt(OAc)_2(PR_3)_2$ (PR_3 = PPh_3, $PPhMe_2$) and the corresponding acid HO–OH, HO_2–O_2H, or ArSH in yields from 80 to 95%. $Pt(OAc)_2(PPh_3)(Et_2S)$ reacted similarly.

Reaction of Iodine with *cis*-Pt(O–O)$(Et_2S)_2$. An equimolar amount of I_2 was added to a stirred $CDCl_3$ solution of *cis*-Pt(O–O)$(Et_2S)_2$ (O–O = 1,2-dioxybenzene or 3,5-di-*tert*-butyl-1,2-dioxybenzene). The ^{1}H NMR spectra showed the almost quantitative formation of *trans*-$PtI_2(Et_2S)_2$ and the free *o*-quinone.[13] Initially a very intense coloring (dark blue-green) was observed, which gradually became less intense. Spectra were in all cases compared with the spectra of original samples (Table II).

Reaction of Iodine with Pt(SPhMe-4)$_2(Et_2S)_2$. An equimolar amount of I_2 was added to a stirred solution of Pt(SPhMe-4)$_2(Et_2S)_2$ in $CDCl_3$. After 1 h the reaction was complete, and the ^{1}H NMR spectrum showed an almost quantitative formation of (4-MePhS–)$_2$ and *trans*-$PtI_2(Et_2S)_2$. Separation of the products was readily accomplished since the first compound was very soluble in pentane, while the latter was virtually insoluble.

Results and Discussion

I. Bis(carboxylato) Compounds of Platinum. Reaction of silver carboxylato compounds, AgO_2CR, with *cis*-$PtCl_2(Et_2S)_2$ (R = CH_3, CF_3, CH_2Cl, $CH(CH_3)_2$) gave new carboxylato

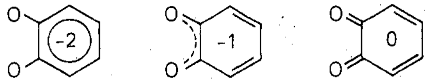

Figure 1. Three formal oxidation states of *o*-quinones.

compounds of platinum in almost quantitative yield according to eq 1. The ^1H NMR data of the compounds are summarized in Table II.

$$PtCl_2(Et_2S)_2 + 2AgO_2CR \rightarrow Pt(O_2CR)_2(Et_2S)_2 + 2AgCl \quad (1)$$

From the broad resonances and the inequivalency of the α protons of Et_2S in $Pt(O_2CR)_2(Et_2S)_2$, it was concluded that the compounds had a cis structure.[14] Turley et al. showed that cis and trans dialkyl sulfide compounds of platinum differ appreciably in kinetic behavior. Interconversion of the magnetically inequivalent α protons of the dialkyl sulfide groups was more rapid for the trans compounds due to the strong trans influence of the sulfide group.[14,15] Since oxygen donors have very weak trans effects, it would be expected that the interconversion rate of cis platinum carboxylato compounds would be even slower than for $PtCl_2(Et_2S)_2$. This has indeed been found. A decrease of this rate was found with increasing acidity of the carboxylic acid. The consequent increase in ionic character of the carboxylato group lowers the trans influence and thus the rate. This was evidenced in the series *cis*-$Pt(O_2CR)_2(Et_2S)_2$ (R = CH_3, CH_2Cl, and CF_3) in which this rate had the order $CH_3 > CH_2Cl > CF_3$. Only in the latter case the two resonances of the α Et_2S protons were not broadened at 30 °C. It is clear that in the case of *trans*-$Pt(O_2CR)_2(Et_2S)_2$, equivalent resonances would be expected as was the case with *trans*-$PtCl_2(Et_2S)_2$ at 30 °C, due to the strong mutual trans influence of the trans diethyl sulfide groups. In the case of *trans*-$Pt(O_2CCF_3)_2(i\text{-}Pr_2S)_2$ the two methyls of the isopropyl group were magnetically equivalent in all solvents tried ($CDCl_3$, CH_2Cl_2, acetone-d_6, C_6D_6) which is the reason the trans structure was assigned to this compound.

II. Substitution of OAc by *o*-Quinones. Both acetato groups of $Pt(OAc)_2(Et_2S)_2$ can be readily substituted and according to ^1H NMR in quantitative yield by *o*-quinones according to eq 2, where HO–OH = 1,2-dihydroquinone (catechol), 3-nitro-, 3-methyl-, or 3,5-di-*tert*-butylcatechol, or 2,3-dihydroxynaphthalene.

$$Pt(OAc)_2(Et_2S)_2 + HO\text{–}OH \rightarrow Pt(O\text{–}O)(Et_2S)_2 + 2HOAc \quad (2)$$

The three modes with different electronic states of this ligand are shown in Figure 1 and naturally similar structures are possible for 2,3-naphthoquinone (from 2,3-dihydroxynaphthalene).

In the case of the divalent platinum compounds described here, the first structure in Figure 1 appears the most appropriate since in the IR spectra a strong CO absorption(s) was (were) found in the region 1250–1300 cm^{-1}. Also a strong absorption was found between 1460 and 1490 cm^{-1}, assigned to a vibration of the quinone ring.[1] On the basis of the chelating character of the *o*-benzoquinones, the platinum compounds are expected to be cis. This is further confirmed by the inequivalency of the α Et_2S protons, which have broadened resonances.[14,15] Consistent with this structure, the two Et_2S groups of $Pt(3,5\text{-}t\text{-}Bu_2\text{-}1,2\text{-benzoquinone})(Et_2S)_2$ were found to be magnetically inequivalent (Table II).

Oxidation of the *o*-benzoquinone (catechol) complexes of platinum with iodine resulted in the formation of the free *o*-quinone as shown in eq 3.

$$Pt(O\text{–}O)(Et_2S)_2 + I_2 \rightarrow trans\text{-}PtI_2(Et_2S)_2 + O\text{–}O \quad (3)$$

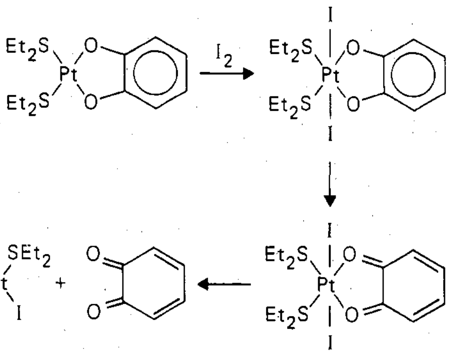

Figure 2. Proposed reaction mechanism for the oxidation of the quinone ligand coordinated to platinum.

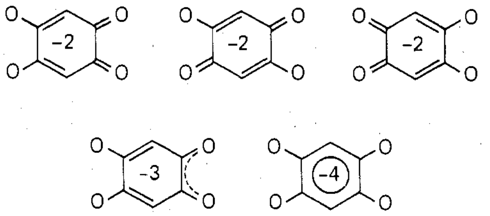

Figure 3. Three possible formal oxidation states of 2,5-dioxy-1,4-benzoquinone and the resonance structures of the dinegative anion.

A likely sequence for this reaction is oxidative addition of I_2 to platinum, giving the intermediate tetravalent platinum compound $PtI_2(O\text{–}O)(Et_2S)_2$ (O–O = 1,2-benzoquinone, 3,5-di-*tert*-butyl-1,2-benzoquinone) followed by electron transfer from the dinegative quinone ligand to platinum and formation of the corresponding divalent platinum compound, which then has a neutral quinone ligand. The preference of divalent platinum for four-coordination then results in the liberation of the free *o*-quinone. The mechanism is shown in Figure 2.

Recently electrochemical oxidations of coodinated *o*-quinones have been studied, and in the case of cobalt, the oxidation proceeds via the formation of the semiquinone complex.[1] One such a complex has been isolated.[16] The very dark initial color of the reaction mixture in the iodine oxidation of $Pt(O\text{–}O)(Et_2S)_2$ may well be the result of an intermediate semiquinone complex, formed when the electron transfer from $O\text{–}O^{2-}$ to Pt^{4+} proceeds via two one-electron processes.

III. Substitution of OAc by Dioxybenzoquinones. Reaction of $HO_2\text{–}O_2H$ ($HO_2\text{–}O_2H$ = 2,5-dihydroxybenzoquinone and 3,6-dichloro- and 3,6-diphenyl-2,5-dihydroxybenzoquinone) with $Pt(OAc)_2(Et_2S)_2$ proceeded according to eq 4, and the new dioxybenzoquinone compounds $Pt(O_2\text{–}O_2)(Et_2S)_2$ were obtained.

$$Pt(OAc)_2(Et_2S)_2 + HO_2\text{–}O_2H \rightarrow Pt(O_2\text{–}O_2)(Et_2S)_2 + 2HOAc \quad (4)$$

Complexes of this ligand have long been of interest in attempted preparations of highly conducting anisotropic transition-metal compounds. These investigations[5-7] led mostly to insoluble materials which were insulating or semiconducting. These materials were most probably polymeric due to the many coordination sites of this type of ligand. Only very few soluble nonpolymeric transition-metal complexes have been isolated, e.g., $L_2Rh(O_2\text{–}O_2)RhL_2$[8] ($O_2\text{–}O_2$ = substituted dioxybenzoquinone). In principle, three different resonance structures for the common (2–) oxidation state of this ligand are possible. In addition, three different formal oxidation states can also be distinguished. This is shown in Figure 3.

The platinum complexes of the substituted dioxybenzoquinones obtained according to reaction 4 were all highly colored due to the many possible resonance structures of this ligand. The two observed, broadened resonances of the α Et_2S protons indicated that the structure was cis. One compound,

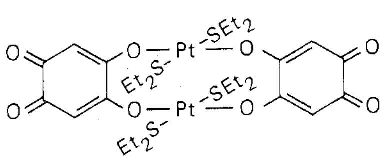

Figure 4. Proposed structure for *trans*-$Pt_2(\mu\text{-}(O_2\text{–}O_2))_2(Et_2S)_4$ (O_2–O_2 = 2,5-dioxy-1,4-benzoquinone).

cis-$Pt(C_6H_2O_4)(Et_2S)_2{\cdot}H_2O$ ($C_6H_2O_4$ = dioxybenzoquinone), could only be obtained crystalline as dark red crystals of the monohydrate by evaporation of solutions in air. However, a very slow conversion to a yellow isomer took place in CH_2Cl_2 or $CHCl_3$ solution. The ^1H NMR spectrum of this much less soluble yellow isomer showed that the α Et_2S protons were sharp and equivalent, which allowed the observation of a $^3J(^{195}Pt\text{–}H)$ coupling of 38 Hz. This low value corresponds with the value found for *trans*-$PtCl_2(Et_2S)_2$ (37.2 Hz; cf. 46.4 Hz for *cis*-$PtCl_2(Et_2S)_2$). Both factors are a strong indication that the Et_2S groups are trans.[14,15,17] A similar difference was found between the purple isomer of *cis*-$Pt(O_2\text{–}O_2)(Et_2S)_2$ (O_2–O_2 = 3,6-dichloro-2,5-dioxybenzoquinone), prepared according to eq 4 and its yellow isomer prepared according to eq 7 (later in this section). On the basis of the trans mode of the Et_2S groups and the fact that a trans chelating mode for the dioxybenzoquinone ligand is extremely unlikely, it is assumed that the yellow isomers have a dimeric structure with two bridging *trans*-dioxybenzoquinone ligands (Figure 4). Unfortunately no molecular weights could be obtained from these yellow isomers (due to their poor solubility).

The change in color from red or purple to yellow going from one isomer to the other must then be due to the fact that the plane of the quinone ligand is no longer parallel to the square-planar coordination plane of platinum. This will no doubt reduce any π overlap between the metal and the ligand and further affect the electron distribution in the ligand. The difference in electron distribution between the different isomers is also shown in the IR spectra (Nujol mull) of the compounds. Whereas the yellow isomers have "ketonic" IR absorptions at 1668 and 1704 cm^{-1} for the unsubstituted compound and at 1680 and 1720 cm^{-1} for the dichloro-substituted dioxybenzoquinone compound, the corresponding frequencies for the red and purple compounds are at 1550, 1605 and ~1540, 1640 cm^{-1}, respectively. The values for the latter two compounds and the corresponding phosphine-substituted compounds described in section V indicate appreciable loss of double bond character of the CO bonds, which results from extensive electron delocalization over all four CO bonds (see Figure 3). The values for the yellow isomers are in the ketonic region and thus indicate that the electrons are hardly delocalized in the bridged configuration.

In this respect, it is of interest to compare these findings with those of the yellow compound obtained from the reaction of $Ag_2(O_2\text{–}O_2)$ (O_2–O_2 = 3,6-dichloro-2,5-dioxybenzoquinone) with K_2PtCl_4, summarized in eq 5 and 6. The latter reaction

$$K_2PtCl_4 + 2Ag_2(O_2\text{–}O_2) \rightarrow K_2(O_2\text{–}O_2) + 4AgCl + (1/n)[Pt(O_2\text{–}O_2)]_n \quad (5)$$

$$K_2(O_2\text{–}O_2) + K_2PtCl_4 + (1/n)[Pt(O_2\text{–}O_2)]_n \rightarrow K_4[Pt_2(\mu\text{-}(O_2\text{–}O_2))_2Cl_4] \quad (6)$$

only takes place when reaction 5 is carried out with equimolar amounts of K_2PtCl_4 and $Ag_2(O_2\text{–}O_2)$. From the data given in the Experimental Section, it is concluded that reaction 5 proceeds most likely via the formation of an intermediate monomeric $PtCl_2(O_2\text{–}O_2)^{2-}$ ion, which is either unstable or immediately reacts further with $Ag_2(O_2\text{–}O_2)$ to give presumably $[Pt(O_2\text{–}O_2)]_n$. This compound then reacts further with K_2PtCl_4 to yield $K_4[Pt_2(\mu\text{-}(O_2\text{–}O_2))_2Cl_4]$ according to eq 6. The formulation of the latter compound was based on the IR absorptions (Nujol) of the CO vibrations at 1666 and 1705 cm^{-1} (as was discussed earlier). These values show that there is little or no electron delocalization over the CO bonds, indicating that the dioxybenzoquinone ligand is not in the square-planar coordination plane of platinum. Also reaction with Et_2S did not afford *cis*-$Pt(O_2\text{–}O_2)(Et_2S)_2$ but gave the yellow trans isomer formulated as *trans*-$Pt_2(\mu\text{-}(O_2\text{–}O_2))_2(Et_2S)_4$ according to eq 7.

$$K_4[Pt_2(\mu\text{-}(O_2\text{–}O_2))_2Cl_4] + 4Et_2S \rightarrow Pt_2(\mu\text{-}(O_2\text{–}O_2))_2(Et_2S)_4 \quad (7)$$

O_2–O_2 = 3,6-dichloro-2,5-dioxybenzoquinone

Attempts were made to obtain the compound $K_2Pt(O_2\text{–}O_2)_2$. Like $K_2Pt(oxalato)_2$,[18] this compound especially could have very interesting electronic properties upon partial oxidation,[18,19] since the dioxybenzoquinone ligand is very polarizable. So far these attempts have been unsuccessful.

A remarkable result of this investigation is, however, finding that the extent of electron delocalization is very dependent upon the coordination mode of this ligand (see also section V). This shows that the orbitals of the metal atom participate in this process to an appreciable extent, and possibly some contribution of a quadrinegative $O_2\text{–}O_2^{4-}$ ionic state is present.

IV. Substitution Reactions with Thiols. First acetato and subsequently diethyl sulfide substitution were observed by reacting $Pt(OAc)_2(Et_2S)_2$ with ArSH (Ar = 4-MePh, 4-ClPh), summarized in eq 8 and 9. These results were obtained by

$$Pt(OAc)_2(Et_2S)_2 + 2ArSH \rightarrow Pt(SAr)_2(Et_2S)_2 + 2HOAc \quad (8)$$

$$Pt(SAr)_2(Et_2S)_2 \rightarrow [Pt(SAr)_2(Et_2S)]_2 \rightarrow [Pt(SAr)_2]_n + Et_2S \quad (9)$$

following the reaction with ^1H NMR. Reaction 9, however, did not go to completion since analytical data for $[Pt(SAr)_2]_2$ were slightly too high in C, H, and S and too low in Pt. This indicated the presence of some residual Et_2S. On the other hand, $Pt(SPhMe\text{-}4)_2(Et_2S)_2$, which was more stable than the 4-ClPh analogue, was slightly too low in C, H, and S and too high in Pt, due to some loss of Et_2S during the preparation. The presence of some Et_2S in $[Pt(SAr)_2]_n$ was confirmed by reaction with PMe_2Ph which sets some Et_2S free (see next section). According to ^1H NMR and elemental analysis, about one molecule of Et_2S was present on every four Pt atoms.[20]

Oxidation of $Pt(SPhMe\text{-}4)_2(Et_2S)_2$ with I_2 resulted in oxidation of the arylthio groups to the corresponding disulfide as shown in eq 10. Although the reaction was slow, it proceeded in almost quantitative yield.

$$Pt(SPhMe\text{-}4)_2(Et_2S)_2 + I_2 \rightarrow PtI_2(Et_2S)_2 + (4\text{-}MePhS\text{–})_2 \quad (10)$$

V. Substitution of Et_2S by Phosphines. Previously it has been shown that the diethyl sulfide groups of $[PtMe_2(Et_2S)]_2$[21] are readily substituted, and the compound is an excellent starting material for many other dimethyl compounds of platinum. In this investigation it was found that the diethyl sulfide compounds of platinum, described in sections I–IV, all react readily in high yield with the phosphines PPh_3 and $PPhMe_2$. With $Pt(OAc)_2(Et_2S)_2$ the substitution of Et_2S is very selective since both the mono- and bis-substituted products could be obtained in high yield as shown in eq 11 and 12.

$$Pt(OAc)_2(Et_2S)_2 + PPh_3 \rightarrow Pt(OAc)_2(PPh_3)(Et_2S) + Et_2S \quad (11)$$

$$Pt(OAc)_2(PPh_3)(Et_2S) + PPh_3 \rightarrow Pt(OAc)_2(PPh_3)_2 + Et_2S \quad (12)$$

The product of reaction 11 has to be formulated as *cis*-$Pt(OAc)_2(Et_2S)(PPh_3)$ since the OAc groups are magnetically inequivalent (Table II). The unusually high-field shift of one acetato group of $Pt(OAc)_2(Et_2S)(PPh_3)$ to 1.45 ppm (Table II) is probably from the acetato group cis to PPh_3. The protons are then close to the phenyl rings of PPh_3, which results in increased shielding. A similar high-field shift of methyl resonances in triphenylphosphine-substituted compounds due to shielding of the phenyl rings has been reported previously for $(PR_3)_2(CO)IrCu(\mu\text{-DMT})Cl$.[22] By use of the same arguments, the compound $Pt(OAc)_2(PPh_3)_2$ has also to be formulated as cis, since both acetato groups have a chemical shift of 1.36 ppm.[23] If the PPh_3 groups were trans to each other, and therefore both cis to the acetato groups, a further high-field shift to about 0.80 ppm would be expected, which is not observed. The corresponding $PPhMe_2$ analogue shows for the methyl groups of $PPhMe_2$ a doublet structure in the ^1H NMR spectra with additional ^{195}Pt couplings, although some virtual phosphorus coupling was present according to the structure of these resonances.[9] This clearly indicates that the compound has to be formulated as *cis*-$Pt(OAc)_2(PPhMe_2)_2$. As expected, no unusual chemical shifts of the acetato groups were observed for this compound.

Reactions of PPh_3 or $PPhMe_2$ with $Pt(O{-}O)(Et_2S)_2$ and $Pt(O_2{-}O_2)(Et_2S)_2$ resulted in a quantitative substitution of Et_2S. This was evidenced by ^1H NMR and by the isolation of the corresponding bis-substituted phosphine compounds (Tables I and II). The methyl groups of $PPhMe_2$ in the compounds $Pt(O{-}O)(PPhMe_2)_2$ and $Pt(O_2{-}O_2)(PPhMe_2)_2$ appear as a doublet (with additional ^{195}Pt couplings) in the ^1H NMR spectra, although again some virtual phosphorus coupling was present. This clearly indicated that their configuration was cis. This configuration was further supported by the fact that in acetone solution the $PPhMe_2$ groups of $Pt(O{-}O)(PPhMe_2)_2$ (O–O = 3,5-di-*tert*-butylcatechol) are magnetically inequivalent. According to ^1H NMR, the substitution of Et_2S proceeded in two steps as was the case with $Pt(OAc)_2(Et_2S)_2$, although somewhat less selective. No attempts were made to isolate the monosubstituted compounds. The IR spectra of *cis*-$Pt(O_2{-}O_2)(PPh_3)_2$ and *cis*-$Pt(O_2{-}O_2)(PPhMe_2)_2$ ($O_2{-}O_2$ = 2,5-dioxybenzoquinone) showed two absorptions at $\sim$1545 and $\sim$1610 cm^{-1}. As was the case with the corresponding Et_2S compounds, these values indicate appreciable electron delocalization over the $O_2{-}O_2$ molecule.

Reactions of PPh_3 or $PPhMe_2$ with $Pt(SAr)_2(Et_2S)_2$ or $[Pt(SAr)_2]_n$ gave *trans*-$Pt(SAr)_2$(phosphine)$_2$, which was evidenced by the triplet structure of the methyl groups of $PPhMe_2$, due to virtual coupling resulting from the relatively large $^{31}P{-}^{31}P$ coupling in trans phosphine compounds. It should be mentioned that these thiolato compounds are analogous to the thiolato compounds of platinum previously reported by Rauchfuss et al.[9]

The same phosphine-substituted compounds of platinum, described earlier in this section, could equally well be obtained by acetato substitution of *cis*-$Pt(OAc)_2(PR_3)_2$ ($PR_3 = PPh_3$, $PPhMe_2$) with HO–OH, $HO_2{-}O_2H$, or ArSH, and in all cases the configurations were also identical. Similar acetato substitutions were observed for *cis*-$Pt(OAc)_2(PR_3)(Et_2S)$.

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Registry No. *cis*-$Pt(OAc)_2(Et_2S)_2$, 69596-67-4; *cis*-$Pt(O_2CCH_2Cl)_2(Et_2S)_2$, 69596-68-5; *cis*-$Pt(O_2CCH(CH_3)_2)_2(Et_2S)_2$, 69596-69-6; *cis*-$Pt(O_2CCF_3)_2(Et_2S)_2$, 69596-70-9; *trans*-$Pt(O_2CCF_3)_2(i\text{-}Pr_2S)_2$, 69596-71-0; *trans*-$PtI_2(Et_2S)_2$, 36389-80-7; 3,5-*t*-$Bu_2$-1,2-benzoquinone, 3383-21-9; 1,2-benzoquinone, 106-51-4; *cis*-$Pt(O\text{-}O)(Et_2S)_2$, 69596-72-1; *cis*-$Pt(t\text{-}Bu_2O\text{-}O)(Et_2S)_2$, 69596-73-2; *cis*-$Pt(NaphthO\text{-}O)(Et_2S)_2$, 69596-74-3; *cis*-$Pt(O_2\text{-}O_2)(Et_2S)_2$, 69596-75-4; *trans*-$Pt_2(\mu\text{-}(O_2\text{-}O_2))_2(Et_2S)_4$, 69596-76-5; *cis*-$Pt(Cl_2O_2\text{-}O_2)(Et_2S)_2$, 69611-31-0; *trans*-$Pt_2(\mu\text{-}(Cl_2O_2\text{-}O_2))_2(Et_2S)_4$, 69611-30-9; *cis*-$Pt(Ph_2O_2\text{-}O_2)(Et_2S)_2$, 69596-77-6; *trans*-$Pt(SPhMe\text{-}4)_2(Et_2S)_2$, 69596-78-7; *cis*-$Pt(OAc)_2(PPh_3)(Et_2S)$, 69596-80-1; *cis*-$Pt(OAc)_2(PPh_3)_2$, 31438-00-3; *cis*-$Pt(OAc)_2(PPhMe_2)_2$, 69596-81-2; *cis*-$Pt(t\text{-}Bu_2O\text{-}O)(PPhMe_2)_2$, 69596-82-3; *cis*-$Pt(O_2\text{-}O_2)(PPhMe_2)_2$, 69596-83-4; *cis*-$Pt(O_2\text{-}O_2)(PPh_3)_2$, 69596-84-5; *cis*-$Pt(NaphthO\text{-}O)(PPh_3)_2$, 69596-85-6; *trans*-$Pt(SPhCl\text{-}4)_2(PPhMe_2)_2$, 69596-86-7; *trans*-$Pt(SPhMe\text{-}4)_2(PPhMe_2)_2$, 69596-87-8; 4-MePhSSPhMe-4, 103-19-5; $K_4[Pt_2(\mu\text{-}(Cl_2O_2\text{-}O_2))_2Cl_4]$, 69596-88-9; $(NH_4)_4[Pt_2(\mu\text{-}(Cl_2O_2\text{-}O_2))_2Cl_4]$, 69596-79-8; $PtCl_2(Et_2S)_2$, 14873-92-8; K_2PtCl_4, 10025-99-7; $[Pt(SPhCl\text{-}4)_2]_n$, 69576-68-7.

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