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ORGANOPLATINUM COMPOUNDS

II *. REDUCTIVE ELIMINATION OF CH_3N_3 FROM $[Me_3PtN_3]_4$ WITH $P(OMe)_3$ YIELDING *cis*-$Me_2Pt[P(OMe)_3]_2$

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Summary

Reaction of $[Me_3PtN_3]_4$ with pure $P(OMe)_3$ yields *cis*-$Me_2Pt[P(OMe)_3]_2$ with reductive elimination of CH_3N_3. IR/Raman and mass spectra of the compound have been obtained and metal-to-ligand vibrations ν(Pt—C) and ν(Pt—P) have been assigned. *Cis*-$Me_2Pt[P(OMe)_3]_2$ was independently synthesized by two different routes: (a) *cis*-$Cl_2Pt[P(OMe)_3]_2$ was treated with MeLi, (b) Me_2PtCOD (COD = cyclooctadiene) was substituted with $P(OMe)_3$.

Results and discussion

Trimethylplatinum(IV) azide has been reported as an example of a covalent organoplatinum(IV)—nitrogen compound [1]; it has been recognized as a tetramer $[Me_3PtN_3]_4$ by its mass spectrum, and X-ray analysis has confirmed a distorted "cubic structure" with the unique feature of an azide group where the α-nitrogen atom is coordinated to three platinum atoms [2].

Covalent organometallic azides react with phosphines in a "Staudinger reaction" with elimination of nitrogen, forming organometallic phosphineimines (eq. 1).

$$L_nM\text{—}N_3 + PR_3 \xrightarrow[\text{Solv.}]{T} L_nM\text{—}N\text{=}PR_3 + N_2 \qquad (1)$$

To extend our knowledge of covalently-bonded platinum nitrogen compounds and in pursuit of our studies on structural aspects of organoplatinum chemistry,

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* Part I see ref. 1.

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we undertook an experiment analogous to eq. 1 (eq. 2).

$$Me_3PtN_3 + PR_3 \not\xrightarrow{T} Me_3Pt{-}N{=}PR_3 + N_2 \qquad (2)$$

With $P(NMe_2)_3$, a strong basic phosphine, no reaction of that type takes place, but a volatile adduct, $Me_3PtN_3 \cdot 4\ P(NMe_2)_3$, b.p. 170°C/$10^{-3}$ Torr, is formed [3]. However, with $P(OMe)_3$ a vigorous exothermic reaction is observed * (eq. 3).

$$Me_3PtN_3 \xrightarrow{\text{excess } P(OMe)_3} \underset{(I)}{Me_2Pt[P(OMe)_3]_2} + N_2 + CH_3N{=}P(OMe)_3 \qquad (3)$$

$Me_2Pt[P(OMe)_3]_2$ (I) is a colourless, air-stable compound which has been fully characterized by elemental and spectroscopic analyses.

Reductive elimination is a well-known reaction in organo-platinum chemistry [4], e.g. pyrolysis of platinum(IV) compounds yields platinum(II) complexes (eq. 4).

$$(CH_3)Cl_3Pt^{IV}[PR_3]_2 \xrightarrow{T} Cl_2Pt^{II}[PR_3]_2 + CH_3Cl \qquad (4)$$

Elimination of RX involves no free radicals or other high-energy intermediates, therefore reactions are rationalized by all electron-pair processes. The nature of the leaving group RX seems to play an important rôle. Standard heats of formation ΔH_f^0 (RX) may be taken as the primary parameter-directing reaction paths (eq. 5).

$$R_3PtX \underset{-2L}{\overset{+2L}{\rightleftharpoons}} R_2PtL_2 + RX \qquad (5)$$

e.g. $\Delta H_f^0(CH_3Cl)_g = -82$ kJ/mol, $\Delta H_f^0(CH_3Br)_g = -36$ kJ/mol and $\Delta H_f^0(CH_3J)_g = +20$ kJ/mol.

We have tried to synthesize I by treatment of $Cl_2Pt[P(OMe)_3]_2$ (assumed to have the *cis*-structure [5]) with CH_3Li prepared from CH_3I and lithium metal, which resulted in halogen—ligand exchange and formation of unidentified products.

Successful preparation of I was carried out by using iodide-free CH_3Li/Et_2O solutions under reaction conditions earlier described by Chatt and Shaw [6] for *cis*-$Me_2Pt[PEt_3]_2$ (eq. 6).

$$cis\text{-}Cl_2Pt[P(OMe)_3]_2 + 2\ MeLi \xrightarrow[-20^\circ C]{Et_2O} 2\ LiCl + \underset{(I)}{cis\text{-}Me_2Pt[P(OMe)_3]_2} \qquad (6)$$

Independently I may be obtained in a ligand-substitution process from Me_2PtCOD with $P(OMe)_3$:

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* *Caution!* Adding $P(OMe)_3$ to a solid sample of $[Me_3PtN_3]_4$ caused a violent explosion, presumably due to metastable CH_3N_3 formed by reductive elimination; $[Me_3PtN_3]_4$ is also known to be explosive when exposed to heat [1].

$$Me_2PtCOD + 2\ P(OMe)_3 \xrightarrow[RT]{Et_2O} cis\text{-}Me_2Pt[P(OMe)_3]_2 + COD \qquad (7)$$

(I)

No attempt has been reported for the preparation of a potentially useful precursor of possible *cis*-Me_2PtL_2 derivatives, e.g. *cis*-$Me_2Pt[C_6H_5CN]_2$; our experiments failed due to reaction of CH_3Li with the benzonitrile ligand:

$$(cis?)\text{-}Cl_2Pt[C_6H_5CN]_2 + 2\ MeLi \xrightarrow[-30°C]{Et_2O} 2\ LiCl + \text{dec. products} \qquad (8)$$

Reactions 3, 6 and 7 yield exclusively the *cis*-complex $Me_2Pt^{II}[P(OMe)_3]_2$; in the literature no starting materials *trans*-$X_2Pt^{II}[PR_3]_2$ and no *trans*-$Me_2Pt^{II}[PR_3]_2$ have been quoted so far [7].

Mass spectra

Spectra of compound I, as synthesized in eq. 3, 6 and 7, were scanned at 70 and 20 eV electron energy with a direct insertion probe; they show no significant differences in their fragmentation patterns (Table 1). The low-mass region of the spectrum is dominated by fragment products of the phosphite ligands, as reported by Braterman [8,9]. In addition, hydrogen and methyl radicals combine with $P(OMe)_3$ to form $[HP(OMe)_3]^+$ at m/e 125 and $[MeP(OMe)_3]^+$ at m/e 139.

In contrast to many organometallics $(Me)_nMX_m$ no alkyl platinum fragments and/or platinum ions Pt^+, $MePt^+$ or Me_2Pt^+ are observed in the mass spectra of $R_3Pt^{IV}X$ or related derivatives [1,10] and the same applies to $R_2Pt^{II}L_2$ complexes [11]; for $Me_2Pt[P(OMe)_3]_2$ only $[PtC_2H_3]^+$ appears with relatively low abundance in the appropriate mass region.

For most ions from m/e 288—458 many alternative structures may be written; the structure of distinct ions and a fragmentation scheme cannot be formulated unambiguously, but among the many structures suggested each seems to be logically derived from Me_2PtL_2 by stepwise fragmentation of both metal-to-carbon and metal-to-ligand sites. The molecular ion appears with only 3% relative abundance, typical for a ligand-stabilized peralkylated platinum(II) complex [11]; in contrast, the $(m - 15)^+$ ion abundance is close to 100% of the base peak.

NMR spectra

High and low resolution [^1H, ^{13}C, ^{31}P] NMR spectra confirm the structure of *cis*-$Me_2Pt[P(OMe)_3]_2$; a detailed analysis of the spectra will appear in a following communication [12].

IR/Raman spectra

Vibrational spectroscopy and measurement of the molecular dipole moment has been widely used to determine *cis*- and *trans*-configurations of square-planar complexes $[X_2Pt^{II}L_2]$; as required by symmetry only one $\nu(Pt—X)$ band was found in the spectra of the *trans*-, and two absorptions ν(Pt—X) in the spectra of the *cis*-complexes [13].

From 3000—750 cm^{-1} IR and Raman spectra show absorptions due to vibrations of the phosphite ligands and of the metal-bonded methyl groups; assignment of $\mathrm{P(OCH_3)_3}$-group frequencies in Table 2 is facilitated by comparing the similar spectra of $\mathrm{(CH_3O)_3P{=}O}$ [14] and of $\mathrm{(CH_3O)_3PNCH_3}$ [15].

Platinum—carbon stretching frequencies, ν(Pt—C), in various complexes have been observed as doublets in *cis*-complexes from 523/536 to 534/545 cm^{-1}, but obviously no *trans*-$\mathrm{Me_2PtL_2}$ derivative has been investigated spectroscopically [16]. We assign ν(Pt—C) from 560—520 cm^{-1} at higher frequencies than in the

TABLE 1 (see also Fig. 1).

MASS SPECTRUM OF $\mathrm{Me_2Pt[P(OMe)_3]_2}$, 70 eV/60°C, PEAKS >3% ONLY

Abundance	*m/e*	Assignment
11.2	63	$\mathrm{HPOMe^+}$
6.4	79	$\mathrm{HP(O)OMe^+}$
79.3	93	$\mathrm{P(OMe)_2{}^+}$
4.7	94	$\mathrm{HP(OMe)_2{}^+}$
8.6	109	$\mathrm{P(O)(OMe)_2{}^+}$
9.2	123	$\mathrm{P(OMe)_2OCH_2{}^+}$
4.1	124	$\mathrm{P(OMe)_3{}^+}$
8.9	125	$\mathrm{HP(OMe)_3{}^+}$
100.0	139	$\mathrm{MeP(OMe)_3{}^+}$ = base peak
3.3	222	$\mathrm{PtC_2H_3{}^+}$
4.8	258	$\mathrm{Pt(HPOMe)^+}$
4.0	273	$\mathrm{MePt(HPOMe)^+}$
23.2	288	$\mathrm{PtP(OMe)_2{}^+/Me_2Pt(HPOMe)^+}$
16.2	289	$\mathrm{PtHP(OMe)_2{}^+/MePtHP(O)OMe^+}$
14.0	318	$\mathrm{Me_2PtHP(OMe)_2{}^+}$
15.2	319	$\mathrm{PtP(OMe)_3{}^+/MePtP(O)(OMe)_2{}^+/Me_2PtHP(OMe)_2{}^+}$
5.2	321	$\mathrm{Pt(HPOMe)_2{}^+}$
33.0	334	$\mathrm{MePtP(OMe)_3{}^+/Me_2PtP(O)(OMe)_2{}^+}$
4.2	337	$\mathrm{Pt(HPOMe)(HP(O)OMe)^+/MePtH(HPOMe)_2{}^+}$
5.3	397	$\mathrm{PtP(OMe)_2P(O)(OMe)_2{}^+/MePtP(OMe)_2PH(OMe)_2{}^+/MePtP(OMe)_3HPOMe^+/Me_2PtHPOMeP(O)(OMe)_2{}^+}$
4.7	398	$\mathrm{PtHP(OMe)_2P(O)(OMe)_2{}^+/PtHP(O)OMeP(OMe)_3{}^+/MePt[HP(OMe)_2]_2{}^+/MePtHP(O)OMeP(O)(OMe)_2{}^+/Me_2PtHP(O)OMeHP(OMe)_2{}^+}$
4.7	411	$\mathrm{Me_2Pt[P(OMe)_2]_2{}^+}$
8.0	412	$\mathrm{PtP(OMe)_2P(OMe)_3{}^+/MePtP(OMe)_2P(O)(OMe)_2{}^+/Me_2PtP(OMe)_2PH(OMe)_2{}^+/Me_2PtHPOMeP(OMe)_3{}^+}$
6.9	413	$\mathrm{Pt[P(O)(OMe)_2]_2{}^+/PtHP(OMe)_2P(OMe)_3{}^+/MePtHP(O)OMeP(OMe)_3{}^+/MePtHP(OMe)_2P(O)(OMe)_2{}^+/Me_2Pt[HP(OMe)_2]_2{}^+/Me_2PtHP(O)OMeP(O)(OMe)_2{}^+}$
9.9	427	$\mathrm{MePtP(OMe)_2P(OMe)_3{}^+/Me_2PtP(OMe)_2P(O)(OMe)_2{}^+}$
7.1	428	$\mathrm{PtP(O)(OMe)_2P(OMe)_3{}^+/MePt[P(O)(OMe)_2]_2{}^+/MePtHP(OMe)_2P(OMe)_3{}^+/Me_2PtHP(OMe)_2P(O)(OMe)_2{}^+/Me_2PtHP(O)OMeP(OMe)_3{}^+}$
10.1	442	$\mathrm{Me_2PtP(OMe)_2P(OMe)_3{}^+}$
9.6	443	$\mathrm{Pt[P(OMe)_3]_2{}^+/MePtP(O)(OMe)_2P(OMe)_3{}^+/Me_2Pt[P(O)(OMe)_2]_2{}^+/Me_2PtHP(OMe)_2P(OMe)_3{}^+}$
94.9	457	$\mathrm{MePtP(OMe)_2OCH_2P(OMe)_3{}^+/Me_2PtP(O)OMeOCH_2P(OMe)_3{}^+}$
92.3	458	$\mathrm{MePt[P(OMe)_3]_2{}^+/Me_2PtP(O)(OMe)_2P(OMe)_3{}^+}$
3.2	473	$\mathrm{Me_2Pt[P(OMe)_3]_2{}^+}$ = molecular ion

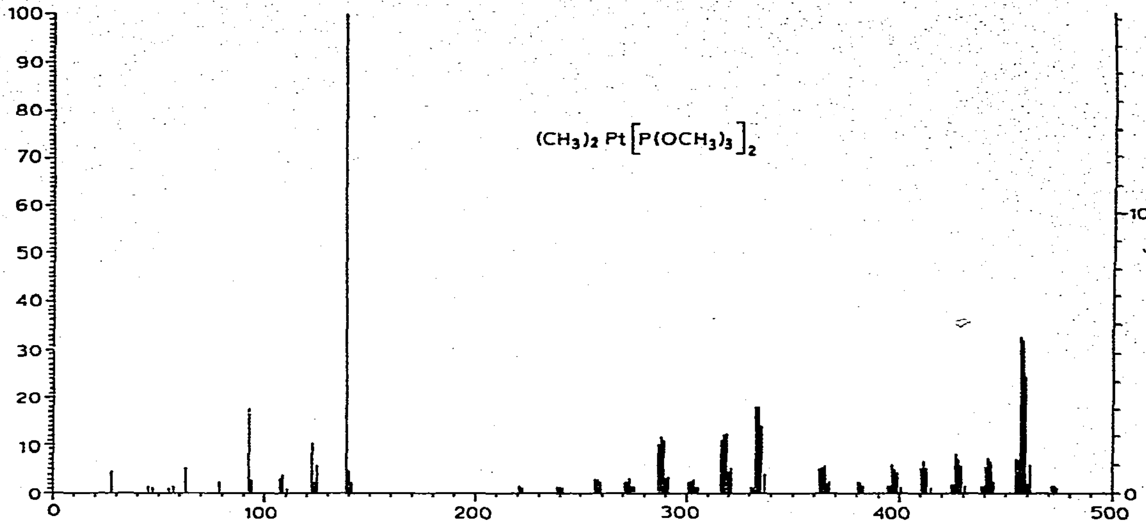

Fig. 1. Mass spectrum of I at 70 eV.

TABLE 2 (see also Fig. 2)

IR/RAMAN SPECTRA OF *cis*-$Me_2Pt[P(OMe)_3]_2$; [cm^{-1}]

Assignment	IR	Raman
ν_s, $\nu_{as}(CH_3)$, (OCH_3)	3000(sh)	3020(sh)
	2950s	2960s
	2880m	2860m
	2840m	2850m
	2820(sh)	2820(sh)
$\delta_{as}(OCH_3)$	1460w(sh)	1465(sh)
$\delta_{as}(CH_3)$	1450m	1445w
	1260w	
$\delta_s(CH_3)$		1215s
$\delta_s(CH_3)$	1195m	1195s
	1188m	
$\nu(OCH_3)$, $\rho(OCH_3)$	1080sh	1075vw
	1060(sh)	1060vw
	1020vs	1015m
$\delta_s(CH_3)$	1005vs	1000m
$\nu_{as}(PO_3)$	800s	815s
$\rho(CH_3)$	780vs	788m
		775s
$\nu_s(PO)_3$	745vs	750s
$\nu(Pt—C)$	560m	552m-s
	540s	522vs
$\delta(PO_3)$	520m	515s
$\nu_{as}(Pt—P_2)$	450w	440vw
δ(POC?)	385w	390m
$\nu_s(Pt—P_2)$	305vw	290m
		250m

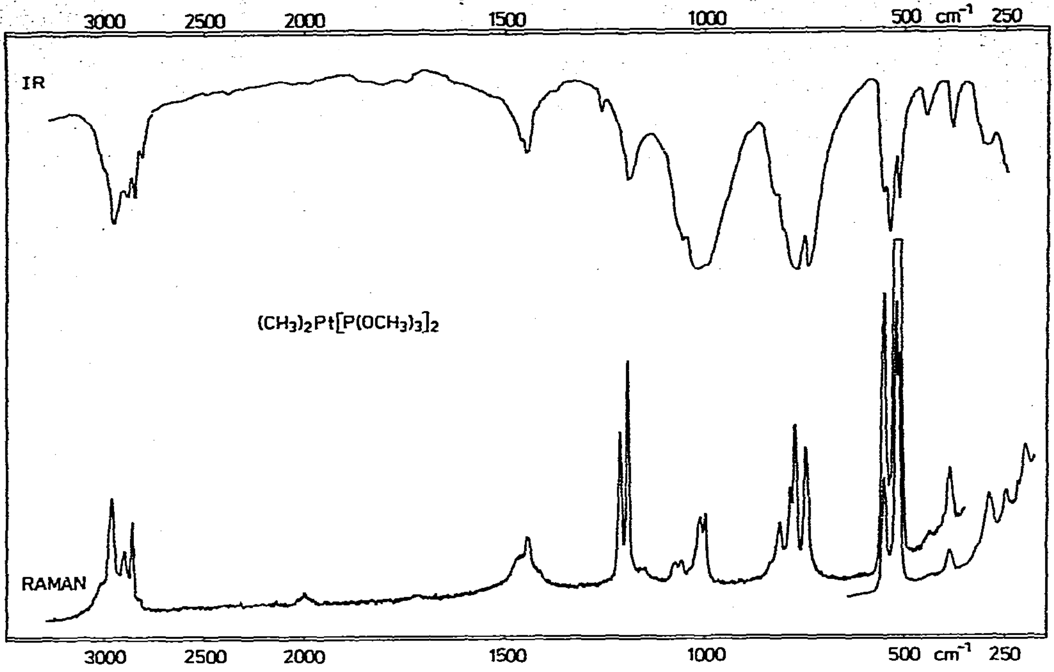

Fig. 2. IR and Raman spectra of I.

corresponding alkylarylphosphine complexes, indicating a higher bond strength in the metal-to-carbon bond. In the Raman effect ν(Pt—C) vibrations are by far the most intense peaks in the whole spectrum characteristic for covalently-bonded alkylmetal groups.

Platinum phosphorous stretching frequencies, $\nu(Pt—P_2)$, are quoted in the literature for *cis*-complexes as doublets from 440/425 to 420/406 cm^{-1} depending on the nature of the phosphine ligand [17], in *cis*-$Me_2Pt[P(OMe)_3]_2$ $\nu(Pt—P_2)$ is found from 450 to 390 cm^{-1}.

Experimental

1. *Spectra and analyses*

All compounds have been fully characterized by IR/Raman, NMR (^1H, ^{31}P, ^{13}C) and mass spectroscopy. The spectroscopic equipment has been described in an earlier communication [1].

Elemental analyses have been performed by A. Bernhardt, Analytical Laboratory, Elbach über Engelskirchen, West Germany, and the analytical facilities of the Fachbereich Chemie, Philipps-Universität, Marburg.

Molecular weights were determined cryoscopically in benzene solution or by mass spectroscopy.

2. *Starting materials*

$[Me_3PtN_3]_4$ [1], *cis*-$Cl_2Pt[C_6H_5CN]_2$[5], cis-$Cl_2Pt[P(OMe)_3]_2$ [5] and Me_2PtCOD [18] were prepared according to standard literature procedures. $P(OMe)_3$ was commercially available and distilled before use: b.p. 110-112°C/760 mm Hg. Methyllithium was prepared from CH_3Cl and lithium in dry ether at —10°C under nitrogen.

3. *Preparation of cis-$Me_2Pt[P(OMe)_3]_2$*

(a) Me_3PtN_3 + $P(OMe)_3$. 25 ml $P(OMe)_3$ are vigorously stirred and 4.6 g (16.3 mmol) Me_3PtN_3 are added in small portions over a period of 30 min; the compound reacts exothermally with evolution of nitrogen (*See Caution Note!*) After addition of the last portion stirring is continued unless the solution becomes clear. To complete the reaction the mixture is refluxed for 30 min; minor amounts of platinum metal are formed. Excess $P(OMe)_3$ is removed in vacuo, the oily residue is fractionally distilled: *cis*-$Me_2Pt[P(OMe)_3]_2$ is obtained as white, crystalline solid, b.p. 140—150°C/0.01 mm Hg; m.p. 60—62°C (uncorr.). Isolated yield: 3.7 g (48%). The compound is stable to air and hydrolysis. Found: C, 20.39; H, 5.19; O, 20.00; P, 12.78; Pt, 40.80. $C_8H_{24}P_2O_6Pt$ calcd.: C, 20.30; H, 5.11; O, 20.28; P, 13.09; Pt, 41.22%. Mol. weight: Found: 520, 530; (benzene); calcd.: 473.

(b) cis-$Cl_2Pt[P(OMe)_3]_2$ + CH_3Li. 50 ml of a 0.43 molar CH_3Li/Et_2O-solution (10.38 mmol) are added dropwise to a stirred suspension of 2.67 g (5.18 mmol) *cis*-$Cl_2Pt[P(OMe)_3]_2$ in 100 ml dry ether, cooled at —20°C. Reaction proceeds with formation of finely crystallized LiCl during 1 h. The mixture is allowed to warm up to room temperature and is quickly hydrolyzed with 50 ml H_2O; small amounts of platinum metal are formed. The ether layer is dried with $CaCl_2$, filtered, and the solvent evaporated in vacuo (crude yield: 1.66 g/67%). The brown-coloured product is dissolved in a minimum of hot CH_3OH, refluxed with charcoal, filtered, and H_2O added dropwise to the hot solution until precipitation occurs. After 24 h at —22°C *cis*-$Me_2Pt[P(OMe)_3]_2$ is crystallized in beautiful long, white needles, m.p. 60—62°C (uncorr.). Isolated yield: 1.02 g (42%). Found: C, 22.09; H, 5.29; P, 12.46; Pt, 40.30. $C_8H_{24}O_6P_2Pt$ calcd.: C, 20.30; H, 5.11; P, 13.09; Pt, 41.22%.

(c) Me_2PtCOD + $P(OMe)_3$. 2.82 ml (23.9 mmol) $P(OMe)_3$ are added dropwise to 3.98 g (11.9 mmol) Me_2PtCOD suspended in 50 ml acetone (15 min). The reaction is slightly exothermic; small amounts of platinum metal are filtered off and all volatiles are removed in vacuo. The residue crystallizes over night and is purified by vacuum distillation (see above). Isolated yield: 2.0 g (35%); colourless needles, m.p. 57—60°C (uncorr.). Found: C, 20.52; H, 4.85. $C_8H_{24}P_2O_6Pt$ calcd.: C, 20.30; H, 5.11%.

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