Polyhedron Vol. 7, No. 5, pp. 353–361, 1988
Printed in Great Britain

0277–5387/88 $3.00+.00
Pergamon Press plc

BRIDGE-SPLITTING REACTION OF A DINUCLEAR PLATINUM(II) COMPLEX CROSS-LINKED BY TETRA-ACETYLETHANE DIANION $[Pt_2(L_2)_2(dahd\text{-}O_2,O_2')][BF_4]_2$ (dahd=TETRA-ACETYLETHANE; L=SEt_2, PMe_2Ph; L_2 = 1,5-CYCLOOCTADIENE); METAL–CARBON BONDED PLATINUM(II) COMPLEX OF TETRA-ACETYLETHANE WITH (C^3,O′)-CHELATE

SHINSAKU YAMAZAKI*

Chemistry Laboratory, Gakuen College Kochi, 292 Asahi Tenjin-cho, Kochi 780, Japan

TOMOHARU AMA

Department of Chemistry, Faculty of Science, Kochi University, 2-5-1 Akebono-cho,
Kochi 780, Japan

and

ZENEI TAIRA

Department of Pharmaceutical Sciences, Tokushima Bunnri University,
180 Boji Yamashiro-cho, Tokushima 770, Japan

(*Received* 10 *April* 1987; *accepted after revision* 16 *September* 1987)

Abstract—A Pt(II) complex of tetra-acetylethane (dahd = 3,4-diacetyl-2,4-hexadiene-2,5-diol) dianion bonding with (C^3,O′)-chelate, Pt(L)(L′)(dahd-C^3,O′){L = L′ = SEt_2; L = L′ = PMe_2Ph; L = SEt_2, L′ = PPh_3; L = L′ = 2,9-R_2-1,10-phen(R = H, Me) where L′ is *trans* to C^3} has been prepared. *cis*-$PtCl_2L_2$(L = SEt_2, PMe_2Ph) reacts with K_2-dahd in CH_3OH to produce a dinuclear cationic complex $[Pt_2L_4(dahd\text{-}O_2,O_2')]^{2+}$ in which dahd is cross-linked with symmetrical bifunctional chelation. An analogous COD (1,5-cyclooctadiene) complex $[Pt_2(COD)_2(dahd\text{-}O_2,O_2')][BF_4]_2$ has been prepared by treating $PtCl_2$(COD) with $AgBF_4$ and H_2-dahd. $[Pt_2L_4(dahd\text{-}O_2O_2')][BF_4]_2$, by treating with K_2-dahd, readily transforms into PtL_2(dahd-C^3,O′) (L = SEt_2, PMe_2Ph). This PtL_2(dahd-C^3,O′)(L = SEt_2, PMe_2Ph) in HBF_4/acetone solution converts to the dinuclear complex $[Pt_2L_4(dahd\text{-}O_2,O_2')][BF_4]_2$, liberating H_2-dahd in a stoichiometric yield.

These anomalous Pt(II) complexes linked by the dahd dianion are characterized using IR, ^1H, ^{13}C-NMR and fast atom bombardment mass spectroscopy, conductance and molecular weight measurements.

Dinuclear Pd(II) and Rh(I) complexes of tetra-acetylethane (dahd = 3,4-diacetyl-2,4-hexadiene-2,5-diol) cross-linking two metal nuclei as bifunctional O_2-chelates have been described before.[1] In them, a reaction of $[Pt_2(PPh_3)_4(dahd\text{-}O_2,O_2')][BF_4]_2$ with the bidentate azaheterocyclic ligand phen have been seen to undergo an anomalous bridge-splitting between the two metal nuclei giving a five-coordinate complex $[Pd(PPh_3)(phen)_2][BF_4]_2$,[2] and concurrently an insoluble complex containing dahd cross-linking of the metal nuclei as an O_1-uni, O_1'-unidentate ligand $[Pd(phen)(dahd\text{-}O_1,O_1')]_n$. The latter product readily transforms into its linkage isomer with a metal–carbon bond Pd(phen)(dahd-

---

*Author to whom correspondence should be addressed.

C^3,O′). Knowing that H_2-dahd itself is stabilized in a dienolate form as a γ,γ'-bis(acetylacetone),[1] the activation of its C(3) to form a M–C bond has been an unexpected result. Some evidence for catena-[Pd(phen)(dahd-O_1,O_1')]$_n$ which somewhat surprisingly accompanies a trace amount of paramagnetic species may indicate that this novel linkage isomerization of the dahd from (O_2,O_2')-chelate to (C_3,O′)-chelate proceeds via a two electron transfer from the dahd ligand to the metal or to the other ligand.

One problem in these Pd(II) complexes is that the reaction products were obtained in low yields as the stoichiometry indicates, in addition to their low solubilities. From these previous findings, we have thus attempted the syntheses and characterizations of dinuclear and mononuclear Pt(II) complexes in which the dahd dianion links Pt(II) as a bidentate O_2-chelate and (C^3,O′)-chelate, using a monodentate SEt_2 or PMe_2Ph and bidentate 1,5-COD as ligands.

EXPERIMENTAL

Preparation of complexes—[$Pt_2(SEt_2)_4$(dahd-O_2,O_2')] $[BF_4]_2$

cis-$PtCl_2(SEt_2)_2$[3] (3.0 g) in acetone containing 1.4 g of H_2-dahd was added with $AgBF_4$ (2.8 g) and the solution after stirring for 2 h, was filtered (2 g of AgCl ppt. 200% per Pt atom). The solution was then evaporated forming a yellow oil. The oil product was washed with water to remove liberated HBF_4. The residue was dried *in vacuo* and crystallized from acetone–diethylether to give white crystals (2.7 g; 71%). Found: C, 27.7; H, 4.6. Calc. for $C_{18}H_{16}O_4B_2F_8$: C, 27.9; H, 4.7%. Conductance (acetone): Λ_M, 224 Ω^{-1} cm^2 mol^{-1}.

[$Pt_2(PMe_2Ph)_4$(dahd-O_2,O_2')] $[BF_4]_2$

cis-$PtCL_2(PMe_2Ph)_2$[4] (0.7 g) was dissolved in mixed solvents of CH_2Cl_2–CH_3OH containing 0.16 g of H_2-dahd. To the solution, 0.52 g of $AgBF_4$ was added. The solution, after stirring for 2 h, was filtered (0.34 g of AgCl ppt. 181% per Pt atom), reduced in volume to $\sim$ 5 cm^3 and addition of diethylether to the residual solution gave pale brown crystals (0.74 g; 87% per Pt atom). Found: C, 37.2; H, 4.3. Calc. for $C_{21}H_{30}O_3BF_4P_2Pt$ (with one water of solvation): C, 37.4; H, 4.5%. ^{1}H NMR{$CDCl_3$-$(CD_3)_2CO$}: δ_H (water of solvate ion), 5.2 $\sim$ 5.3 ppm(vb). The signal due to the hydrogen from water which is always concomitant with the solvent $(CD_3)_2CO$ is observed at $\sim$ 3.00 ppm and is relatively sharp. Conductance (acetone): Λ_M, 236 Ω^{-1} cm^2 mol^{-1}.

[$Pt_2(COD)_2$(dahd-O_2,O_2')] $[BF_4]_2$

$PtCl_2(COD)$[5] (1.3 g) was dissolved in CH_2Cl_2 containing 0.4 g of H_2-dahd. To this solution, an acetone solution of $AgBF_4$ (1.3 g) was added. The solution, after stirring overnight, was filtered (0.9 g of AgCl ppt. 185% per Pt atom). The filtrate was then added to silica gel and filtered. The solution was reduced in volume to $\sim$ 5 cm^3 under pressure, and addition of diethylether to the residual solution gave pale brown crystals (1.1 g; 63% per Pt atom). Found: C, 31.3; H, 3.7. Calc. for $C_{13}H_{20}O_3BF_4Pt$ (with one water of solvation): C, 30.9; H, 4.0%. ^{1}H NMR{$(CD_3)_2CO$}: δ_H(H_2O of solvation), 3.0 ppm(vb). Conductance (acetone): Λ_M, 226 Ω^{-1} cm^2 mol^{-1}.

$Pt(SEt_2)_2$(dahd-C^3,O′)

cis-$PtCl_2(SEt_2)_2$ (0.3 g) in CH_3OH was mixed with 0.2 g of K_2-dahd[1] and a few drops of NEt_3. The solution was stirred for 16 h and then filtered. The filtrate was evaporated. The residue was dissolved in about 20 cm^3 of CH_2Cl_2 and the solution was transferred to a separating funnel. After addition of an equi-volume of H_2O, the solution was vigorously shaken to mix. The CH_2Cl_2 phase was transferred to a round bottom flask and the solvent was removed under reduced pressure to give a yellow oil. After drying *in vacuo*, the product was crystallized from CH_2Cl_2–diethylether to give pale brown micro-crystals (0.13 g; 34%). When the reaction oily product is not washed with H_2O, the yield of crystal product is raised to 78%. Found: C, 37.8; H, 5.6. M.W. (cryoscopic method in $C_6H_5NO_2$), 381. Calc. for $C_{18}H_{32}O_4S_2Pt$: C, 37.8; H, 5.6%. M = 572. ^{1}H, ^{13}C NMR are in *vide infra*. The low molecular weight measurement in nitrobenzene suggests that one SEt_2 of the complex is displaced in solution by the nitrobenzene solvent. FABMS: $M^+ = 572$ (*vide infra*).

$Pt(SEt_2)_2$(dahd-C^3,O′) was also obtained by treating [$Pt_2(SEt_2)_4$(dahd-O_2,O_2')] $[BF_4]_2$ with K_2-dahd in CH_3OH. When [$Pt_2(SEt_2)_4$(dahd-O_2,O_2')] $[BF_4]_2$ (0.75 g) was added to K_2-dahd (0.2 g) in CH_3OH the pale yellow solution turned dark yellow. The solution, after stirring for a day, was filtered to separate a small amount of dark white ppt. The solvent was then removed under reduced pressure to give a pale brown oil, which was washed with water and decanted. The oily residue, after being dried *in vacuo*, was crystallized from CH_2Cl_2–diethylether to give white crystals (0.64 g; 84% per Pt atom).

$Pt(PPh_3)(SEt_2)$(dahd-C^3,O′)

$Pt(SEt_2)_2$(dahd-C^3,O′) (0.24 g) in CH_2Cl_2 was added to 0.22 g of PPh_3. The solution was stirred for 1 day and reduced in volume under pressure to about 5 cm^3. Addition of diethylether and *n*-hexane to the residual solution gave a pale yellow solid, which was recrystallized from CH_2Cl_2 and diethylether (0.24 g; 79%). Found: C, 51.3; H, 5.0. M.W. (vapour pressure osmometry in CH_2Cl_2) 680. Calc. for $C_{32}H_{37}O_4PSPt$: C, 51.7; H, 5.0. M = 744.

Pt(phen)(dahd-C^3,O′)

$Pt(SEt_2)_2$(dahd-C^3,O′) (0.11 g) was dissolved in CH_2Cl_2 and to the solution 0.05 g of phen · H_2O was added. The solution was stirred for about a week giving a pale orange precipitate. The product was crystallized from CH_2Cl_2 using isothermal vaporization (0.09 g; 82%). Found: C, 47.0; H, 3.6; N, 5.0. M.W. (vapour pressure osmometry in CH_2Cl_2) 532. Calc. for $C_{20}H_{24}N_2O_4Pt$: C, 46.2; H, 3.5; N, 4.9%. M = 574.

Pt(2,9-Me_2-phen)(dahd-C^3,O′)

$Pt(SEt_2)_2$(dahd-C^3,O′) (0.12 g) in CH_2Cl_2–acetone was added with 2,9-Me_2-phen · $0.5H_2O$ (0.06 g). The solution was refluxed for about a week and then diethylether and *n*-hexane were added. On allowing the solution to stand in a refrigerator overnight an orange solid with CH_2Cl_2 of solvate (0.08 g; 55%) was produced. Found: C, 44.0; H, 3.9; N, 4.1. Calc. for $C_{25}H_{26}Cl_2N_2O_4Pt$: C, 43.9; H, 3.8; N, 4.1%. ^1H NMR ($CDCL_3$): δ_{CH_2}(CH_2Cl_2 of solvate) 5.23 ppm.

$Pt(PMe_2Ph)_2$(dahd-C^3,O′)

cis-$PtCl_2(PMe_2Ph)_2$ (0.63 g) was suspended in CH_3OH and 0.3 g of Na_2-dahd-$(CH_3OH)_x$ and NEt_3 (0.25 g) was added, giving a homogeneous solution. The solution, after stirring for 5 days (the time required to produce a small amount of dark white solid) was filtered. The solvent was removed under reduced pressure to give a pale green oil, which was added to water and allowed to stand for a day to give pale green crystals with one water of solvation (0.4 g; 50%). Found: C, 45.6; H, 5.1. Calc. for $C_{26}H_{36}O_5P_2Pt$: C, 45.6; H, 5.3%.

IR spectra were recorded on a Hitachi 260-10 infrared spectrophotometer. Spectrometers used for NMR studied were: ^1H NMR, JEOL JNM-MH-100, Hitachi R-90H FT-NMR spectrometers; ^{13}C NMR: Hitachi R-90H FT-NMR (22.66 MHz). Molecular weights were obtained using a Corona Molecular Weight Apparatus M-117 (vapour pressure osmometry) in CH_2Cl_2 at 30°C. Electroconductivity was measured in a dried acetone solution (*ca* 1×10^{-3} M) using a DKK AO-6 instrument. FABMS spectra was produced using a JEOL HX-100. Elemental analyses were performed by the Micro-Analytical Centre, Department of Pharmaceutical Sciences, Kyoto University.

RESULTS AND DISCUSSION

Dinuclear Pt(II) complex cross-linked by the dahd(3,4-diacetyl-2,4-hexadiene-2,5-diol) dianion $[Pt_2(L_2)_2(\text{dahd-}O_2,O'_2)][BF_4]_2$ {L = SEt_2, PMe_2Ph, or L_2 = 1,5-cyclooctadiene(COD)} is formed by treating *cis*-$PtCl_2L_2$ (L = SEt_2, PMe_2Ph) and $PtCl_2$(COD) with $AgBF_4$ in the presence of H_2-dahd in acetone or CH_3OH. IR and ^1H NMR data of $[Pt_2(L_2)_2(\text{dahd-}O_2,O'_2)][BF_4]_2$, is given in Table 1 and shows that dahd bonds the Pt(II) nuclei by symmetrical O-bonding bifunctional chelation. These spectral data agree well with those of the corresponding Pd(II) and Rh(I) complexes $[M_2(L_2)_2(\text{dahd-}O_2,O'_2)][BF_4]_n$ (M = Pd, L = PPh_3, L_2 = bdpe{1,2 - bis(diphenylphosphino)ethane}, *n* = 2; M = Rh, L = CO, *n* = O).[1]

$[Pt_2L_4(\text{dahd-}O_2,O'_2)][BF_4]_2$ (L = SEt_2,PMe_2Ph), by treating with K_2-dahd or Na_2-dahd in CH_3OH, readily transforms into PtL_2(dahd). PtL_2(dahd) was directly obtained in a moderate yield by reacting *cis*-$PtCl_2L_2$ with K_2-dahd or Na_2-dahd in the presence of NEt_3.

IR, ^1H and ^{13}C NMR spectra of PtL_2(dahd) {L = SEt_2, PMe_2Ph, PPh_3; L_2 = 2,9-R_2-phen (R = H, Me)} are shown in Fig. 2 (L = SEt_2) and Tables 1 and 2. ^1H NMR spectrum of $Pt(SEt_2)_2$(dahd) shows that two Me groups of the dahd are equivalent, while the other two are non-equivalent. A resonance occurs at 2.51 in the lower field region close to that proposed for an acetyl group of, for example, γ-carbon-bonded β-diketonate Pt(II) complexes,[6] while the resonance at 2.10 is consistent with one carbonyl bound to Pt(II) in the enol form. This indicates that one acetylacetonate group of the dahd contains a localized (C═C) group. Characteristic IR absorption bands are consistent with those, in which 1502 cm^{-1} is due to ν(C—O), 1636 cm^{-1} to ν(C═C), and two bands at 1728 and 1670 cm^{-1} are due to ν(C═O). The ^1H NMR also exhibits magnetically non-equivalency of the two sulphur atoms. A $^{13}C\{^1H\}$ NMR spectrum of $Pt(SEt_2)_2$(dahd) obtained when operating in the Fourier Transform Mode (with 30,000 of pulse acquisition and 4 s of pulse intervals) agrees well with these observations. The satellites due to the ^{195}Pt splitting at 73.1 is due to the 3-carbon nucleus

Table 1. IR and ^{1}H NMR data

Complex	Characteristic bands (IR)^a				^{1}H^b		
	ν(C═O)		ν(C═C)	$\nu(C\cdots C)+\nu(C\cdots O)$ or ν(C—O)	δ_{Me}		
[Pt$_2$(SEt$_2$)$_4$(dahd)][BF$_4$]$_2$^{c}				1562(vs)			2.10
[Pt$_2$(PMe$_2$Ph)$_4$(dahd)][BF$_4$]$_2$^{d}				1556(vs)			2.13
[Pt$_2$(COD)$_2$(dahd)][BF$_4$]$_2$^{e}				1542(vs)			2.15
Pt(SEt$_2$)$_2$(dahd)^f	1728(w)	1670(vs)	1636(m)	1502(vs)	2.51(1)	2.15(2)	2.10(1)
Pt(PPh$_3$)(SEt$_2$)(dahd)^g	1719(w)	1673(vs)	1632(m)	1501(vs)	2.18(2)	2.08(1)	1.99(1)
Pt(PMe$_2$Ph)$_2$(dahd)^h		1673(vs)	1627(s)	1515(s)	2.40(1)	2.14(2)	1.96(1)
Pt(phen)(dahd)^i	1735(w)	1680(vs)	1632(m)	1547(vs)	2.47(1)	2.14(2)	2.07(1)
Pt(2.9-Me$_2$-phen)(dahd)^j		1680(vs)	1632(m)	1503(vs)	2.26(1)	2.10(2)	1.95(1)

[a] Measured in nujol mulls.

[b] Measured in CDCl$_3$ unless otherwise indicated. Chemical shifts are relative to Me$_4$Si at 0.00.

[c] δ_{Me}(SEt$_2$) 1.47(t), δ_{CH_2}(SEt$_2$) 3.04 with [$J(^{195}Pt—H)$] = 35 Hz, $J_{H;H'}$ = 7 Hz.

[d] δ_{Me}(PMe$_2$Ph) 1.71 with [$J(^{195}Pt—H)$] = 34 Hz, $J_{P,H}$ = 13 Hz. Measured in (CD$_3$)$_2$CO-CDCl$_3$.

[e] Measured in (CD$_3$)$_2$CO. δ_{CH}(COD) 5.93 with [$J(^{195}Pt—H)$] = 74 Hz. δ_{CH_2}(COD) 2.5 ~ 2.9 (multiplet).

[f] δ_{Me}(SEt$_2$) 1.44(t) 1.33(t), δ_{CH_2}(SEt$_2$) 3.05 (q, $J_{H,H'}$ = 7 H, $J_{Pt,H}$ = 28 Hz) 2.67(q); [$^4J(^{195}Pt—H)$] (Me-protons at 1,8-positions of dahd^2) = 5 Hz.

[g] δ_{Me}(SEt$_2$) 0.91(t), δ_{CH_2}(SEt$_2$) 2.56(q, $J_{H,H}$ = 8 Hz) where $J_{Pt,H}$ = ~ 35 Hz. [$^4J(^{195}Pt—H)$] (Me-protons at 6-position of dahd) = 6 Hz.

[h] δ_{Me}(PMe$_2$Ph) 1.60(d) with $J_{P,H}$ = 12 Hz, $J_{Pt,H}$ = 37 Hz. 1.44(d) with $J_{P,H}$ = 11 Hz, $J_{Pt,H}$ = 24 Hz. [$^4J(^{195}P—H)$] (Me-protons at 1,8-positions of dahd) = 7 Hz.

[i] δ of the azaheterocyclic ligand: 2,9-H 10.18(d) 9.40(d), 4,7-H 8.60(d) 8.41(d), 5,6-H 7.90(s) where ^{195}Pt satellites could not be discerned.

[j] δ of the azaheterocyclic ligand: 4,7-H 8.38(d), 5.6-H 7.74(s) 3,8-H 7.64(d) 7.52(d), 2,9-Me 3.10(s), 3.03(s).

Table 2. $^{13}C\{^1H\}$ NMR data[a]

Complex	dahd								SEt$_2$		PMe$_2$PH	
	C^{2,7}	C^5	C^9	C^4	C^3	C^{1,8}	C^{10}	C^6	C^1	C^2		
Pt(SEt$_2$)$_2$(dahd)	201.8	194.3	188.5	120.1	73.1	30.3	28.6	24.3	31.4	13.1		
	[51.1]	[41.5]	[28.3]	[40.1]	[489.2]			[42.2]	[22.1]	[15.2]		
									30.6	12.5		
Pt(PPh$_3$)(SEt$_2$)(dahd)	201.8	195.5	191.1	118.3	81.5	30.5	28.7	24.2	27.9	12.9		
									[15.2]			
	(6.2)	(4.5)			(60.0)							
Pt(PMe$_2$Ph)$_2$(dahd)	202.4	196.0	190.7	117.8	80.7	30.4	28.8	25.7			12.6	11.8
	[34.2]							[64.8]				
	(6.2)	(4.8)	(9.7)	(4.8)	(56.0)			(5.5)			(34.6)	(40.8)
Pt(phen)(dahd)[b]	205.4	195.4	—	—	—	30.2	28.5	23.9				
Pt(2,9-Me$_2$-phen)(dahd)[c]	207.0	193.7	189.7	118.9	60.2	29.6	28.7	23.8				
	[49.9]				[313.5]			[75.3]				

[a] Chemical shifts are relative to Me$_4$Si at 0.00. The solvent used is CDCl$_3$. [$J(^{195}Pt—H)$] are in braces; J(P—C) in parentheses; the other resonances and their coupling constants which are not described in the table were not discernible owing to the low solubilities or insufficient S/N ratio.

[b] Resonances due to azaheterocyclic ligand are as the following: C^2, C^9 153.3 149.0; C^3, C^8 128.0 125.0; C^4, C^7 138.3 137.0; C^{5,6} 126.6; C^{13}, C^{14} 130.2 130.0; C^{11}, C^{12} 147.6 145.1.

[c] Resonances due to azaheterocyclic ligand are as the following; C^2, C^9 167.5 162.5; C^3, C^8 125.8 125.5; C^4, C^7 127.0 126.7; C^5, C^6 137.1 136.9; C^{13}, C^{14} 127.6 127.3; C^{11}, C^{12} 149.2 147.4; *Me*-C^2, *Me*-C^9 28.5 24.3.

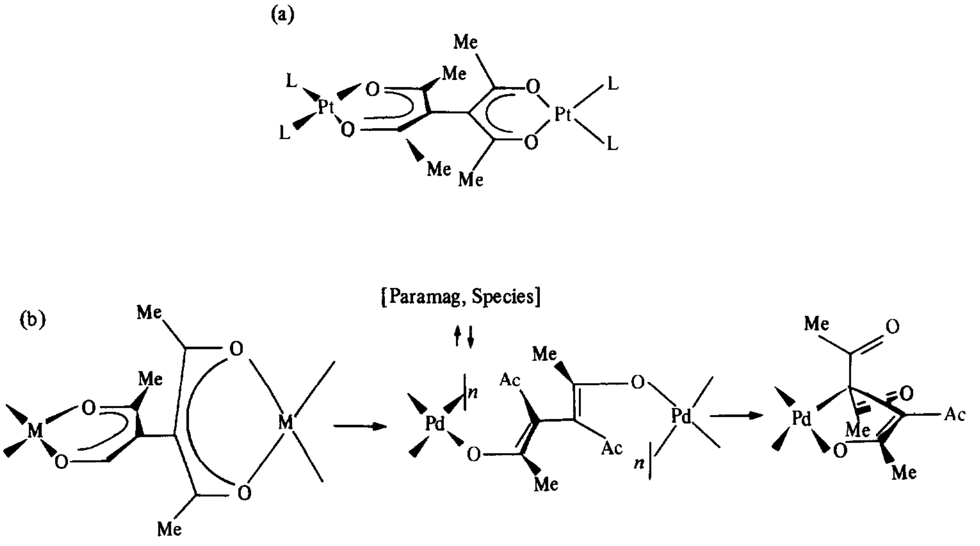


Fig. 1. (a) Proposed structure of $[Pt_2(L_2)_2(dahd\text{-}O_2,O_2')]^{2+}$. (b) Linkage modes of tetra-acetylethane dianion given by a bridge splitting reaction of $[M_2(L_2)_2(dahd\text{-}O_2,O_2')][BF_4]_n$ (M = Pd, L = PPh_3, $n = 2$; M = Rh, L = CO, $n = 0$); Ac = CH_3CO-.

of the dahd and the large coupling constant $[^1J(^{195}Pt—^{13}C)] = 489.2$ Hz is consistent with C-3 atom directly bonding to Pt(II),[7] while $[^2J(^{195}Pt—C^4)]$ was obtained as 40.1 Hz at 120.1.

These spectral data of $Pt(SEt_2)_2(dahd)$ agree with a structure having low symmetry in which dahd bonds to Pt(II) with a (C^3,O')-chelate as proposed in Fig. 3. Interestingly, ^{13}C NMR resonances due to one SEt_2 could be observed with ^{195}Pt satellites, while the other has no ^{195}Pt satellites.

It has been reported from variable temperature ^1H NMR evidence that *cis*-$PtCl_2\{S(CH_2C_6H_5)_2\}_2$[8] undergoes dynamic inversion motion at the pyramidal sulphur. In the present case, one sulphide in $Pt(SEt_2)_2(dahd\text{-}C_3,O')$ is assumed likely to be undergoing analogous dynamic behaviour at an ambient temperature, but lower temperature NMR spectra have not been obtained. However, ^{13}C NMR data of the analogous central carbon-bonded Pt(II) complexes of acetylacetone, Pt(acac-O)(acac-C^3)(py) and $Pt(acac\text{-}C^3)_2(py)_2$[9] may be useful for the arrangement of sulphides in $Pt(SEt_2)_2(dahd\text{-}C^3,O')$. From the magnitude of the coupling constant $^{195}Pt—C^3$, observed for the acetylacetonate complexes, where $J(^{195}Pt—C^3)$ for Pt(acac-O)(acac-C_3)(py) is 619 Hz and for $Pt(acac\text{-}C^3)_2(py)_2$ is 369 Hz, *s*-bonding character of C-3 is apparently correlated with a *trans* labilizing effect:[10] O(acac) < C(3)(acac). Thus, the sulphur being stereochemically nonrigid in $Pt(SEt_2)_2(dahd\text{-}C^3,O')$ can be explained by an arrangement which is *trans* to C(3) (a resonance in the higher field region) and not to O. FABMS of $Pt(SEt_2)_2(dahd\text{-}C^3,O')$ is given in Fig. 4 as an explicit pattern, in which the basal peak is $M^+(m/z = 572)$ and the isotopic ion distribution patterns agree well with the calculated ones.

A sulphide of $Pt(SEt_2)_2(dahd\text{-}C^3,O')$ is readily displaced by PPh_3 to give $Pt(PPh_3)(SEt_2)(dahd\text{-}C^3,O')$. ^{13}C NMR spectrum of the complex with a relatively large $[^2J(P—C)] = 60.0$ Hz is as expected, consistent with PPh_3 being arranged at the *trans* position to C^3. In addition, NMR resonances due to the CH_2 group of SEt_2 with ^{195}Pt satellites may be due to the stereochemical rigidity being arranged *trans* to O.

^1H and ^{13}C NMR of $Pt(PMe_2Ph)_2(dahd)$ is comparable with $Pt(SEt_2)_2(dahd\text{-}C^3,O')$, and they exhibit non-equivalency of the two phosphorus atoms. The chemical shifts due to the dahd carbons of $Pt(PMe_2Ph)_2(dahd)$ agree with those obtained for $Pt(SEt_2)_2(dahd\text{-}C^3,O')$. The weak resonances at 81.8 and 79.4 Hz, the latter of which was partially overlapped with that of the solvent $CDCl_3$ are tentatively assigned to the C^3 nucleus coupled to the *trans* phosphorus nucleus. Its chemical shift and two bond coupling constant $[^2J(^{31}P—C^3)] = 56.7$ Hz are however comparable with those obtained for $Pt(PPh_3)(SEt_2)(dahd\text{-}C^3,O')$.

$Pt(SEt_2)_2(dahd\text{-}C^3,O')$ reacts with the bidentate azaheterocyclic ligand phen to give Pt(phen)(dahd-C^3,O'). IR, ^1H and ^{13}C NMR spectral data of this complex agree very closely with those of $PtL_2(dahd\text{-}C^3,O')$(L = SEt_2, PMe_2Ph) and also with Pd(phen)(dahd-C^3,O').[1] ^{13}C NMR of an analogous 2,9-Me_2-phen complex was more informative than the phen complex, because we could raise its solubility, and the data are compatible with the proposed structure (Fig. 3).

The bridge-splitting reaction of the dinuclear

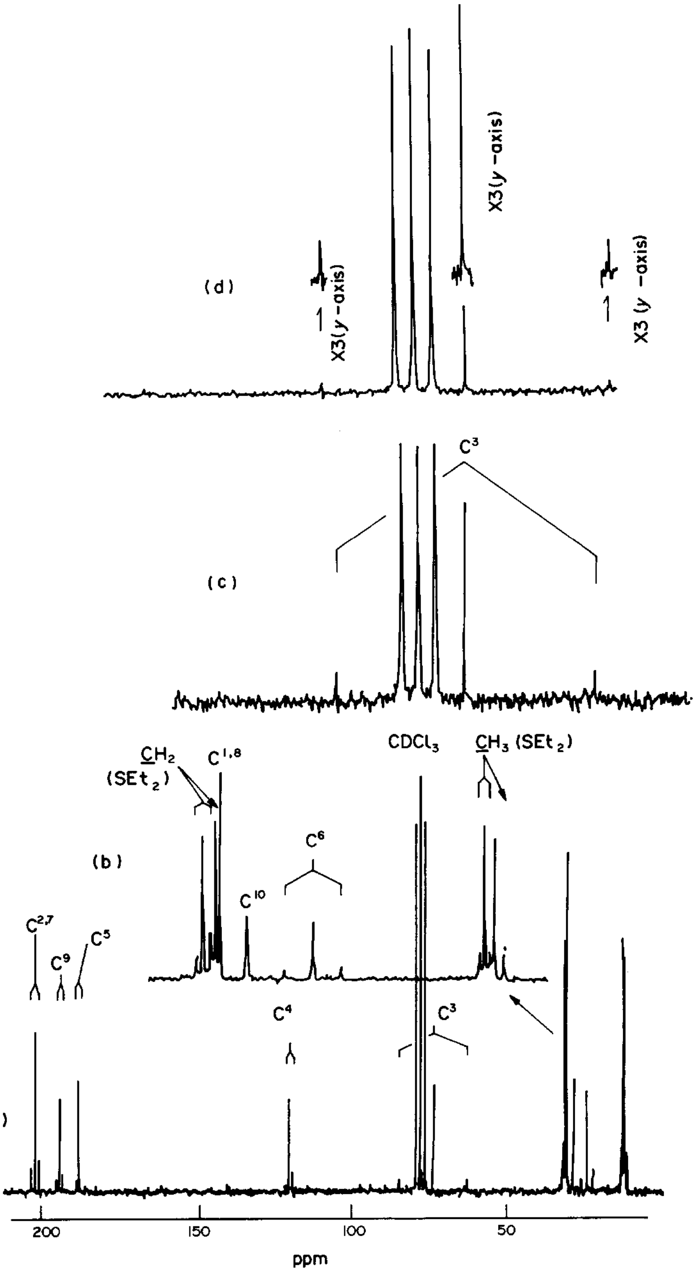


Fig. 2. (a) $^{13}C\{^{1}H\}$ NMR spectrum of $Pt(SEt_2)_2(dahd\text{-}C^3,O')$ in $CDCl_3$; (b) expanded in the range of $0 \sim 50$ ppm; (c) expanded (× 3) in the range $50 \sim 100$ ppm; (c) expanded in the range $50 \sim 100$ ppm; (d) expanded (× 3) through y-axis. *Due to impurity included.

Pt(II) complex cross-linked by the dahd dianion as an (O_2,O'_2)-chelate by the attack of basic K_2-dahd, may firstly proceed via an uptake of the counter anion (KBF_4) and concurrent insertion of the dahd dianion into the inner sphere (Scheme 1). On the other hand, by treating PtL_2(dahd-C3,O′) (L = SEt_2, PMe_2Ph) with an equivalent amount of HBF_4 in aqueous acetone, $[Pt_2L_4(dahd)][BF_4]_2$ (L = PMe_2Ph, yield 73%) and H_2-dahd (46%) were obtained.

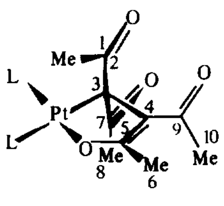


Fig. 3. Proposed structure of $PtL_2(dahd\text{-}C^3,O')$\{L = SEt_2, PMe_2Ph, L_2 = 2,9-R_2-phen(R = H, Me)\}.

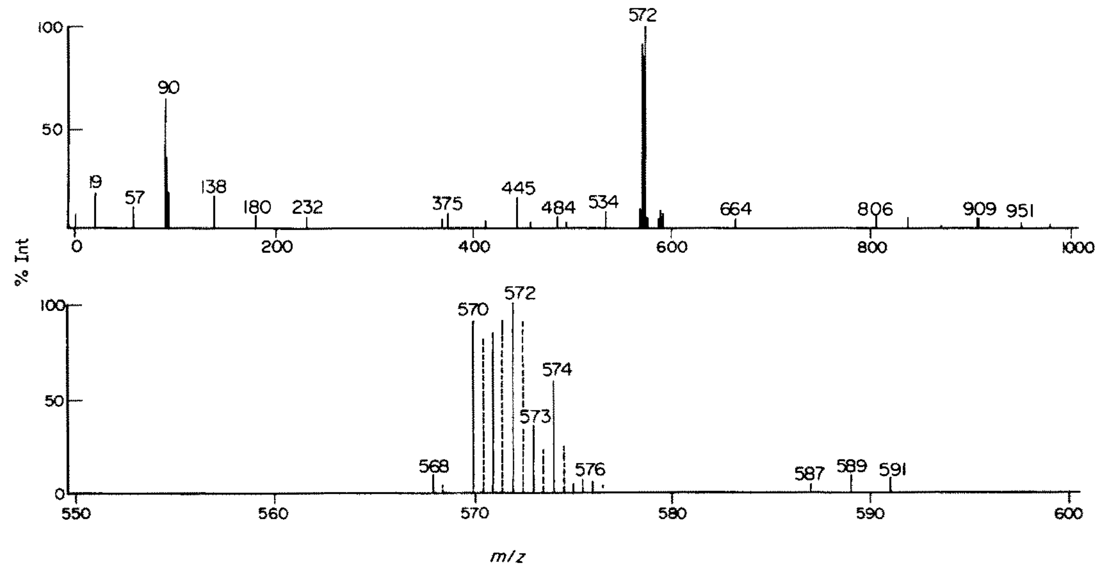
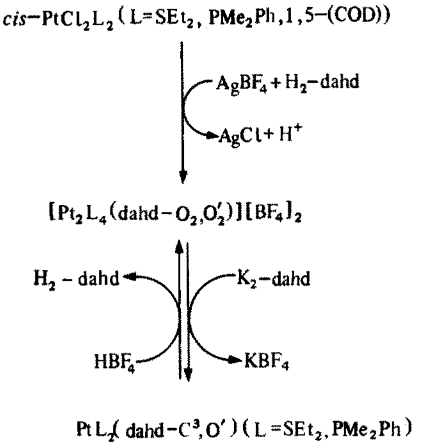


Fig. 4. FABMS of Pt(SEt$_2$)$_2$(dahd-C^3,O′).

These indicate that linkage modes of the dahd dianion to Pt(II) in acidic conditions favour the bifunctional (O$_2$,O$'_2$)-chelate, while in basic conditions it prefers the (C^3,O′)-chelate. It has so far been known that deprotonation of β-diketonate Pt(II) complexes, Pt(tfac)$_2$(PPh$_3$) (tfac = 1,1,1- trifluoroacetylacetone),[11] PtCl(acac-O)(π-val) (val = vynylalcohol)[12] and PtCl(acac-O)(acac)[12] favours carbon-bonded complexes of the β-diketone at C-3 and up to C-1. Considering that dahd itself is γ,γ'-bis(acetylacetonate) and stabilized in the dienol–dienolate form both in H$_2$-dahd[13] and [M$_2$(L$_2$)$_2$(dahd)][BF$_4$]$_n$ (M = Pd, L = PPh$_3$, L$_2$ = bdpe, $n = 2$; M = Rh, L = CO, $n = 0$; M = Pt, L = SEt$_2$, PMe$_2$Ph, L$_2$ = COD, $n = 2$), an activation of C-3 of the dahd forming metallation should still be noteworthy. Unfortunately, an intermediate, such as [PtL$_2$(dahd-O$_1$,O$'_1$)]$_n$ or any paramagnetic species as found for catena-[Pd(phen)(dahd-O$_1$,O$'_1$)]$_n$, have not been isolated.

Interestingly, the linkage mode of the dahd dianion to Pt(II) as a (C^3,O′)-chelate is comparable with the Pt(II) complex of Vitamin C Pt(*cis*-dach) (ascorbate) (dach = diaminocyclohexane),[14] having antitumor properties which Hollis *et al.* established by X-ray analysis, in addition to their similar frameworks.

Acknowledgement—An author (S. Y.) is grateful to Y. Tanaka (Hitachi Ltd, Naka Engineering Centre, Ibaragi) for obtaining ^{13}C NMR spectra.



Scheme 1.

REFERENCES

1. S. Yamazaki, *Polyhedron* 1986, **5**, 1183.
2. S. Yamazaki, *Polyhedron* 1985, **4**, 1915; S. Yamazaki, *Bull. Chem. Soc. Jpn.* 1987, **60**, 1155.
3. G. B. Kauffman and D. O. Cowan, *Inorg. Synth.* 1960, **6**, 211.
4. J. M. Jenkins and B. L. Shaw, *J. Chem. Soc.* (A) 1966, 770.
5. J. X. McDermott, J. F. White and G. M. Whitesides, *J. Am. Chem. Soc.* 1976, **98**, 6521.
6. J. Lewis and C. Oldham, *J. Chem. Soc.* (A). 1966, 1456; S. Kawaguchi, *Coord. Chem. Rev.* 1986, **70**, 51.
7. B. E. Mann and B. F. Taylor, *^{13}C NMR Data for Organometallic Compounds*. Academic Press, London (1981).

8. P. Haake and P. C. Turley, *Inorg. Nucl. Chem. Lett.* 1966, **2**, 173; P. Haake and P. C. Turley, *J. Am. Chem. Soc.* 1967, **89**, 4611.
9. T. Ito. T. Kiriyama, Y. Nakamura and A. Yamamoto, *Bull. Chem. Soc. Jpn.* 1976, **49**, 3257.
10. A. Yamamoto, *Organometallic Chemistry.* Syokabo, Tokyo (1986); F. Basolo and R. G. Pearson, *Mechanism of Inorganic Reactions* 2nd edn. John Wiley, New York (1967).
11. S. Okeya, Y. Nakamura and S. Kawaguchi, *Bull. Chem. Soc. Jpn.* 1981, **54**, 3396.
12. J. Hills, J. Francis, M. Mori and M. Tsutsui, *J. Am. Chem. Soc.* 1974, **96**, 4800.
13. L. F. Power and K. E. Turner, *Inorg. Nucl. Chem. Lett.* 1972, **8**, 313; J. P. Schaefer and P. J. Wheatley, *J. Chem. Soc.* 1966, 528.
14. L. S. Hollis, A. R. Amundsen and E. W. Stern, *J. Am. Chem. Soc.* 1985, **107**, 274.