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Syntheses and Characterization of 2,4-Dioxo-3,3-pentanediselenolato Platinum(II) Complex and Its Dithiolato Analog Prepared by Se–C and S–C Bond Cleavages of 2,3-Diseleno-1,1,4,4-tetraacetylbutane and 2,3-Dithio-1,1,4,4-tetraacetylbutane

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Synopsis. 2,4-Dioxo-3,3-Pentanediselenolato(Se_2-ac) platinum(II) complex [Pt(Se_2-ac)(PMe_2Ph)$_2$] and its dithiolato analog [Pt(S_2-ac)(PMe_2Ph)$_2$] have been prepared by treating *cis*-[$PtCl_2(PMe_2Ph)_2$] with 2,3-diseleno-1,1,4,4,-tetraacetylbutane and 2,3-dithio-1,1,4,4-tetraacetylbutane in a KOH/acetone-methanol mixed solution. The IR, ^{1}H, ^{13}C, and ^{31}P NMR and mass spectra of these complexes are discussed.

In our previous paper, a 2,4-dioxo-2-pentene-3-thiolato Pt(II) complex was prepared via the S–S bond cleavage of 2,3-dithio-1,1,4,4-tetraacetylbutane under basic conditions.[1] We have newly synthesized a 2,4-dioxo-3,3-pentanediselenolato Pt(II) complex and its dithiolato analog by treating *cis*-[$PtCl_2(PMe_2Ph)_2$] with 2,3-diseleno-1,1,4,4-tetraacetylbutane and 2,3-dithio-1,1,4,4-tetraacetylbutane in a KOH/acetone-methanol mixed solution. These novel Pt(II) complexes, which were produced via S–C and Se–C bond cleavages, were rather unstable in solution. Their IR, ^{1}H, ^{13}C, and ^{31}P NMR and mass spectra are discussed in this paper.

Experimental

Bis-(dimethylphenylphosphine)(2,4-dioxo-3,3-pentane diselenolato)platinum(II), [Pt(Se_2-ac)(PMe_2Ph)$_2$]: To *cis*-[$PtCl_2(PMe_2Ph)_2$] (0.51 g) in acetone charged with N_2 was added 0.33 g of 2,3-diseleno-1,1,4,4-tetraacetylbutane,[2] followed by KOH (ca. 0.11 g) in methanol. The solution, after stirring overnight, was evaporated to produce a brownish-orange solid. The product was developed with TLC(SiO_2) in acetone-CH_2Cl_2. An eluate of the brownish-orange band was developed again with TLC. The eluate was evaporated to produce a brownish-orange residue, which was crystallized from CH_2Cl_2-hexane to give brownish-orange needles (0.25 g: 37%). Anal. Found: C, 34.68; H, 3.90%. Calcd for $C_{21}H_{28}O_2P_2Se_2Pt$: C, 34.67; H, 3.88%. Electron impact mass spectrum (In-beam direct method at 70 eV). *m/z* 727 M$^+$, 684 [M-CH_3CO]$^+$, 648 [M-Se]$^+$. [Pt(Se_2-ac)(PMe_2Ph)$_2$] is soluble in $CHCl_3$, CH_2Cl_2, and acetone, but is insoluble in diethylether and hexane. The complex in CH_2Cl_2 or $CHCl_3$, by allowing the solution to stand fo several hours, undergoes a decompositon.

Bis-(dimethylphenylphosphine)(2,4-dioxo-3,3-pentane dithiolato)platinum(II), [Pt(S_2-ac)(PMe_2Ph)$_2$]: To *cis*-[$PtCl_2(PMe_2Ph)_2$] (0.6 g) in acetone charged with N_2 was added 0.29 g of 2,3-dithio-1,1,4,4-tetraacetylbutane,[3,4] followed by KOH (ca. 0.13 g) in methanol. After stirring the solution for 2 d, a white precipitate was filtered, and the filtrate was evaporated. A brownish-orange product was developed with TLC(SiO_2) in acetone-CH_2Cl_2. A brownish-orange band was eluted by acetone-methanol. The eluate, after the addition of diethylether and hexane, was allowed to stand in a refrigerator for 3 d to give a brownish-orange solid (0.41 g: 52% yield). Anal. Found: C, 39.82; H, 4.47%. Calcd for $C_{21}H_{28}O_2P_2S_2Pt$: C, 39.81; H, 4.45%. The complex is soluble in CH_2Cl_2, $CHCl_3$, and acetone, but is insoluble in hexane. The complex gradually decomposes in CH_2Cl_2 or $CHCl_3$ and changes into an insoluble white solid whose empirical formula is [Pt(SCO-ac)(PMe_2Ph)$_2$], with its molecular ion at *m/z* 628 (100) by SIMS. This white product has not been characterized. SIMS of [Pt(S_2-ac)(PMe_2Ph)$_2$](3-nitrobenzyl alcohol). *m/z* 633 (5) M$^+$, 602 (13) [Pt(S-ac)(PMe_2Ph)$_2$]$^+$, 471 (12) [Pt(PMe_2Ph)$_2$]$^+$, 336 (56) [Pt(PMe_2Ph)]$^+$. The other intense peaks at 455 (100) and 488 (56) were assigned to [Pt($C_6H_4NO_2$)(PMe_2Ph)]$^+$ and [PtS($C_6H_4NO_2$)(PMe_2Ph)]$^+$ which may be formed by a decomposition in the matrix. In addition, a peak was observed at *m/z* 628 (38).

Elemental analyses were performed at the micro Analytical Center, Kyoto University. ^{1}H NMR spectra at 90.04 MHz and ^{13}C NMR spectra at 22.66 MHz were recorded on a Hitachi R-90-H FT NMR spectrometer operating Fourier transform modes in sealed tubes saturated with N_2. The IR spectra were recorded on a Hitachi 260-10 infrared spectrometer. An electron impact mass spectrum was, recorded on a Hitachi M-80 mass spectrometer and secondary ion mass spectra were produced using 3-nitrobenzyl alcohol as a matrix and Xe gas as the first ion source.

Results and Discussion

2,3-Diseleno-1,1,4,4-tetraacetylbutane[2] has been obtained from 2,2,4,4-tetraacetyl-1,3-diselenetane[2,3] by reducing it with aq HI. 2,3-Diseleno-1,1,4,4-tetraacetylbutane has a dienolic from both in solid and solution, which is analogous with 2,3-diseleno-1,1,4,4-tetraacetylbutane.[3,4] These bis(β-dicarbonyls) ligands linked by selenium or sulfur atoms between the two β-diketones under basic conditions readily undergo a cleavage of the M–M or M–C (M=S or Se) bond. We have thus prepared a 2,4-dioxo-2-pentene-3-thiolato Pt(II) complex[1] via an S–S bond cleavage of 2,3-dithio-1,1,4,4-tetraacetylbutane. A treatment of *cis*-[$PtCl_2(PMe_2Ph)_2$] with 2,3-diseleno-1,1,4,4-tetraacetylbutane and 2,3-dithio-1,1,4,4-tetraacetylbutane in a KOH/acetone–methanol mixed solution gave 2,4-dioxo-3,3-pentanediselenolato (Se_2-ac) and -dithiolato (S_2-ac) Pt(II) complexes, [Pt(Se_2-ac)(PMe_2Ph)$_2$] and [Pt(S_2-ac)(PMe_2Ph)$_2$] via a Se–C′ and an S–C′ bond cleavage of the corresponding bis(β-dicarbonyls) respectively.

Table 1. ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR and IR spectral data for [Pt(M_2-ac)(PMe_2Ph)$_2$] (M=S, Se)

Compound	IR[a)] (C=O)		^{1}H NMR[b)] δ_{Me}	δ_{Me} (PMe_2Ph)	^{13}C NMR[c)] δ_{CO}	δ_{Me}	δ_{C^3}	δ_{Me} (PMe_2Ph)	^{31}P NMR[d)]
DSTAB[e)]			2.43						
TADSN[f)]	1687(vs)	1673(vs)	2.63			24.67			
[Pt(Se_2-ac)(PMe_2Ph)$_2$]	1699(vs)	1656(vs)	2.64	1.51 (9.78) [33.98] (0.18) [34.07]	205.59 [18.66]	24.39	59.0 [53.89]	13.32 (19.69) [39.38]	−21.13 [2947.41]
[Pt(S_2-ac)(PMe_2Ph)$_2$]	1700(vs)	1670(vs)	2.52	1.52 (9.00)	206.66 [22.8]	23.69	82.2 [55.97]	13.08 (19.69) [58.72]	

a) In cm^{-1}; Measured in CH_2Cl_2. b) Measured in $CDCl_3$; Chemical shifts are relative to $SiMe_4$. J(P-H) and J(Pt-H) are in parentheses and brackets respectively. c) Measured in $CDCl_3$; Chemical shifts are relative to $SiMe_4$. J(P-C) and J(Pt-C) are in parentheses and brackets respectively. d) Measured in $CDCl_3$; Chemical shift is relative to 85% H_3PO_4. J(^{195}Pt-P) is in bracket. e) 2,3-Diseleno-1,1,4,4-tetraacetylbutane is abbreviated as DSTAB. f) 2,2,4,4-Tetraacetyl-1,3-diselenetane is abbreviated as TADSN.

The ^{1}H, ^{13}C, and ^{31}P NMR and IR spectral data of [Pt(M_2-ac)(PMe_2Ph)$_2$] (M=Se, S) are given in Table 1. Carbonyl stretching absorption bands observed for [Pt(Se_2-ac)(PMe_2Ph)$_2$] are at 1699 and 1656 cm^{-1}, and exhibit two carbonyls of the 2,4-pentanedione group in the keto form. The other absorption pattern very closely resembles those of 2,2,4,4-tetraacetyl-1,3-diselenetane. ^{1}H NMR resonance arising from methyl protons of the 2,4-pentanedione in the complex at 2.64 is appreciably close to 2.63 of 2,2,4,4-tetraacetyl-1,3-diselenetane. These spectral data indicate that two acetyl group of the 2,4-pentanedione is symmetrically arranged in the complex. A ^{13}C NMR resonance arising from its C^3 at 59.0 is in a region which is sufficiently higher field as observed for the central carbon bonded complexes of 2,4-pentanedione[5)] and 1,1,2,2-tetraacetylethane.[6)] J(^{195}Pt-C) 53.89 found in [Pt(Se_2-ac)(PMe_2Ph)$_2$] apparently exhibits no Pt-C bond included, but Se-C^3 bonds maintained.[7)] Resonance arising from methyl carbons of the 2,4-pentanedione group in the complex, as is consistent with its ^{1}H NMR, shows a singlet at 24.39, which is also noticeably close to 24.67 of 2,2,4,4-tetraacetyl-1,3-diselenetane. On the other hand, the ^{13}C NMR resonance arising from the methyl carbons of PMe_2Ph unexpectedly exhibits an ABC spin system (Fig. 1), but no AB spin system as predicted for the phosphines arranged at a cis-position mutually. The spectrum is in good agreement with the simulated lines of [ABC(3.5)+ABCM(1)] with $J_{AB}=J_{AC}=19.69$ Hz and $J_{AM}=39.38$ Hz. This ABC spin system which arises from ^{31}P-^{31}P coupling could not be discerned in its ^{1}H NMR spectra as observed in *trans*-[PtI_2(PMe_2Ph)$_2$] and [Pd(PMe_2Ph)$_3$(2,9-R_2-phen)][BF_4]$_2$.[9)] The ^{13}C NMR at the present case suggests that two phosphines in the complex are symmetrically arranged with the P-Pt-P bond angle fairly unusually expanded from 90° to give a ^{31}P-^{31}P coupling magnetically. Its ^{31}P NMR with J(Pt-P)=2947 Hz is consistent with the ^{13}C NMR, and the J(Pt-P) is intermediate between 2379 Hz for *trans*-[$PtCl_2$(PMe_3)$_2$][10)] and 3480 Hz for *cis*-[$PtCl_2$(PMe_2Ph)$_2$],[11)] in addition to 2311 and 3407 Hz for [PtCl(PMe_2Ph)$_3$][PF_6].[1)] [Pt(Se_2-ac)(PMe_2Ph)$_2$] is relatively unstable in solution. Its EIMS by In-beam direct method, however, explicitly shows a molecular ion peak at m/z 727. The structure of [Pt(Se_2-ac)(PMe_2Ph)$_2$] is supposed to have a high symmetry with a diselenetane framework in which the 2,4-dioxo-3,3-pentanediselenolate ligand bonds to Pt(II) as a (η^2-Se_2)-linkage, as is found in a diselenocarbonate Rh(III) complex.[12)] Any other conceivable structure

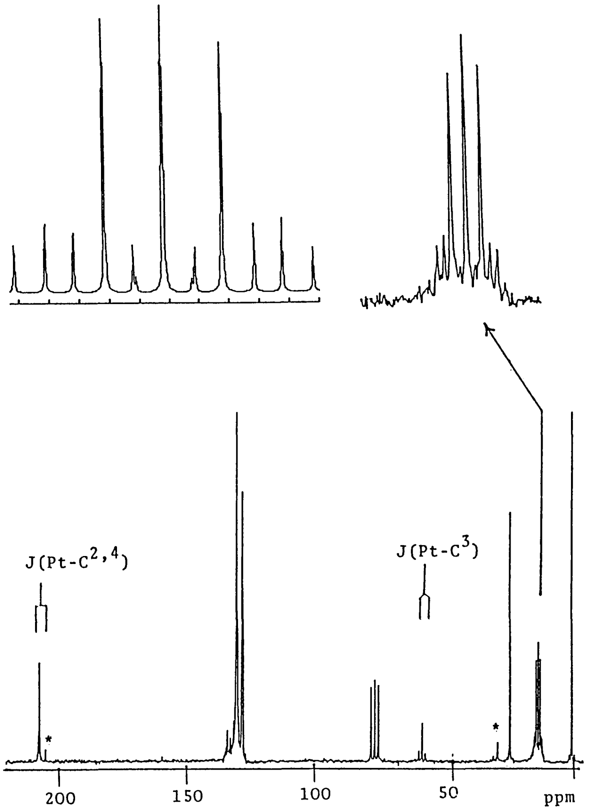


Fig. 1. ^{13}C{^{1}H} NMR spectrum of [Pt(η^2-Se_2-ac)(PMe_2Ph)$_2$] in $CDCl_3$ and a simulated line as ABC spin system (expanded) of Me-carbons of PMe_2Ph. *An acetone impurity included.

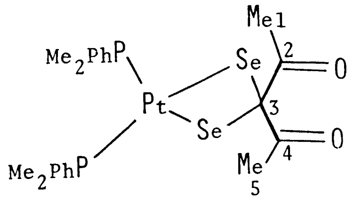
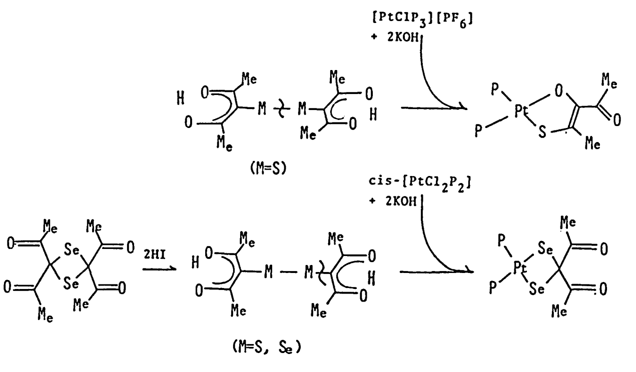


Fig. 2. A supposed structure of [Pt(Se_2-ac)($PMe_2Ph)_2$].

for [Pt(Se_2-ac)($PMe_2Ph)_2$], in which a 3-acetyl-4-oxo-1,2-pentanediselenolate ligand may bond to Pt(II) as a (C^3, Se)-chelate, can be excluded since no corresponding J(Pt-C^3) could be obtained and the ^{31}P NMR datum explicitly shows an equivalency of the phosphines. It is also unlikely that the 2,4-dioxo-3,3-pentanediselenolate ligand with a diselenetane framework having a Se-Se bond can coordinate Pt(O) through its oxygen atoms, since $J(\text{Pt-C}^{2,4})=18.66$ Hz observed in [Pt(Se_2-ac)($PMe_2Ph)_2$] is quite different from such a presumed configuration.[13]

[Pt(S_2-ac)($PMe_2Ph)_2$] is less stable than the corresponding diselenolato Pt(II) complex, and gradually decomposes in $CHCl_3$ producing an insoluble white precipitate(uncharacterized). The ^{1}H and ^{13}C NMR data of [Pt(S_2-ac)($PMe_2Ph)_2$] listed in Table 1 involve resonances due to this white species(10—15% included under the condition). The predominant resonances due to [Pt(S_2-ac)($PMe_2Ph)_2$] are however sufficiently comparable with those of [Pt(Se_2-ac)($PMe_2Ph)_2$]. SIMS datum of [Pt(S_2-ac)($PMe_2Ph)_2$] exhibited a molecular ion peak at m/z 633 with a relatively weak intensity(5), although the spectrum was accompanied by an intense peak at m/z 628 due to the white product already formed by a decomposition in the matrix (experimental section).

[Pt(η^2-M_2-ac)($PMe_2Ph)_2$] (M=S, Se) produced via a Se′-C′ or S′-C′ bond cleavage of 2,3-diseleno-1,1,4,4-tetraacetylbutane and 2,3-dithio-1,1,4,4-tetraacetylbutane may be given by supposing subsequent reaction steps: a Se′-C′ or S′-C′ bond cleavage of the 3,3′-diseleno or -dithiobis (β-dicarbonyls) and a synchronous Se′-C or S′-C bond formation causes a Se-Se′ or S-S′ bond cleavage resulting in the formation of M_2-ac^{2-}, and a following metathesis of the complex. A 2,4-dioxo-2-pentene-3-thiolato Pt(II) complex[1] was previously isolated via an S-S′ bond cleavage of 2,3-dithio-1,1,4,4-tetraacetylbutane under basic conditions. In the present case, no analogous 2,4-dioxo-2-pentene-3-selenolato Pt(II) complex was obtained, which may be formed via a Se-Se′ bond cleavage of 2,3-diseleno-1,1,4,4-tetraacetylbutane. It should also be noticed that 2,2,4,4-tetraacetyl-1,3-diselenetane undergoes a cleavage of the Se-C′ bonds by reducing with aq HI to afford 2,3-diseleno-1,1,4,4-tetraacetylbutane with a Se-Se′ bond. Accordingly, a supposed rearrangement forming (η^2-M_2)-bonding to the metal interestingly seems to be a reversed pattern from the reaction cited above (Scheme 1). Yet, J(Pt-P) obtained in [Pt(Se_2-ac)($PMe_2Ph)_2$] may be valid only in the configuration of a d-8 electron species.



Scheme 1. (Reaction scheme of S-S, S-C, and Se-C bond cleavages of 2,3-dithio-1,1,4,4-tetraacetylbutane and 2,3-diseleno-1,1,4,4-tetraacetylbutane).

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