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Synthesis and Characterization of a 2,4-Pentanedione-3-selenolato Pt(II) Complex. Oxidation Reaction of Tetrakis(triphenylphosphine)platinum(0) with 2,2,4,4-Tetraacetyl-1,3-diselenetane

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A new Pt(II) complex of 2,4-pentanedione-3-selenolate dianion(Se-ac), [Pt(Se-ac-O, Se)(PPh_3)$_2$], has been prepared by reacting tetrakis(triphenylphosphine)platinum(0) with 2,2,4,4-tetraacetyl-1,3-diselenetane. The complex has been characterized from IR, ^1H, ^{13}C, and ^{31}P NMR spectroscopy.

The bis(β-diketones) linked by sulfur and selenium atoms between the two β-dicarbonyls, 2,3-dithio-1,1,4,4-tetraacetylbutane and 2,3-diseleno-1,1,4,4-tetraacetylbutane, are in dienol form[1,2] and they relatively readily undergo S-S, S-C, and Se-C bond cleavages in presence of OH^- in preference to Se-Se bond cleavage. In the previous papers, Pt(II) complexes of 2,4-pentanedione-3-thiolate(2-) with an (O, S)-chelate and 2,4-dioxo-3,3-pentanedithiolate(2-) and 2,4-dioxo-3,3-diselenolate(2-) with a (η^2-M_2)(M=S, Se)-bond fashion have been prepared[3,4] by treating *cis*-[$PtCl_2$(PMe_2Ph)$_2$] with the dienolic bis(β-diketones) in basic conditions. In the present paper, a new Pt(II) complex of 2,4-pentanedione-3-selenolate(2-) with an (O, Se)-chelate has been prepared from a novel oxidation reaction of $Pt(PPh_3)_4$ with the bis(β-diketones), 2,2,4,4-tetraacetyl-1,3-diselenetane which is in diketo form.[2] This complex could not have been obtained by the similar method following the preparation of the thiolato complex.

$Pt(PPh_3)_4$ in $CHCl_3$ *in situ* degassed of air in *vacuo* was added with an *equi*-molar quantity of 2,2,4,4-tetraacetyl-1,3-diselenetane. The solution, after sirring overnight, was reduced in volume under reduced pressure to ≈ 10 cm^3, and addition of diethylether and hexane to the solution gave an orange crude product(≈ 74% yield). The product was then developed on TLC(SiO_2) with CH_2Cl_2-acetone. An eluate of an orange band in acetone gave an orange crystalline solid of the complex. The result of the elemental analysis was in agreement with the calculated values as $[Pt(Se\text{-}ac)(PPh_3)_2]$(Se-ac =2,4-pentanedione-3-selenolate dianion). IR, ^1H, ^{13}C, and ^{31}P NMR of the complex are consistent with a 2,4-pentanedione-3-selenolate(2-), formed by a reduction of 2,2,4,4-tetraacetyl-1,3-diselenetane *via* its Se-C bond cleavages, bonding to Pt(II) with an (O, Se)-chelate and they are quite com parable to those of $[Pt(S\text{-}ac\text{-}O, S)(PMe_2Ph)_2]$.[3] Two ^1H NMR resonances arising from Me-protons of the Se-ac(2-) in $[Pt(Se\text{-}ac)(PPh_3)_2]$ exhibit that a structure of the complex has low symmetry in which the Se-ac^{2-} bonds Pt(II)

Table 1. IR, ^1H, ^{13}C, and ^{31}P NMR of $[Pt(Se\text{-}ac\text{-}O, Se)(PPh_3)_2]$

IR(cm^{-1})[a]	^1H NMR[b]		^{31}P NMR[c]	^{13}C NMR{ppm, ( )=Hz}[d]				
ν(C=O)	{ppm, ( )=Hz}		{ppm, ( )=					
ν(C=C)	$\delta_{C^5H_3}$	$\delta_{C^1H_3}$	[ ]=Hz	C-2	C-4	C-3	C-5	C-1
ν(C-O)								
1614(s)	2.27(3)	1.90(3)	20.91 6.70	194.50	182.19	102.98	30.90	26.03
1592(m)	(1.52)	(1.52)	(22.8)(22.8)	(d)	(8.55,	(dd)	(1.83)	(4.89)
1484(vs)			[2871.7][3610.2]		2.44)			

a)Measured in CH_2Cl_2. b)Measured in $CDCl_3$. Chemical shifts are relative to $SiMe_4$. J(P-H) are in parentheses. c)Measured in $CDCl_3$. Chemical shifts are relative to $P(OMe)_3$ at 140.0. J(P-P) and J(^{195}Pt-P) are in parentheses and brackets, respectively. d)Measured in $CDCl_3$. Chemical shifts are relative to $SiMe_4$. J(P-C) are in parentheses.

with an (O, Se)-chelate. Its ^{31}P NMR shows an AB spin system explicitly, as is expected from the ^{1}H NMR, with $J(^{195}Pt\text{-}P)=2871$ and 3610 Hz. These values are rather close to a *cis*-configuration for the two phosphorous atoms than a *trans* one. One of the J(Pt-P) with a relatively small value may be explained by a distortion in the bond angle P-Pt-P deviating from an ideal angle 90° of a square planar structure, as found for $[Pt(S\text{-ac-}O, S)(PMe_2Ph)_2]$[3] and $[Pt(\eta^2\text{-}Se_2\text{-ac})(PMe_2Ph)_2]$.[4] ^{13}C NMR of $[Pt(Se\text{-ac-}O, Se)(PPh_3)_2]$ is consistent with a localized structure of the $Se\text{-ac}^{2-}$ coordinating to Pt(II) with an (O, Se)-chelate. The IR spectrum of the complex, in fact, shows three characteristic absorption bands in which two absorption bands observed at 1484 and 1592 cm^{-1} were assigned due to ν(C–O) and ν(C=C), respectively, while a strong band at 1614 cm^{-1} is due to ν(C=O). The relatively lower frequency region due to the carbonyl stretching at the present case is comparable with 1613 cm^{-1} observed for $[Rh(acac\text{-}O_1)(CO)(PPr^i_3)_2]$[5] possesing an O-unidentate 2,4-pentanedione and 1621 cm^{-1} for $[Pt(S\text{-ac-}O, S)(PMe_2Ph)_2]$.[3]

2,2,4,4-Tetraacetyl-1,3-Diselenetane by reducing with *aq* HI undergoes its Se-C bond cleavages to afford 2,3-diseleno-1,1,4,4-tetraacetylbutane with Se-Se bond.[2] $[Pt(Se\text{-ac-}O, Se)(PPh_3)_2]$ may accordingly be formed *via* two reaction paths: one, a reduction of 2,2,4,4-tetraacetyl-1,3-

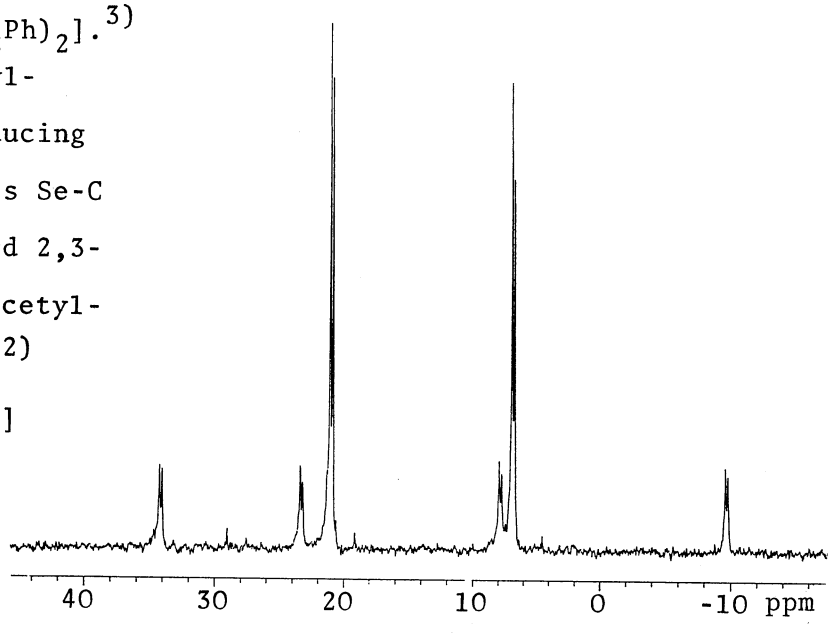
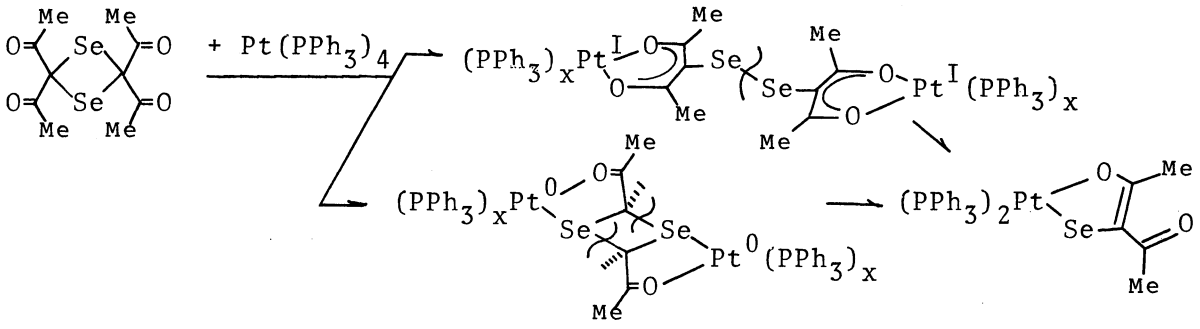


Fig. 1. ^{31}P NMR of $[Pt(Se\text{-ac-}O, Se)(PPh_3)_2]$.

diselenetane by $Pt(PPh_3)_4$ forms 2,3-diseleno-1,1,4,4-tetraacetylbutane(2-), first, which may cross-links two Pt(I) nuclei with an (O_2, O'_2)-chelate, as found for 1,1,2,2-tetraacetylethane complexes,[6] and a succeeding Se-Se bond cleavage occurs *via* an electron transfer resulting a Pt-O bond disso ciation and a concurrent Pt-Se bond formation; the other, a dinuclear Pt(0) complex cross-linked by 2,2,4,4-tetraacetyl-1,3-diselenetane with an (O, Se)-chelates undergoes two electron transfers by one step from the respective metals to the ligand accompanying simultaneous Se-C bond cleavages.



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