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A SERIES OF HYDRIDOPLATINUM(II) COMPLEXES STABILIZED WITH TRIBENZYLPHOSPHINES: THEIR PREPARATION, AND AN EMPIRICAL APPROACH TO THE MUTUAL INFLUENCE OF LIGANDS

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Summary

The preparation, IR and NMR spectra of 123 platinum hydrides of the general formula, *trans*-$PtHX(PBz_3)_2$ or *trans*-$PtHL(PBz_3)_2BPh_4$ (X = a uninegative anionic ligand, L = a neutral donor molecule, Bz = benzyl), are described. Neutral platinum hydrides have been synthesized by the reduction of *trans*-$PtCl_2(PBz_3)_2$ with $NaBH_4$, by the Michaelis—Arbuzov rearrangement, or by metathesis. Cationic hydridoplatinum(II) complexes are obtained from the reaction of *trans*-$PtHX(PBz_3)_2$ (X = Cl or NO_3) with a donor molecule (L) in the presence of $NaBPh_4$, or by coordinating a donor molecule through use of $PtH(PBz_3)_2BPh_4 \cdot \frac{1}{2}CH_2Cl_2$. The observed trends in ν(Pt—H), τ(H), ^1J(Pt—H) and ^1J(Pt—P) in a series of the hydridobenzylphosphineplatinum(II) complexes are discussed in terms of "*trans*- or *cis*-influences", defined as the ability of a ligand to weaken the bond *trans* or *cis* to itself. The data support the view that a donor atom *trans* to the hydridic ligand is important in determining the strength of the Pt—H bond in this series. Some remarks on the distinctive characteristics of some complexes, e.g., dissociation of coordinated cycloalkanone from platinum(II) or stereochemical non-rigidity of the *sym*-dimethylurea ligand, are included. Tricyclohexylphosphine analogs also have been prepared for comparison.

Introduction

In recent years, many platinum hydrides containing tertiary phosphines as stabilizing ligands have been prepared [1—5], and further studies to obtain a measure of the *trans*-influence for a series of the complexes, *trans*-$PtHX(PR_3)_2$ or *trans*-$PtHL(PR_3)_2Y$ (R_3 = Et_3, Ph_2Me, or Ph_3, Y = ClO_4^- or PF_6^-), have led to a comprehensive understanding of various ligands [6]. However, correlations and differences between the *trans*-influence series obtained by IR and NMR techniques have been limited mainly to three hydridoplatinum(II) systems stabilized

(a) (b)

Fig. 1. Two types of d^8-16e-hydridoplatinum(II)-dg:
(a) a neutral hydridoplatinum(II) complex;
(b) a cationic hydridoplatinum(II) complex.
X = a univalent anionic ligand; L = a donor molecule; P = tribenzylphosphine (abbreviated as PBz_3 in this paper).

with PEt_3, PPh_2Me, and PPh_3 [6]. Recent studies of steric and electronic effects in phosphine—transition metal complexes [7—9] clearly demonstrate that organic substituent groups of phosphine ligands often exert significant influences on the properties of the complexes. It is necessary, therefore, to extend such research to closely related platinum hydrides containing other tertiary phosphines.

From this point of view, it was of interest to prepare a large number of new platinum hydrides using tribenzylphosphine. In a previous paper [10], we have briefly reported that some *trans*-monohydridobenzylphosphineplatinum(II) complexes can be prepared by a novel synthetic path from *trans*-$PtCl_2(PBz_3)_2$ via dihydridoplatinum(II). It seems reasonable to assume that tribenzylphosphine as a stabilizing ligand is suitable for the systematic preparation of a number of square planar platinum hydrides differing only in the X or L substituent (Fig. 1), because relatively small degrees of steric constraint for both PBz_3 (cone angle 136°) [8] and H^- permit even a fairly large ligand (X or L) to be accommodated between the two PBz_3 groups *trans* to each other. The use of PBz_3 for the synthesis of platinum hydrides has the added advantage that the ^1H NMR spectrum of the methylene groups in PBz_3, as well as the ^1H NMR spectrum of hydridic protons and the ^{31}P NMR spectrum provide stereochemical information as to whether the two phosphine ligands attached to platinum are mutually *cis* or *trans*.

In this paper, we describe a systematic approach to the preparation of 123 hydridobenzylphosphineplatinum(II) complexes, and discuss their spectroscopic characteristics (ν(Pt—H), τ(H), ^1J(Pt—H), and ^1J(Pt—P)) for the purpose of an empirical systematization of the mutual influence of ligands through platinum(II).

Results and discussion

1. Preparation and characterization of hydridobenzylphosphineplatinum(II) complexes

Two types of complexes, neutral (Fig. 1a, Nos. 1—24) and cationic hydridoplatinum(II) (Fig. 1b, Nos. 26—123), have been prepared. Donor atoms (within anions X and molecules L) were as follows: hydrogen (X = H), carbon (X = CN, L = CO), tin (X = $SnCl_3$), nitrogen (X = NO_2, N_3, NCS, NCO, L = NH_3, NH_2R, NHR_2, NCR, diazole derivatives, pyridine derivatives), phosphorus (X = P(O)RR′, L = PR_3, $P(OR)_3$, $P(OMe)_2Ph$), arsenic (L = $AsPh_3$), antimony (L = $SbPh_3$), oxygen (X = ClO_4, NO_3, L = pyridine-*N*-oxides, urea derivatives, amides, cycloalkanones), sulfur (X = SCN, SR, $S(O)_2C_6H_4$-4-Me, L = SR_2, thiourea derivatives, thioacetamide, *N*-methylthiourethane), selenium (X = SeCN), chlorine (X = Cl), bromine (X = Br), iodine (X = I). Analytical and spectroscopic data for all the

(continued on p. 348)

TABLE 1

ANALYTICAL AND INFRARED DATA ON A SERIES OF HYDRIDOBENZYLPHOSPHINEPLATINUM(II) COMPLEXES

No.	Compound [a]	M.p. (°C)	Analysis (Found (calcd), wt. %)			ν(PtH) (cm^{-1}) [e]	Others (cm^{-1})
			C	H	Halogen or N		
1	$PtHCl(PBz_3)_2$	161—163	60.0 (60.0)	5.0 (5.2)	Cl 4.0 (4.2)	2210(2226 br) [f]	
2	$PtHBr(PBz_3)_2$	180—182	56.9 (57.0)	4.8 (4.9)	Br 9.1 (9.0)	2221(2222 br) [f]	
3	$PtHI(PBz_3)_2$	202—204	54.0 (54.1)	4.8 (4.7)	I 13.6 (13.6)	2192(2204 br) [f]	
4	$PtH(NCO)(PBz_3)_2$	170—172	61.1 (61.0)	5.6 (5.1)	1.9 (1.7)	2273	ν_a(NCO) 2223; ν_s(NCO) 1319
5	$PtH(SCN)(PBz_3)_2$	197—199	59.8 (59.9)	5.0 (5.0)	1.6 (1.6)	—SCN 2203 —NCS 2272	ν(CN) 2102 ν(CN) 2070
6	$PtH(SeCN)(PBz_3)_2$	186—188	56.8 (56.8)	4.9 (4.8)	1.4 (1.5)	2199	ν(CN) 2102
7	$PtH(SnCl_3)(PBz_3)_2$	205—207	48.7 (49.0)	3.9 (4.2)	Cl 10.3 (10.3)	2162	
8	$PtH(N_3)(PBz_3)_2$	127—129	59.5 (59.6)	5.3 (5.1)	5.0 (5.0)	2222	$\nu_a(N_3)$ 2033
9	$PtH(CN)(PBz_3)_2$	119—121	62.6 (62.2)	5.2 (5.2)	1.4 (1.7)	2059	ν(CN) 2130
10	$PtH(ClO_4)(PBz_3)_2$	205—207	55.9 (55.8)	4.8 (4.8)		[h]	ν(ClO) 1128, 1056, 937
11	$PtH(NO_3)(PBz_3)_2$ [b]	172—174	58.2 (58.2)	5.0 (5.0)	1.5 (1.6)	2283	$\nu(NO_3)$ 1449, 1284, 1015
12	$PtH(NO_2)(PBz_3)_2$	147—149	59.1 (59.3)	5.1 (5.1)	1.4 (1.7)	2200	$\nu(NO_2)$ 1351, 1323, 873
13	$PtH(SH)(PBz_3)_2$	137—139	60.2 (60.2)	5.8 (5.3)		2106	
14	$PtH(SMe)(PBz_3)_2$	129—131	60.2 (60.6)	5.8 (5.4)		2082	
15	$PtH(SBu\text{-}t)(PBz_3)_2 \cdot CH_2Cl_2$	134—136	57.7 (57.7)	5.7 (5.6)		2146, 2098 (2126 br) [g]	
16	$PtH(SBz)(PBz_3)_2$	110—112	63.3 (63.4)	5.8 (5.4)		2159	
17	$PtH(SC_6H_4\text{-}4\text{-}Me)(PBz_3)_2$	102—104	63.6 (63.4)	5.6 (5.4)		2169	
18	$PtH[SC(O)Me](PBz_3)_2$	150—152	60.2 (60.1)	5.3 (5.3)		2169	ν(CO) 1600
19	PtH(2-mercaptobenzothiazole)-$(PBz_3)_2$	174—176	60.7 (60.6)	4.9 (4.9)		2189	
20	$PtH(SO_2C_6H_4\text{-}4\text{-}Me)(PBz_3)_2$	167—169	61.6 (61.3)	5.3 (5.3)		2163	
21	$PtH[(MeO)_2P(O)](PBz_3)_2$	132—135	57.6 (57.8)	5.5 (5.4)		2087	ν(PO) 1125
22	$PtH[(EtO)_2P(O)](PBz_3)_2$	144—146	59.1 (58.7)	5.6 (5.6)		2061	ν(PO) 1134
23	$PtH[(MeO)PhP(O)](PBz_3)_2$	154—157	60.9 (61.3)	5.2 (5.4)		2106	ν(PO) 1112
24	$PtH_2(PBz_3)_2$	Not analyzed				1734	
25	$PtH(PBz_3)_2BPh_4 \cdot \frac{1}{2}CH_2Cl$ or $\frac{1}{4}CH_2Cl_2$	100—103	68.3 (68.5) 69.2 (69.5)	6.2 (5.5) 5.9 (5.6)	Cl 2.5 (3.0)	[h]	

(continued)

TABLE 1 (continued)

No.	Compound [a]	M.p. (°C)	Analysis (Found (calcd), wt. %)			ν(PtH) (cm^{-1}) [e]	Others (cm^{-1})
			C	H	Halogen or N		
26	$PtH(NH_3)(PBz_3)_2BPh_4$	145—146	68.7 (69.5)	5.9 (5.8)	1.2 (1.2)	2256	ν(NH) 3339, 3257
27	$PtH(NH_2Me)(PBz_3)_2BPh_4$	145—147	69.8 (69.7)	6.0 (5.9)	1.4 (1.2)	2260	ν(NH) 3327, 3287
28	$PtH(NHMe_2)(PBz_3)_2BPh_4$	101—102	70.0 (69.9)	6.1 (6.0)	1.3 (1.2)	2270	ν(NH) 3285
29	$PtH(NH_2Et)(PBz_3)_2BPh_4$	142—144	70.0 (69.7)	6.1 (6.0)	1.0 (1.2)	2258	ν(NH) 3317, 3267
30	$PtH(NH_2Pr\text{-}n)(PBz_3)_2BPh_4$	120—122	70.0 (70.0)	6.3 (6.1)	1.1 (1.2)	2267	ν(NH) 3305, 3261
31	$PtH(NH_2Pr\text{-}i)(PBz_3)_2BPh_4$	137—139	70.0 (70.0)	6.3 (6.1)	1.2 (1.2)	2281	ν(NH) 3306, 3263
32	$PtH(NH_2Bu\text{-}n)(PBz_3)BPh_4$	119—121	69.7 (70.2)	6.2 (6.2)	1.1 (1.2)	2265	ν(NH) 3317, 3266
33	$PtH(NH_2Bu\text{-}sec)(PBz_3)_2BPh_4$	128—130	69.9 (70.2)	5.9 (6.2)	1.2 (1.2)	2263	ν(NH) 3297, 3254
34	$PtH(NH_2Bu\text{-}i)(PBz_3)_2BPh_4$	137—139	70.8 (70.2)	6.3 (6.2)	1.3 (1.2)	2241	ν(NH) 3312, 3268
35	$PtH(NH_2Cy)(PBz_3)_2BPh_4$	120—122	71.0 (70.7)	6.4 (6.3)	1.1 (1.2)	2269	ν(NH) 3297, 3254
36	$PtH(NH_2\text{-}2\text{-}butenyl)(PBz_3)_2BPh_4$	122—124	70.1 (70.2)	6.2 (6.0)	1.4 (1.2)	2258	ν(NH) 3305, 3257
37	$PtH(NH_2CH_2CH_2Ph)(PBz_3)_2BPh_4$	143—145	72.0 (71.4)	6.2 (6.0)	1.2 (1.1)	2248	ν(NH) 3306, 3265
38	$PtH(NH_2Bz)(PBz_3)_2BPh_4$	144—146	71.7 (71.2)	5.9 (5.9)	1.0 (1.1)	2269	ν(NH) 3307, 3268
39	$PtH(NHMeBz)(PBz_3)_2BPh_4$	135—137	70.8 (71.4)	6.3 (6.0)	1.3 (1.1)	2270	ν(NH) 3268
40	$PtH(NH_2Ph)(PBz_3)_2BPh_4$	135—137	70.8 (71.1)	5.9 (5.8)	1.1 (1.2)	2295	ν(NH) 3301, 3239
41	$PtH(NH_2C_6H_4\text{-}4\text{-}Me)(PBz_3)_2BPh_4$	145—147	71.4 (71.2)	5.9 (5.9)	1.2 (1.1)	2297	ν(NH) 3303, 3255
42	$PtH(NH_2C_6H_4\text{-}3\text{-}Me)(PBz_3)_2BPh_4$	136—138	71.1 (71.2)	6.0 (5.9)	1.3 (1.1)	2287	ν(NH) 3298, 3248
43	$PtH(NH_2C_6H_4\text{-}2\text{-}Me)(PBz_3)_2BPh_4$	131—133	71.2 (71.2)	5.9 (5.9)	1.0 (1.1)	2282	ν(NH) 3299, 3255
44	$PtH[NH_2CH_2C(O)OEt](PBz_3)_2BPh_4$	133—136	68.5 (68.5)	5.9 (5.9)	1.0 (1.1)	2276	ν(NH) 3316, 3270; ν(CO) 1744
45	$PtH(NCMe)(PBz_3)_2BPh_4$	138—140	69.9 (70.1)	5.9 (5.7)	1.2 (1.2)	[h]	ν(NC) 2274
46	$PtH(NCBz)(PBz_3)_2BPh_4$	153—155	71.4 (71.6)	5.9 (5.7)	1.4 (1.1)	[h]	ν(NC) 2273
47	$PtH(NCPh)(PBz_3)_2BPh_4$	145—147	71.3 (71.5)	5.5 (5.6)	1.2 (1.1)	[h]	ν(NC) 2252
48	$PtH(NCC_6H_4\text{-}4\text{-}OMe)(PBz_3)_2BPh_4$	140—142	70.9 (70.7)	5.7 (5.6)	1.0 (1.1)	[h]	ν(NC) 2241
49	$PtH(NCC_6H_4\text{-}4\text{-}Me)(PBz_3)_2BPh_4$	137—138	71.8 (71.6)	5.8 (5.7)	1.2 (1.1)	[h]	ν(NC) 2256
50	$PtH(NCC_6H_4\text{-}3\text{-}Me)(PBz_3)_2BPh_4$	147—149	71.4 (71.6)	6.0 (5.7)	1.1 (1.1)	[h]	ν(NC) 2254
51	$PtH(NCC_6H_4\text{-}2\text{-}Me)(PBz_3)_2BPh_4$	141—143	71.1 (71.6)	5.9 (5.7)	1.3 (1.1)	[h]	ν(NC) 2251
52	$PtH(NCCHCH_2)(PBz_3)_2BPh_4$	125—127	69.7 (70.5)	5.7 (5.7)	1.3 (1.2)	[h]	ν(NC) 2246

(continued)

TABLE 1 (continued)

No.	Compound [a]	M.p. (°C)	Analysis (Found (calcd), wt.%)			ν(PtH) (cm^{-1}) [e]	Others (cm^{-1})
			C	H	Halogen or N		
53	PtH(NCCHCHMe)$(PBz_3)_2BPh_4$	118—120	70.8 (70.6)	5.8 (5.8)	1.2 (1.2)	[h]	ν(NC) 2236
54	PtH[NCC(Me)CH_2]$(PBz_3)_2BPh_4$	141—143	70.8 (70.6)	5.7 (5.8)	1.3 (1.2)	[h]	ν(NC) 2251
55	PtH[NCC(Cl)CH_2]$(PBz_3)_2BPh_4$	131—133	67.8 (68.4)	5.4 (5.4)	1.3 (1.2)	[h]	ν(NC) 2246
56	PtH(NCSMe)$(PBz_3)_2BPh_4$	123—125	68.3 (68.2)	5.5 (5.6)	1.0 (1.2)	[h]	ν(NC) 2171
57	PtH(Py)$(PBz_3)_2BPh_4$	158—160	70.8 (70.9)	5.7 (5.7)	1.2 (1.2)	2290	
58	PtH(2-Me-py)$(PBz_3)_2BPh_4$	150—152	71.2 (71.1)	5.8 (5.8)	1.1 (1.2)	2261	
59	PtH(3-Me-py)$(PBz_3)_2BPh_4$	156—158	71.7 (71.1)	5.9 (5.8)	1.1 (1.2)	2256	
60	PtH(4-Me-py)$(PBz_3)_2BPh_4$	122—124	70.9 (71.1)	5.9 (5.8)	0.9 (1.2)	2269	
61	PtH(2-Et-py)$(PBz_3)_2BPh_4$	134—136	70.9 (71.2)	5.8 (5.9)	1.0 (1.1)	2256	
62	PtH(4-Ph-py)$(PBz_3)_2BPh_4$	147—149	71.9 (72.3)	6.0 (5.7)	1.0 (1.1)	2262	
63	PtH(3,5-lut)$(PBz_3)_2BPh_4$	151—153	70.6 (71.2)	5.9 (5.9)	1.1 (1.1)	2286	
64	PtH(2,6-lut)$(PBz_3)_2BPh_4$	135—137	71.4 (71.2)	6.0 (5.9)	1.1 (1.1)	2223	
65	PtH(2,5-lut)$(PBz_3)_2BPh_4$	146—148	71.4 (71.2)	6.0 (5.9)	1.2 (1.1)	2259	
66	PtH(2,4-lut)$(PBz_3)_2BPh_4$	149—151	71.2 (71.2)	6.0 (5.9)	1.2 (1.1)	2266	
67	PtH(2,3-lut)$(PBz_3)_2BPh_4$	153—155	71.1 (71.2)	6.2 (5.9)	1.3 (1.1)	2253	
68	PtH(γ-collidine)$(PBz_3)_2BPh_4$	148—150	70.9 (71.1)	5.9 (6.1)	1.2 (1.1)	2211	
69	PtH(quinoline)$(PBz_3)_2BPh_4$	145—147	72.1 (71.9)	5.7 (5.6)	1.2 (1.1)	2205	
70	PtH(isoquinoline)$(PBz_3)_2BPh_4$	157—159	72.7 (71.9)	5.7 (5.6)	1.1 (1.1)	2264	
71	PtH(iz)$(PBz_3)_2BPh_4$	168—170	69.4 (69.6)	5.7 (5.7)	2.2 (2.4)	2255	ν(NH) 3323
72	PtH(benz-iz)$(PBz_3)_2BPh_4$	140—141	70.5 (70.6)	5.8 (5.6)	2.3 (2.3)	2265	ν(NH) 3290
73	PtH(1-Me-iz)$(PBz_3)_2BPh_4$	136—138	69.9 (69.7)	5.9 (5.8)	2.2 (2.3)	2268	
74	PtH(2-Me-iz)$(PBz_3)_2BPh_4$	167—169	69.7 (69.7)	5.9 (5.8)	2.3 (2.3)	2199	ν(NH) 3334
75	PtH[2,5(4)-Me_2-iz]$(PBz_3)_2BPh_4$	168—170	69.7 (69.9)	5.9 (5.9)	2.5 (2.3)	2203	ν(NH) 3338
76	PtH(pz)$(PBz_3)_2BPh_4$	173—175	69.2 (69.6)	5.7 (5.7)	2.3 (2.4)	2272	ν(NH) 3348
77	PtH[5(3)-Me-pz]$(PBz_3BPh_4$	179—181	69.7 (69.7)	5.6 (5.8)	2.5 (2.3)	2276	ν(NH) 3359
78	PtH(3,5-Me_2-pz)$(PBz_3)_2BPh_4$	183—184	69.6 (69.9)	6.0 (5.9)	2.6 (2.3)	2262	ν(NH) 3362
79	PtH(3,4,5-Me_3-pz)$(PB_3)_2BPh_4$	172—173	69.9 (70.1)	6.2 (6.0)	2.4 (2.3)	2260	ν(NH) 3392
80	PtH(3,5-Me_2-4-Br-pz)$(PBz_3)_2BPh_4$	154—156	65.9 (65.6)	5.5 (5.4)	1.9 (2.2)	2282	ν(NH) 3379

(continued)

TABLE 1 (continued)

No.	Compound [a]	M.p. (°C)	Analysis (Found (calcd), wt.%)			ν(PtH) (cm^{-1}) [e]	Others (cm^{-1})
			C	H	Halogen or N		
81	PtH[3(5)-Ph-5(3)-Me-pz](PBz$_3$)$_2$BPh$_4$	182—184	71.3 (71.2)	5.6 (5.7)	2.4 (2.2)	2279	ν(NH) 3354
82	PtH(1,3,4,5-Me$_4$-pz)(PBz$_3$)$_2$BPh$_4$	165—167	70.3 (70.2)	5.8 (6.1)	2.4 (2.2)	2210	
83	PtH(1,3,5-Me$_3$-pz)(PBz$_3$)$_2$BPh$_4$	141—142	70.2 (70.1)	5.9 (6.0)	2.0 (2.3)	2213	
84	PtH(1-Ph-3,4,5-Me$_3$-pz)(PBz$_3$)$_2$BPh$_4$	169—171	71.3 (71.5)	5.8 (5.9)	2.5 (2.1)	2270	
85	PtH(allyl-pz)(PBz$_3$)$_2$BPh$_4$	134—136	70.2 (70.2)	6.1 (5.8)	2.3 (2.3)	2268	
86	PtH(PBz$_3$)$_3$BPh$_4$	195—196	73.6 (73.2)	6.0 (5.9)		2145	
87	PtH(PPh$_3$)(PBz$_3$)$_2$BPh$_4$ [c]	191—193	72.6 (72.8)	5.6 (5.7)		2140, 2123	
88	PtH(PPh$_3$)(PBz$_3$)$_2$ClO$_4$	226—228	61.8 (61.8)	5.0 (5.0)		2156, 2131	ν(ClO) 1085
89	PtH(PPh$_3$)(PBz$_3$)$_2$(tcsyl)	211—213	65.0 (65.0)	5.3 (5.3)		2135(2147, 2136) [d]	
90	PtH(PPh$_2$Me)(PBz$_3$)$_2$BPh$_4$	181—182	70.9 (71.7)	6.0 (5.8)		2130	
91	PtH(PPhMe$_2$)(PBz$_3$)$_2$BPh$_4$	185—188	70.4 (70.4)	6.0 (5.8)		2127	
92	PtH[P(OMe)$_3$](PBz$_3$)$_2$BPh$_4$	158—160	65.9 (66.4)	6.0 (5.8)		2117	
93	PtH[P(OPh)$_3$](PBz$_3$)$_2$BPh$_4$	150—152	60.0 (70.3)	5.7 (5.5)		2165	
94	PtH[PPh(OMe)$_2$](PBz$_3$)$_2$BPh$_4$	167—169	68.8 (68.7)	5.5 (5.8)		2153	
95	PtH(AsPh$_3$)(PBz$_3$)$_2$BPh$_4$	170—172	70.6 (70.5)	5.5 (5.5)		2154	
96	PtH(SbPh$_3$)(PBz$_3$)$_2$BPh$_4$	166—168	68.1 (68.3)	5.2 (5.3)		2141	
97	PtH(CO)(PBz$_3$)$_2$BPh$_4$	146—148	69.8 (69.9)	5.6 (5.5)		2207	ν(CO) 2074
98	PtH(py-*N*-oxide)(PBz$_3$)$_2$BPh$_4$	134—136	70.2 (70.0)	5.8 (5.6)	1.1 (1.2)	*h*	
99	PtH(4-Me-py-*N*-oxide)(PBz$_3$)$_2$BPh$_4$	130—132	69.5 (70.1)	5.8 (5.7)	1.0 (1.1)	*h*	
100	PtH[OC(NH$_2$)$_2$](PBz$_3$)$_2$BPh$_4$	108—110	67.8 (68.0)	5.9 (5.7)	2.2 (2.4)	*h*	ν(NH) 3479, 3433, 3340; ν(CO) 1631
101	PtH[OC(NH$_2$)NHMe](PBz$_3$)$_2$BPh$_4$	127—128	68.1 (68.2)	6.0 (5.8)	2.3 (2.3)	*h*	ν(NH) 3439, 3373, 3338; ν(CO) 1611
102	PtH[OC(NHMe)$_2$](PBz$_3$)$_2$BPh$_4$	128—130	68.2 (68.4)	6.0 (5.9)	2.4 (2.3)	*h*	ν(NH) 3393; ν(CO) 1613
103	PtH[OCH(NH$_2$)](PBz$_3$)$_2$BPh$_4$	110—112	69.3 (68.8)	5.8 (5.7)	1.2 (1.2)	*h*	ν(NH) 3410, 3320, 3295; ν(CO) 1659
104	PtH[OCH(NHMe)](PBz$_3$)$_2$BPh$_4$	98—100	69.0 (69.0)	5.7 (5.8)	1.1 (1.2)	*h*	ν(NH) 3354; ν(CO) 1632
105	PtH[OCH(NMe$_2$)](PBz$_3$)$_2$BPh$_4$	78—81	69.1 (69.2)	5.8 (5.9)	1.2 (1.2)	*h*	ν(CO) 1649

(continued)

TABLE 1 (continued)

No.	Compound [a]	M.p. (°C)	Analysis (Found (calcd), wt.%)			ν(PtH) (cm^{-1}) [e]	Others (cm^{-1})
			C	H	Halogen or N		
106	$PtH[OCMe(NH_2)](PBz_3)_2BPh_4$	80—83	68.8 (69.0)	5.8 (5.8)	1.1 (1.2)	h	ν(NH) 3435, 3327; ν(CO) 1632
107	$PtH[OCMe(NHMe)](PBz_3)_2BPh_4$	118—120	69.2 (69.2)	6.0 (5.9)	0.9 (1.2)	h	ν(NH) 3361; ν(CO) 1606
108	$PtH[OCMe(NMe_2)](PBz_3)_2BPh_4$	125—127	69.5 (69.4)	5.9 (6.0)	1.2 (1.1)	h	ν(CO) 1594
109	$PtH(2\text{-pyrrolidone})(PBz_3)_2BPh_4$	126—128	69.4 (69.5)	5.9 (5.8)	1.3 (1.2)	h	ν(NH) 3335; ν(CO) 1641
110	PtH(N-Me-2-pyrrolidone) $(PBz_3)_2BPh_4$	96—98	69.4 (69.7)	5.9 (5.9)	0.9 (1.1)	h	ν(CO) 1630
111	$PtH(\epsilon\text{-caprolactam})(PBz_3)_2BPh_4$	129—131	69.9 (69.9)	6.1 (5.9)	1.2 (1.1)	h	ν(NH) 3279; ν(CO) 1607
112	$PtH(cyclohexanone)(PBz_3)_2BPh_4$	103—107	67.1 (67.1)	6.0 (5.8)		h	ν(CO) 1717 (free), 1637
113	$PtH(cyclopentanone)(PBz_3)_2BPh_4 \cdot CH_2Cl_2$	99—104	66.7 (66.9)	5.7 (5.7)			ν(CO) 1747 (free), 1672
114	$PtH(SMe_2)(PBz_3)_2BPh_4$	150—152	68.5 (68.9)	5.9 (5.9)		2219	
115	PtH(tetrahydrothiophene) $(PBz_3)_2BPh_4$	155—157	69.3 (69.4)	5.9 (5.9)		2231	
116	$PtH[S(Me)Ph](PBz_3)_2BPh_4$	147—148	70.3 (70.2)	5.8 (5.7)		2211	
117	$PtH([SC(NH_2)_2](PBz_3)_2BPh_4$	170—172	67.4 (67.1)	5.8 (5.6)	1.9 (2.3)	2205	ν(NH) 3467, 3407, 3319, 3205
118	$PtH[SC(NH_2)NHMe]$ $(PBz_3)_2BPh_4$	186—187	67.3 (67.3)	5.6 (5.7)	2.4 (2.7)	2205	ν(NH) 3394 (br), 3312 3290(sh), 3255(sh)
119	$PtH[SC(NHMe)_2](PBz_3)_2BPh_4$	179—181	67.2 (67.5)	6.0 (5.8)	2.5 (2.3)	2194	ν(NH) 3362; ν(CN) + + δ(NCS) 1575
120	$PtH[SC(NHMe)NMe_2](PBz_3)_2BPh_4$	166—167	68.0 (68.2)	6.1 (6.0)	2.2 (2.3)	2216	ν(NH) 3371, 3300; ν(CN) + δ(NCS) 1557
121	$PtH[SC(NMe_2)_2](PBz_3)_2BPh_4$	167—168	68.0 (67.9)	6.3 (6.0)	2.2 (2.3)	2197	ν(CN) + δ (NCS) 1547
122	$PtH[SCMe(NH_2)](PBz_3)_2BPh_4$	181—183	67.5 (68.1)	6.0 (5.7)	1.2 (1.2)	2203	ν(NH) 3342, 3291
123	$PtH[SC(OEt)NHMe](PBz_3)_2BPh_4$	166—168	67.7 (67.6)	5.9 (5.8)	1.3 (1.1)	2199	ν(NH) 3349; ν(CN) + δ (NCS) 1557

[a] Me, methyl; Et, ethyl; Pr, propyl; Bu, butyl; Cy, cyclohexyl; Ph, phenyl; Bz, benzyl; lut, lutidine; iz, imidazole; pz, pyrazole; py, pyridine. [b] Conductivity 73.8 ohm^{-1} cm^2 $equiv^{-1}$ in nitromethane at 20.1°C. Conductivity 44.2 ohm^{-1} cm^2 $equiv^{-1}$ in nitromethane at 20.1°C. [d] A crude product before recrystallization. [e] Nujol Mull, experimental error ± 4 cm^{-1}. [f] In $CHCl_3$. [g] In CH_2Cl_2. [h] Not observed.

TABLE 2

NMR DATA ON A SERIES OF HYDRIDOBENZYLPHOSPHINEPLATINUM(II) COMPLEXES

Compound		Hydride proton			Methylene proton in Bz			^{31}P		Others: τ (ppm) and J(Hz)
No.	Ligand (X or L)	τ(H) [a] (ppm)	^1J(Pt—H) [b] (Hz)	^2J(P—H) [c] (Hz)	τ(H) [a] (ppm)	^3J(Pt—CH_2) [c] (Hz)	J(P—CH_2) [c,d] (Hz)	δ [e] (ppm)	^1J(Pt—P) (Hz) [b]	
The neutral complexes: trans-PtHX(PBz$_3$)$_2$ in $CDCl_3$										
1	Cl	27.86	1290	12.0	6.75	31.5	3.5	−23.4	2969	C_6H_5 2.81(singlet)
2	Br	26.47	1345	12.0	6.74	32.0	3.5	−21.1	2925	C_6H_5 2.81(singlet)
3	I	23.62	1359	10.0	6.68	32.0	3.5	−18.5	2882	C_6H_5 2.83(singlet)
4	-NCO	28.07	1050	13.0	6.93	33.0	3.0			C_6H_5 2.91(singlet)
5	-SCN	23.58	1186	11.0	6.83	33.5	3.5			
	-NCS	28.21		13.0	6.87	33.0	4.0			
6	-SeCN	23.02	1200	10.5	6.78	33.0	3.5	−22.3	2925	C_6H_5 2.83(quintet)
7	$SnCl_3$	[f]			[f]					
8	N_3	28.75	1154	13.5	6.85	32.0	3.5			C_6H_5 3.01(singlet)
9	CN	16.69	776	13.0	6.69	32.0	3.5			C_6H_5 2.79(singlet)
10	ClO_4	36.47	1518	11.5	6.86	33.5	3.5			C_6H_5 2.81(quintet)
11	NO_3	34.39	1330	12.5	6.91	33.5	4.0	−27.2	3094	C_6H_5 2.81(singlet)
12	-NO_2	30.32	1008	14.0	6.82	33.0	4.0			C_6H_5 2.78(singlet)
13	SH	21.03	992	13.0	6.74	32.5	3.5			C_6H_5 2.80(singlet; SH 11.39(br, singlet)
13	(in CH_2Cl_2)	21.02	993	13.0	6.79	32.5	3.5			C_6H_5 2.82(singlet); SH 11.54; ^2J(HS—Pt) 58.5 ^3J(HS—P) 8.5
14	SMe	21.20	938	14.5	6.73	32.0	3.5			C_6H_5 2.82(singlet), Me 7.92; ^3J(Me—Pt) 30.0; ^4J(Me—H) 1.5
15	SBu-t	22.61	966	14.5	6.65	32.5	3.0			C_6H_5 2.84(singlet); Me 8.73
16	SBz	21.29	981	13.5	6.71	31.5	3.0			SCH_2 6.50; ^3J(CH_2S—Pt) 23.5
17	SC_6H_4-4-Me	21.47	983	12.5	6.92	31.5	3.5			Me 7.79; 3,5-CH 3.25; ^{3}(CH—CH) 8
18	SC(O)Me	21.65	996	11.5	6.86	33.0	3.5			C_6H_5 2.82(singlet); Me 7.52; ^4J(Me—Pt) 6
19	2-mercapto-benzothiazole	22.62	1086	11.5	6.78	33.0	3.0			4- or 7-CH 2.32 or 2.51; ^3J(CH—CH) 7
20	$SO_2C_6H_4$-4-Me	23.07	876	14.5	6.80	30.5	3.0			Me 7.77
21	$(MeO)_2P(O)$	16.26	690	14.0 227 [f]	6.63	30.0	3.5			C_6H_5 2.83(singlet); OMe 6.67; ^3J(Me—P) 10.5
22	$(EtO)_2P(O)$	16.16	675	14.5 225 [f]		[f]				Me 8.90; ^3J(Me—CH_2) 7

23	(MeO)PhP(O)	16.18	712	11.5 213 [j]	6.73	35.5	3.5			OMe 6.61; ^3J(Me—P) 10.0
24	H	12.40	800	19.0	6.81	34.5	3.5			
25	BPh_4 [f]	17.42	852	9.5		[k]		−14.7	2615	
The cationic complexes: trans-$PtHL(PEt_3)_2BPh_4$ (except 88, 89) in CH_2Cl_2										
26	NH_3	28.16	1042	13.5	7.03	34.5	3.5	−21.8	2928	NH_3 8.63(br)
27	NH_2Me	28.59	1002	15.0	6.88	35.5	3.5	−19.7	2921	Me 8.88(multiplet); NH_2 9.08(br)
28	$NHMe_2$	29.71	956	15.5	6.87	34.5	3.5	−19.9	2974	Me 8.5(sextet); NH 8.44(br)
29	NH_2Et	28.35	1002	15.5	6.84	34.5	3.5			NCH_2 8.70(multiplet); NH_2 9.08(br); Me 9.78; $^3J(CH_2—Me)$ 6.5
30	NH_2Pr-n	28.32	1009	16.0	6.80	35.0	3.5			NCH_2 8.81(br); NH_2 9.05(br); CCH_2C 9.60(multiplet); Me 9.64
31	NH_2Pr-i	28.20	995	15.5	6.84	35.0	3.5			NCH 8.15(multiplet); NH_2 9.05; Me 9.64; ^3J(Me—CH) 6.5
32	NH_2Bu-n	28.30	1009	15.5	6.81	35.5	3.5			NCH_2 8.74(br); NH_2 9.08(br); CCH_2CH_2C 9.56(multiplet); Me 9.38
33	NH_2Bu-s	28.21	997	15.5	6.89	36.0	3.5			NH_2 9.02, NCH 9.02(br), $NCCH_2$ 9.54(multiplet); NCMe 9.70; ^3J(Me—CH) 6; NCCMe 9.68
34	NH_2Bu-i	28.30	1022	15.5	6.82	35.5	3.5			NH_2 9.10(br); NCH_2 8.95; $^3J(CH_2—CH)$ 5.0; NCCH 9.52(br); CCMe 9.80; ^3J(Me—CH) 6.0
35	NH_2Cy	28.11	996	15.5	6.82	35.0	3.5			NH_2 8.98; Cy 8.4—10.2
36	NH_2-2-butenyl	28.38	1024	15.0	6.88	34.5	3.5			NH_2 9.01; NCH_2 8.11; $NCCCH_2$ 4.66(multiplet), 4.34(multiplet)
37	$NH_2CH_2CH_2Ph$	28.35	1028	15.0	6.94	35.5	3.0			NH_2 9.0(br); NCH_2 8.32(br); $NCCH_2$ 8.21; 2,6-CH 3.49(multiplet)
38	NH_2Bz	28.34	1030	15.5	6.84	34.5	3.5			NH_2 8.80(br); NCH_2 7.52; $^3J(CH_2—NH_2)$ 7.5
39	NHMeBz	29.68	977	16.0	6.89	34.5	3.5	−19.4	2934	NH 7.61(br); Me 8.6(multiplet); NCH_2 7.61(br); 2,6-CH 3.48(multiplet)
40	NH_2Ph	29.75	1100	14.5	7.01	36.5	3.5	−21.7	2961	NH_2 8.74(br)
41	$NH_2C_6H_4$-4-Me	29.64	1091	14.0	6.98	37.5	3.5			4-Me 7.85; 2,6-CH 4.04; ^3J(CH—CH) 8.0
42	$NH_2C_6H_4$-3-Me	29.79	1097	15.0	7.02	37.0	3.5			3-Me 7.92; 2,6-CH 4.14(br)
43	$NH_2C_6H_4$-2-Me	29.64	1111	14.0	7.10	36.0	3.5			2-Me 8.36; 6-CH 3.85(br)
44	$NH_2CH_2C(O)OEt$	28.88	1046	14.5	6.88	36.0	3.5			NCH_2 8.36(quintet); OCH_2 6.09; $^3J(CH_2—Me)$ 8; Me 8.83

(continued)

TABLE 2 (continued)

Compound		Hydride proton			Methylene proton in Bz			^{31}P		Others: τ (ppm) and J(Hz)
No.	Ligand (X or L)	τ(H) [a] (ppm)	^1J(Pt—H) [b] (Hz)	^2J(P—H) [c] (Hz)	τ(H) [a] (ppm)	^3J(Pt—CH_2) [c] (Hz)	J(P—CH_2) [c,d] (Hz)	δ [e] (ppm)	^1J(Pt—P) (Hz) [b]	
44	(in $CDCl_3$)				6.97	36.5	3.0			NCH_2 8.42; OCH_2 6.09; ^3J(CH—CH_2) 7; Me 8.90
45	NCMe	28.24	1147	12.0	6.85	36.5	3.5			Me 8.91; ^4J(Me—Pt) 3.5
46	NCBz	28.17	1159	12.0	7.01	34.5	3.5			$NCCH_2$ 7.13
47	NCPh	27.77	1157	12.0	6.84	36.5	3.5	−23.8	2916	
48	NCC_6H_4-4-OMe	27.80	1146	12.0	6.83	36.0	3.5			Me 6.32
49	NCC_6H_4-4-Me	27.77	1148	12.0	6.92	34.5	3.5			Me 7.74
50	NCC_6H_4-3-Me	27.77	1151	12.0	6.90	35.0	3.5			Me 7.77
51	NCC_6H_4-2-Me	27.74	1149	12.5	6.90	34.5	3.5			Me 8.04
52	$NCCHCH_2$	27.93	1152	12.0	6.92	35.5	3.5			$CHCH_2$ 4.22, 4.33, 4.51; $CHCH_2$ 4.39, 4.50, 4.65
52	(in $CDCl)_3$									
53	NCCHCHMe	27.90	1149	12.0	6.92	35.0	3.5			Me 8.4(quintet); CHCH 4.31
54	$NCC(Me)CH_2$	27.82	1158	12.0	6.89	36.0	3.5			Me 8.51(multiplet); CH_2 4.42
54	(in $CDCl_3$)	27.84	1159	12.0	7.06	35.0	3.5			Me 8.66(multiplet); CH_2 4.68, 4.94
55	$NCC(Cl)CH_2$	27.76	1175	12.0	6.91	35.5	3.5			CH_2 4.24, 4.55; ^2J(HCH) 4
56	NCSMe	28.19	1152	12.0	6.83	36.5	3.5			Me 8.12
57	py	28.89	1022	14.0	6.99	34.5	3.5	−21.1	2919	
58	2-Me-py	28.58	1032	13.5		*k*				2-Me 7.98
59	3-Me-py	28.79	1015	14.0	6.95	34.5	3.5			3-Me 8.20
60	4-Me-py	28.77	1017	14.0	7.01	34.0	3.5			4-Me 7.93
61	2-Et-py	28.59	1038	13.0	7.03	36.0	3.0			Me 8.98; CH_2 7.53; ^3J(Me—CH_2) 7.5
62	4-Ph-py	28.67	1017	14.0	6.97	34.5	3.5			
63	3,5-lut	28.69	1007	14.5	7.02	34.5	3.0	−20.7	2911	3, 5-Me 8.35; 2, 6-CH 4.06; ^3J(CH—Pt) 23.5
63	(in $CDCl_3$)				7.01	34.0	3.0			3,5- Me 8.32; 2, 6-CH 3.95; ^3J(CH—Pt) 22.0
64	2, 6-lut	28.13	1058	14.5	7.08	33.5	3.5			2,6 -Me 8.06
65	2, 5-lut	28.47	1027	13.5		*k*				2-Me 8.00; 5-Me 8.16; 3-CH 3.27, 6-CH 3.46; ^3J(CH—Pt) 21.5
66	2, 4-lut	28.47	1028	13.5		*k*		−19.5	2902	2-Me 7.99, 4-Me 7.87
67	2, 3-lut	28.70	1032	13.5		*k*				2,3-Me 7.97

68	γ-collidine	27.99	1053	15.0	7.13	34.0	3.5	−13.9	2861	2,6-Me 8.05; ^4J(Me—Pt) 5.0; 4-Me 7.86; 3, 5-CH 3.32
68	(in $CDCl_3$)	27.97	1058	15.0						2, 6-Me 8.13; ^4J(Me—Pt) 4.5; 4-Me 7.86; 3,5-CH 3.44
69	quinoline	28.18	1051	13.5	7.09	33.5	3.5	−19.9	2884	
70	isoquinoline	28.63	1013	14.0	6.99	35.0	3.5			
71	iz	27.71	994	13.5	7.60	35.0	3.5	−23.0	2945	4-CH 4.11(br)
72	benz-iz	27.16	1013	13.5	7.17	31.0	3.0			2-CH 4.60; ^3J(CH—Pt) 11.5
73	1-Me-iz	27.66	1008	14.0	6.99	35.0	3.5			Me 6.99; 4-CH 3.60
74	2-Me-iz	27.28	997	13.0	7.13	34.5	3.5			2-Me 8.77; ^4J(CH—Pt) 4; 4-CH 3.95
75	2, 5(4)-Me_2-iz	27.21	987	13.5	7.13	34.0	3.5			2-Me 8.75; ^4J(CH—Pt) 4; 5-Me 8.36
76	pz	28.24	1060	13.0	7.06	34.5	3.0	−25.8	2916	4-CH 3.90
77	5-Me-pz	28.12	1048	13.5	7.01	38.5	4.0	−25.7	2928	5-Me 8.19; 4-CH 4.20
	3-Me-pz	Not observed			Not observed					3-Me 8.12; 4-CH 3.98
78	3,5-Me_2-pz	27.78	1016	13.0		*k*		−25.0	2923	3-Me 8.16; ^4J(Me—Pt); 3,5-Me 8.21; 4-CH 4.26
78	(in $CDCl_3$)									3-Me 8.27; ^4J(Me—Pt) 3; 5-Me 8.31; 4-CH 4.36
79	3,4,5-Me_3-pz	27.80	1030	13.0		*k*		−25.3	2921	3-Me 8.37; 4-Me 8.40; 5-Me 8.33
80	3,5-Me_2-4-Br-pz	28.15	1051	13.5		*k*				3-Me 8.52; 5-Me 8.28
81	3-Me-5-Ph-pz	27.69	1051	13.0						3-Me 8.15; ^4J(Me—Pt) 4; 4-CH 3.83
	5-Me-3-Ph-pz	28.24	1043	12.5		*k*		−24.7	2935	5-Me 8.10; 4-CH 3.70
82	1,3,4,5-Me_4-pz	27.21	1067	14.0	7.05	35.0	3.0	−19.7	28.30	1-Me 7.33; 3-Me 8.36; 4-Me 8.28; 5-Me 8.17
83	1,3,5-Me_3-pz	27.29	1076	14.0	7.05	34.5	3.0	−19.7	2830	1-Me 7.37, 3-Me 8.27, 5-Me 8.08
84	1-Ph-3,4,5-Me_3-pz	28.39	1054	13.0		*k*		−18.9	2892	3-Me 8.43, 4-Me 8.05, 5-Me 7.92
85	allyl-pz	28.08	1082	13.0	7.11	35.0	3.5			NCH_2 6.14; $^3J(CH_2—CH_2)$ 5, NCCH 4.66; $NCCCH_2$ 4.9; 4-CH 4.80; 3,5-CH 4.0
86	PBz_3	17.28	714	14.0	7.12	32.0	3.0	−14.6	2682	^2J(P—P′) 24 *m*
				164 *l*	7.45	16.0	8.0			
87	PPh_3	16.87	783	11.5	7.23	32.5	3.5	−16.5	2717	^2J(P—P′) 25 *m*
				158 *l*						
88	PPh_3 *g*	16.83	*i*	*i*	6.99	33.0	3.5			
89	PPh_3 *h*	16.80	789	12.0	7.02	34.5	3.5			4-Me 7.72
				158 *l*						
90	PPh_2Me	16.49	756	12.5	7.03	34.0	3.0			Me 8.71; ^2J(Me—P) 8; ^3J(Me—Pt) 24
				159 *l*						
91	$PPhMe_2$		*i*		6.90	32.5	4.0			Me 9.01; ^2J(Me—P) 8; ^3J(Me—Pt) 16.5
92	$P(OMe)_3$	15.58	749	11.0	6.85	32.5	3.5	−23.2	2663	Me 6.81; ^3J(Me—P) 12.0; ^2J(P—P′) 30 *m*
				262 *l*						

(continued)

TABLE 2 (continued)

Compound		Hydride proton			Methylene proton in Bz			^{31}P		Others: τ (ppm) and J(Hz)
No.	Ligand (X or L)	τ(H) [a] (ppm)	^{1}J(Pt—H) [b] (Hz)	^{2}J(P—H) [c] (Hz)	τ(H) [a] (ppm)	^{3}J(Pt—CH_2) [c] (Hz)	J(P—CH_2) [c,d] (Hz)	δ [c] (ppm)	^{1}J(Pt—P) (Hz) [b]	
93	$P(OPh)_3$	15.85	758	11.0 285 [f]	6.97	32.5	3.5	−20.8	2620	
94	$P(OMe)_2Ph$	15.32	[f]	11.0 175 [f]	6.81	33.5	3.5			
95	$AsPh_3$	18.85	1009	11.0	7.15	33.5	3.5	−18.5	2708	
96	$SbPh_3$	17.75	1173	9.0	6.98	34.0	3.0	−19.5	2632	
97	CO	16.12	840	10.0	6.83	35.5	3.5			
98	py-*N*-oxide	33.62	1294	13.5	7.00	36.0	3.5	−28.8	3027	
99	4-Me-py-*N*-oxide	33.60	1280	13.5	7.04	35.0	3.0			4-Me 7.96; 2,6-CH 3.59; ^{3}J(CH—CH) 6.5
100	$OC(NH_2)_2$	33.90	[f]	14.5	7.07	34.5	3.5			
101	$OC(NH_2)NHMe$	33.99	[f]	[f]	7.01	33.5	3.0			Me 7.91; ^{3}J(Me—NH) 4
102	$OC(NHMe)_2$	33.78	1317	13.5	6.98	35.5	3.5			Me 7.93(br); NH 6.10
102	(at −60°C)				6.90	34.5	3.5			Me 7.58, 8.29; ^{3}J(Me—NH) 45; NH 5.86(br)
103	$OCH(NH_2)$	34.19	[f]	[f]	6.20	34.5	3.5			NH_2 6.20, 6.63
104	OCH(NHMe)	34.93	1359	13.5	7.03	33.5	3.0			Me 8.09; ^{3}J(Me—NH) 5; NH 5.41
105	$OCH(NMe_2)$	34.89	1354	13.0	6.97	36.0	3.5			Me 7.70, 7.73; OCH 4.40(br)
106	$OCMe(NH_2)$	33.81	1337	13.0	7.01	33.5	3.5	−29.2	3015	Me 8.72; NH_2 5.98(br)
107	OCMe(NHMe)	34.59	1338	13.5	7.05	33.0	3.0			NMe 7.98; ^{3}J(Me—NH) 5, OCMe 9.37; NH 5.91
108	$OCMe(NMe_2)$	34.59	1337	13.5	6.87	35.0	3.5			NMe 7.48, 7.52; OCMe 8.92
109	2-pyrrolidone	33.98	1331	13.0	6.96	36.0	3.5			5-CH_2 7.38; ^{3}J(CH_2—CH_2) 6.5, 4-CH_2 8.36(multiplet); 3-CH_2 8.22; ^{3}J(CH_2—CH_2) 6.0; NH 6.16
110	N-Me-2-pyrrolidone	34.61	1342	14.5	7.14	35.5	3.5			Me 7.71; 3-CH_2 8.67; ^{3}J(CH_2—CH_2) 7.5; 4-CH_2 8.95; 5-CH_2 7.14

111	ε-Caprolactam	33.18	1315	13.5	6.94	34.0	3.5			7-CH_2 7.63, 3-CH_2 7.89; 4,5,6-CH_2 7.72
112	Cyclohexanone	34.12	*l*	*l*	7.07	35.0	3.5			
113	Cyclopentanone	33.82	*l*	*l*	6.95	35.5	3.5			
114	SMe_2	23.30	1094	11.5	6.85	33.5	3.0	−21.1	2820	Me 8.52; ^3J(Me—Pt) 25.2; ^4J(MePt—H) 1.5
115	Tetrahydro-thiophene	23.36	1090	13.0	6.86	34.0	3.5	−20.9	2838	2,5-CH_2 7.86; 3,4-CH_2 8.57
116	S(Me)Ph	23.51	1124	12.0	6.93	35.0	3.5			Me 8.18; ^3J(Me—Pt) 24.0; ^4J(MePt—H) 1.5
117	$SC(NH_2)_2$	22.09	1134	10.0	6.99	31.5	3.5			NH_2 6.21(br)
118	$SC(NH_2)NHMe$		*l*		6.98	33.5	3.5			Me 7.70; ^3J(Me—NH) 5.5; NH or NH_2 6.22
119	$SC(NHMe)_2$	21.68	1130	10.5	6.86	32.0	3.5	−24.0	2817	Me 7.38(br) 8.47(br)
119	(in $CDCl_3$)				6.94	32.0	3.0			Me 7.57(br) 8.80(br); NH_2 5.23, 5.67
119	(at −60°C)				6.86	30.0	3.5			Me 7.34, 8.59; ^3J(Me—NH) 4.5; NH 5.07, 5.32
120	$SC(NHMe)NMe_2$	23.53	1170	11.0	6.93	33.0	3.0			Me 7.61(multiplet)
120	(in $CDCl_3$)				7.01	32.5	3.0			NMe_2 7.83; NMe 7.69; ^3J(Me—NH) 5
121	$SC(NMe_2)_2$	23.38	1112	10.5	6.91	32.5	3.0			Me 7.34
121	(in $CDCl_3$)				6.97	32.0	3.5			Me 7.54
122	$SCMe(NH_2)$	21.42	1104	10.0	6.91	31.5	3.5	−25.8	2801	Me 8.41; NH_2 6.3(br)
123	SC(OEt)NHMe	21.89	1157	10.5	6.80	33.0	3.0			NMe 7.87; ^3J(Me—NH) 6; OCMe 8.67; ^3J(Me—CH_2) 7; OCH_2 5.64

[a] Experimental error ± 0.05 ppm. [b] Experimental error ± 5 Hz. [c] Experimental error ± 0.5 Hz. [d] Virtual coupling. [e] Chemical shift referred to 85% H_3PO_4, experimental error ± 0.2 ppm. [f] Chemical formula: $PtH(PBz_3)_2BPh_4 \cdot \frac{1}{2}CH_2Cl_2$. The spectrum was measured in dichloromethane. [g] Chemical formula: *trans*-$PtH(PPh_3)(PBz_3)_2ClO_4$. [h] Chemical formula: *trans*-$PtH(PPh_3)(PBz_3)_2$(tosyl). [i] The spectrum was not observed because of poor solubility of the sample in $CDCl_3$. [j] No determination due to overlapping of the methylene signal in PBz_3 with that of ethoxy groups. [k] Complex multiplet: τ 6.0—8.0 ppm. [l] Coupling of hydride with phosphorus in X or L *trans* to H^-. [m] Coupling between ^{31}P in PBz_3 and ^{31}P in X or L. [n] Experimental error in parentheses.

TABLE 3

ANALYTICAL AND INFRARED DATA ON SOME HYDRIDOCYCLOHEXYLPHOSPHINEPLATINUM(II) COMPLEXES

No.	Compound	M.p. (°C)	Analysis (Found (calcd), wt.%)			ν(PtH) (cm^{-1}) [a]	Others (cm^{-1})
			C	H	N		
124	$PtHCl(PCy_3)_2$	228—230	54.3 (54.6)	8.5 (8.5)		2179	
125	$PtH(NO_3)(PCy_3)_2$	186—188	52.5 (52.8)	8.3 (8.3)	1.7 (1.7)	2248	$\nu(NO_3)$ 1228
126	$PtH(NCS)(PCy_3)_2$	242—244	54.4 (54.5)	8.4 (8.3)	1.8 (1.7)	2202	ν(CN) 2099
127	$PtH(SH)(PCy_3)_2$	196—198	54.0 (54.7)	8.9 (8.7)		2079	
128	$PtH(CN)(PCy_3)_2$	230—232	56.6 (56.8)	8.6 (8.6)	1.8 (1.8)	2037	ν(CN) 2123
129	$PtH[OC(NHMe)_2](PCy_3)_2BPh_4$	160—162	64.6 (65.0)	8.3 (8.2)	2.4 (2.4)	Not observed	ν(NH) 3398, ν(CO) 1613

[a] Nujol mull, experimental error ± 4 cm^{-1}

hydridobenzylphosphineplatinum(II) complexes are listed in Tables 1 and 2. Data for some hydridocyclohexylphosphineplatinum(II) complexes also are shown in Tables 3 and 4.

1.1. Synthetic routes to a series of hydridobenzylphosphineplatinum(II) complexes (Nos. 1—123*)*

Because of the wide variety of hydridoplatinum(II) complexes, it was necessary to use several different preparative methods: (i) The reduction of *trans*-$PtCl_2(PR_3)_2$ with $NaBH_4$ [10]. This successful preparation using the *trans*-isomer of $PtCl_2(PR_3)_2$ has recently been reported for the *trans*-$PtCl_2(P\text{-}i\text{-}Pr_3)_2$—hydrazine system [11]. (ii) The Michaelis—Arbuzov rearrangement. Many transition metal complexes of the uninegative phosphorus donor ligands of the type $R_2(O)P^-$

TABLE 4

NMR DATA ON SOME HYDRIDOCYCLOHEXYLPHOSPHINEPLATINUM(II) COMPLEXES

No.	Compound	Hydride proton			Others: τ(ppm) and J(Hz)
		τ(H) (ppm) [c]	^1J(Pt—H) (Hz) [d]	^2J(P—H) (Hz) [e]	
124	*trans*-$PtHCl(PCy_3)_2$ [a]	28.76	1277	13.0	
125	*trans*-$PtH(NO_3)(PCy_3)_2$ [a]	35.01	1388	13.5	
126	*trans*-$PtH(NCS)(PCy_3)_2$ [a]	28.57	1087	12.5	
127	*trans*-$PtH(SH)(PCy_3)_2$ [a]	22.08	997	13.5	SH 11.24; ^2J(HS—Pt) 43.0; ^3J(HS—P) 9.5; ^3J(HSPt—H) 2
128	*trans*-$PtH(CN)(PCy_3)_2$ [a]	18.80	777	13.5	
129	*trans*-$PtH[OC(NHMe)_2](PCy_3)_2BPh_4$ [b]	34.41	Not observed	12.5	NCH_3 7.57(br, singlet)

[a] In $CDCl_3$. [b] In CH_2Cl_2. [c] Experimental error ± 0.05 ppm. [d] Experimental error ± 5 Hz. [e] Experimental error ± 0.5 Hz.

have so far been prepared by this rearrangement [12,13]. However, few examples have been reported for hydridoplatinum(II) complexes; Roundhill and coworkers [14] have prepared some hydridophosphinatoplatinum(II) complexes by solvolysis of zerovalent platinum compounds. (iii) The metathesis in platinum hydride synthesis. Since the first report by Chatt and Shaw [15], the metathesis has been used often for the preparation of platinum hydrides [16]. (iv) The reaction of *trans*-$PtHX(PR_3)_2$ (X = Cl or NO_3) with a donor molecule (L) in the pressence of $NaBPh_4$. This type of reaction is a conventional method used for the preparation of the cationic hydridoplatinum(II) complexes such as *trans*-$PtH(L)(PEt_3)_2ClO_4$ [17] or *trans*-$PtH(L)(PPh_2Me)_2PF_6$ [16]. (v) The direct synthesis of cationic platinum hydrides from dihydridoplatinum(II) [10]. (vi) The insertion reaction of $SnCl_2$ into the Pt—Cl bond in *trans*-$PtHCl(PR_3)_2$. This type of insertion within a platinum hydride has been used for the preparation of *trans*-$PtH(SnCl_3)(PEt_3)_2$ [18].

The application of methods i—v to the preparation of hydridobenzylphosphineplatinum(II) complexes will be discussed in turn (as well as that of the insertion reaction (vi), see Experimental).

1.1.1. The reduction of trans-$PtCl_2(PBz_3)_2$ with $NaBH_4$. Several neutral hydridoplatinum(II) complexes (Nos. 1—3, 9, 10, 24 in Tables 1 and 2), one of which (No. 10) is new, have been prepared by the method already reported [10] (eq. 1). The species produced from the reaction of *trans*-dichlorobis(tribenzylphosphine)-

$$\textit{trans}\text{-}PtCl_2(PBz_3)_2 \xrightarrow[CH_2Cl_2/THF]{NaBH_4} [\textit{trans}\text{-}PtH_2(PBz_3)_2] \xrightarrow{HX}$$

$$[PtH_3X(PBz_3)_2] \xrightarrow[benzene]{-H_2\uparrow} \textit{trans}\text{-}PtHX(PBz_3)_2 \qquad (1)$$

(X = Cl, Br, I, NO_3, or ClO_4)

platinum(II) with sodium tetrahydroborate has the spectroscopic properties characteristic of *trans*-dihydridoplatinum(II); the NMR spectrum of the hydridic proton shows the values listed in Table 2 (No. 24), and a strong absorption appears near 1730 cm^{-1} in the IR spectrum. These spectroscopic data conform closely to the empirical rule derived by Shaw and Uttley [19], namely that stable platinum(II) dihydrides show the IR band and NMR resonance due to the hydridic proton within the following values; ν(Pt—H) 1710—1750 cm^{-1}, τ(H) 12—13.15 ppm; ^2J(P—H) 16—18 Hz; ^1J(Pt—H) 780—802 Hz. Therefore, even though its analytical characterization was not possible, the species produced from *trans*-$PtCl_2(PBz_3)_2$ and $NaBH_4$ seems to be *trans*-dihydridobis(tribenzylphosphine)platinum(II) (*trans*-$PtH_2(PBz_3)_2$). Treatment of this species with aqueous inorganic acid caused evolution of hydrogen with the formation of monohydridoplatinum(II) (*trans*-$PtHX(PBz_3)_2$). This fact provides evidence that a trihydridoplatinum(IV) ($PtH_3X(PBz_3)_2$) may also be produced as an unstable intermediate.

1.1.2. The Michaelis—Arbuzov rearrangement in platinum hydride synthesis. New hydridoplatinum(II) complexes of phosphonite or phosphinite (Nos. 21—23) have been synthesized by the Michaelis—Arbuzov rearrangement (eq. 2), or by addition of sodium hydroxide in the presence of hydridochloroplatinum(II)

and diethyl phosphite (eq. 2'). Since cationic hydridoplatinum(II) complexes

$$trans\text{-}PtHCl(PBz_3)_2 + PR(OMe)_2 \xrightarrow{CH_2Cl_2} trans\text{-}PtH[R(MeO)P(O)](PBz_3)_2 + MeCl \quad (2)$$

$$trans\text{-}PtHCl(PBz_3)_2 + P(OEt)_2(OH) + NaOH \xrightarrow{\text{benzene/ethanol}} trans\text{-}PtH[(EtO)_2P(O)](PBz_3)_2 + NaCl + H_2O \quad (2')$$

(No. 92 or 94) containing a neutral donor molecule $PR(OMe)_2$ can be isolated from the initial stage of reaction 2, it is evident that the reaction proceeds via the cationic hydride. So far as we know, this is the first clear example of the use of the Michaelis—Arbuzov rearrangement for platinum hydride synthesis. We have also attempted the Arbuzov rearrangement of $P(OMe)_3$ with *trans*-$PtHCl(PR_3)_2$ (R = Cy (cyclohexyl) or Ph), but only the starting hydride was recovered. Perhaps the steric bulk of PCy_3 or PPh_3 [7,8] prevents the arrangement in this case.

1.1.3. The metathesis in platinum hydride synthesis. Several neutral hydridobenzylphosphineplatinum(II) complexes (Nos. 2—6, 8—20) have been prepared by metathesis. The four platinum hydrides (Nos. 2, 3, 9, 10) which have been prepared by the reaction 1 as described previously, are also obtained from this

$$trans\text{-}PtHCl(PBz_3)_2 + MX \xrightarrow{\text{benzene/ethanol}} trans\text{-}PtHX(PBz_3)_2 + MCl \quad (3)$$

(a) M = Na, X = Br, I, NCO, N_3, NO_2, $S(O)_2C_6H_4$-4-Me, SR(R = H, Me, t-Bu, CH_2Ph, C_6H_4-4-Me, C(O)Me, 2-benzothiazolyl)
(b) M = K, X = SCN, SeCN, CN
(c) M = Ag, X = NO_3, ClO_4

method in high yields. While oxidative addition of HSR (R = H or aryl) to platinum(0) complexes has so far been adopted for the preparation of hydridosulfidoplatinum(II) [20,21], the metathesis provides a convenient route to new hydridosulfidoplatinum(II) complexes (Nos. 13—19, reaction 3a, X = SR).

1.1.4. The reaction of trans-$PtHX(PBz_3)_2$ (X = Cl or NO_3) with a donor molecule (L) in the presence of $NaBPh_4$. Most of the cationic platinum hydrides (Nos. 26—44, 47—71, 73—99, 101—123) containing PBz_3 have been prepared by replacing a chloride or nitrate group in neutral hydridoplatinum(II) complexes with a donor molecule L (eq. 4).

$$trans\text{-}PtHX(PBz_3)_2 + L + NaBPh_2 \xrightarrow{\text{benzene/ethanol}} trans\text{-}PtH(L)(PBz_3)_2BPh_4 + NaX \quad (4)$$

(a) X = NO_3, L = CO, NH_3, NH_2R, NHR_2, NCR, diazole derivatives, pyridine derivatives, pyridine-*N*-oxide, urea derivatives, amides, cycloalkanones, *N*-methylthiourethane.
(b) X = Cl, L = PR_3, $P(OR)_3$, $P(OMe)_2Ph$, $AsPh_3$, $SbPh_3$, SR_2, thiourea derivatives, $SCMe(NH_2)$.

In the absence of the donor molecule L, this reaction of hydridonitratoplati-

num(II) with $NaBPh_4$ was found to lead to the novel platinum hydride, $PtH(PBz_3)_2BPh_4$, as shown in eq. 5. This white complex tends to include the recrystal-

$$trans\text{-}PtH(NO_3)(PBz_3)_2 + NaBPh_4 \xrightarrow{\text{benzene/ethanol}} PtH(PBz_3)_2BPh_4 + NaNO_3 \quad (5)$$

lization solvent, e.g., dichloromethane, and has a strong ability to coordinate an additional donor molecule L. Making use of this property, we have prepared four cationic complexes (Nos. 45, 46, 72, 100), for which the direct synthesis according to reaction 4 was difficult.

$$PtH(PBz_3)_2BPh_4 + L \xrightarrow{CH_2Cl_2} trans\text{-}PtH(L)(PBz_3)_2BPh_4 \quad (6)$$

1.1.5. The direct synthesis of cationic platinum hydrides from dihydroplatinum(II). The two cationic platinum hydrides (88, 89) having a counter ion different from BPh_4^- have been obtained directly from dihydridoplatinum(II). During this reaction (eq. 7), hydrogen gas was slowly evolved. It therefore seems

$$trans\text{-}PtH_2(PBz_3)_2 + PPh_3 + HY \xrightarrow{-H_2\uparrow} trans\text{-}PtH(PPh_3)(PBz_3)_2Y$$

$Y = ClO_4$ or tosyl (7)

most likely that reaction 7 proceeds via a trihydridoplatinum(IV) species, $PtH_3Y(PBz_3)_2$, similarly to the case of reaction 1.

1.2. The characterization of hydridobenzylphosphineplatinum(II) complexes

All the neutral platinum hydrides (Nos. 1—24) examined, excepting only complex No. 7, are very soluble in chloroform and dichloromethane, and their hydridic protons, as well as their phosphine-methylene protons, show "triplet" NMR spectra indicative of the *trans*-form [15,16,22].

Similarly, the NMR spectra for all the cationic hydridoplatinum complexes (Nos. 26—123) show patterns assignable to the *trans*-form, and as shown in the case of $L = PPh_3$ (Nos. 87—89), a change of the anion Y ($Y = BPh_4$, ClO_4, or tosyl) in cationic platinum hydrides does not alter the chemical shift (τ(H)) or coupling constant (^1J(Pt—H)) of the hydridic ^1H NMR. This situation has already been noted for $PtH(PPh_3)_3X$ (X = a uninegative anion) [5].

The ^1H NMR spectra provide evidence that all complexes, excepting only No. 10 with $X = SnCl_3$, have the *trans*-square-planar geometry. Other notable features of the complexes are described below.

1.2.1. The coordination mode of some ligands ($X = ClO_4$ or $S(O)_2C_6H_4$-4-Me, L = chelating olefin, ureas, amides, thioureas, thioacetamide, or N-methylthiourethane). For some cationic hydridoplatinum(II) complexes (Nos. 36, 52—55, 85) containing olefins such as acrylonitrile, allylamine, or allylpyrazole, the hydridic ^1H NMR showed values of τ(H) and ^1J(Pt—H) similar to those for hydridoplatinum(II) complexes (Nos. 57—70) containing a pyridine derivative, or to those for hydridoamineplatinum(II) complexes (Nos. 26—44). In addition, ^1H NMR spectra of the complexes containing potentially chelating olefin, did not show a high field shift, indicating that the olefinic group itself was not coordi-

nated, because a coordinated olefin usually shows a remarkable shielding of olefinic protons [23]. Therefore, in these complexes the "bifunctional" olefins coordinate to platinum solely through the nitrogen in a simple donor fashion. Similar types of platinum complexes, *trans*-$PtH(allylamine)(PPh_3)_2ClO_4$ [24] or *trans*-$PtCl_2(allylpyrazole)_2$ [25], have recently been reported.

Infrared studies on the bis(urea) complex $PtCl_2(NH_2C(O)NH_2)_2$ indicate that each urea coordinates through a single nitrogen in unidentate fashion [26]. On the other hand, the hydride complex *trans*-$PtH(urea)(PBz_3)_2BPh_4$ (No. **100**), shows a decrease in the C = O stretching frequency but no appreciable changes in N—H stretching frequencies, compared with free urea. This pattern is the opposite to that shown by $PtCl_2(urea)_2$, and indicates that coordination has occurred through oxygen. A particularly high value of τ(H) also suggests the existence of a Pt—O bond, since it parallels the case of *trans*-$PtH(acetone)(PPh_2Me)_2PF_6$, for which Clark and Kurosawa observed a high value of τ(H) and a large coupling constant ^1J(Pt—H) [16]. Moreover, for other urea derivatives and amide complexes (Nos. **101—111**), the decrease in ν(C = O), the high value of τ(H), and the large coupling constant ^1J(Pt—H) confirm that these donors coordinate solely through oxygen. In the perchlorate compound (No. **10**), coordination through a perchlorate oxygen is evidenced by the appearance of three chlorine—oxygen stretching bands (ν(Cl—O)) characteristic of a unidentate perchlorate having C_{3v} symmetry, as well as by the high values of τ(H), and the large ^1J(Pt—H) coupling constant.

A *para*-toluenesulfinate anion (X = $S(O)_2C_6H_4$-4-Me) in platinum hydride (No. **20**) acts as a unidentate ligand bonding through sulfur, as can be seen from the similarity of hydridic ^{1}H NMR data to those of apparently *S*-bonded platinum hydrides (Nos. **13—18, 114—116**).

In the case of thiourea, thioacetamide, and *N*-methylthiourethane complexes (Nos. **117—123**), coordination through sulfur is confirmed by the ^{1}H NMR data.

1.2.2. Evidence for the stereochemistry of the potentially cationic platinum hydride (No. 25). The platinum hydride $PtH(PBz_3)_2BPh_4$ shows a triplet NMR signal from the hydridic proton, accompanied by ^{195}Pt satellites. This triplet, together with a ^{195}Pt—P coupling constant derived from ^{31}P NMR indicates [15,16,27] that the two phosphine ligands are mutually *trans*. From the values of τ(H) and ^1J(Pt—H), which are similar to those for apparently *C*-bonded complexes, *trans*-$PtH(CN)(PBz_3)_2$ (No. 9) and *trans*-$PtH(CO)(PBz_3)_2BPh_4$ (No. **97**), it is deduced further that the position *trans* to H^- is probably surrounded by carbon donors (cf. section 2.3, 2.4).

1.2.3. Linkage isomerism of tautomerism in platinum hydrides (X = SCN, L = a diazole molecule). Among ambidentate ligands, the thiocyanate ion is well known for exhibiting linkage isomerism in hydrido-tertiary-phosphineplatinum-(II) [16,28,29] with the -NCS to -SCN ratio always greater than unity. It is believed that steric crowding of tertiary phosphines may favor the linear - NCS rather than the bent-SCN, and indeed, for the platinum hydride *trans*-$PtH(NCS)(PCy_3)_2$ (No. **126**) containing a bulky phosphine, the NMR spectrum shows the presence of only the *N*-bonded isomer. However, for hydridobenzylphosphineplatinum-(II) (No. 5), the NMR intensities of both the hydridic protons and the phosphine-methylene protons show the -NCS and -SCN forms to be present in almost equal concentrations. No other instance of the presence of a large proportion of the

-SCN isomer in hydridometal systems [30] has been reported as yet.

In some diazole hydride complexes (Nos. 75, 77, 81) containing 3(5)-methyl-5(3)-phenyl pyrazole, 3(5)-methylpyrazole, or 2,5(4)-dimethylpyrazole, two separate tautomers were observed in the ^{1}H NMR spectrum. The ratios of the two forms were determined from the signal intensities of hydridic or methyl ^{1}H NMR as: 3-methyl-5-phenylpyrazole/5-methyl-3-phenylpyrazole = 1/3, 3-methylpyrazole/5-methylpyrazole = 1/6, and 2,5-dimethylimidazole >> 2,4-dimethyl imidazole. These observations provide the first evidence for separate tautomers in platinum hydrides.

1.2.4. Dissociation of ligands from platinum hydrides. In the IR spectrum of *trans*-PtH(cyclohexanone)$(PBz_3)_2BPh_4$ (No. 112) (in nujol mull), there is a strong ν(C = O) band at 1637 cm^{-1} arising from coordinated cyclohexanone, together with the weak signal from free cyclohexanone (ν(C=O) 1717 cm^{-1}). The latter band becomes stronger in a dichloromethane solution through dissociation of the cyclohexanone—platinum bond. In dichloromethane solution between —60 and 30°C, the NMR spectrum shows a very weak triplet due to the hydridic proton, while the spectrum intensities in the low field region (τ = 1—10) indicate the molar ratio of cyclohexanone to tribenzylphosphines to be 1/2. Moreover, repeated recrystallization from dichloromethane/diethyl ether produced the potentially cationic platinum hydride (No. 25). The results point to the following equilibrium in dichloromethane:

trans-PtH(cyclohexanone)$(PBz_3)_2BPh_4 \rightleftharpoons$

$PtH(PBz_3)_2BPh_4$ + cyclohexanone

Similar results are obtained for the cyclopentanone complex (No. 113).

Several workers reported that rapid dissociation of the coordinated phosphine PPh_3 in some platinum hydrides, occurs in $CDCl_3$ at room temperature [20,21]. In *trans*-PtH(SR)$(PBz_3)_2$ (Nos. 13—19), this type of dissociation has not been found. The hydridic ^{1}H NMR spectra of these complexes show a phosphorus-coupling pattern at room temperature, and the phosphine-methylene ^{1}H NMR spectra also exhibits a triplet split due to virtual coupling [22]. These observations indicate that two phosphines (PBz_3) in these hydrides do not undergo a rapid dissociation similar to that shown by the triphenylphosphine complexes cited above. The absence of dissociation seems to be due to a stronger donor property of PBz_3 than that of PPh_3. Indeed, no rapid dissociation of strong donor PCy_3 was observable from the ^{1}H-NMR spectrum of trans-PtH(SH)$(PCy_3)_2$ (No. 127) at room temperature. This is fully consistent with our interpretation.

1.2.5. Stereochemical non-rigidity of sym-dimethylurea or sym-dimethylthiourea in platinum hydrides. Evidence for stereochemical non-rigidity of *sym*-dimethylurea and *sym*-dimethylthiourea linked to hydridoplatinum(II) (Nos. 102, 119) has been observed in the ^{1}H NMR spectra as shown in Fig. 2. The methyl signal of *sym*-dimethylurea in the platinum hydride consists solely of a broad singlet at room temperature, and this splits into a pair of doublets at —60°C, accompanied by the narrowing of the line width in the hydridic signal. The methyl groups in the *sym*-dimethylthiourea complex also show a temperature-dependent ^{1}H NMR spectrum. The peak separation between the two methyl signals, which are not in this case split by an NH proton, is observed even at room

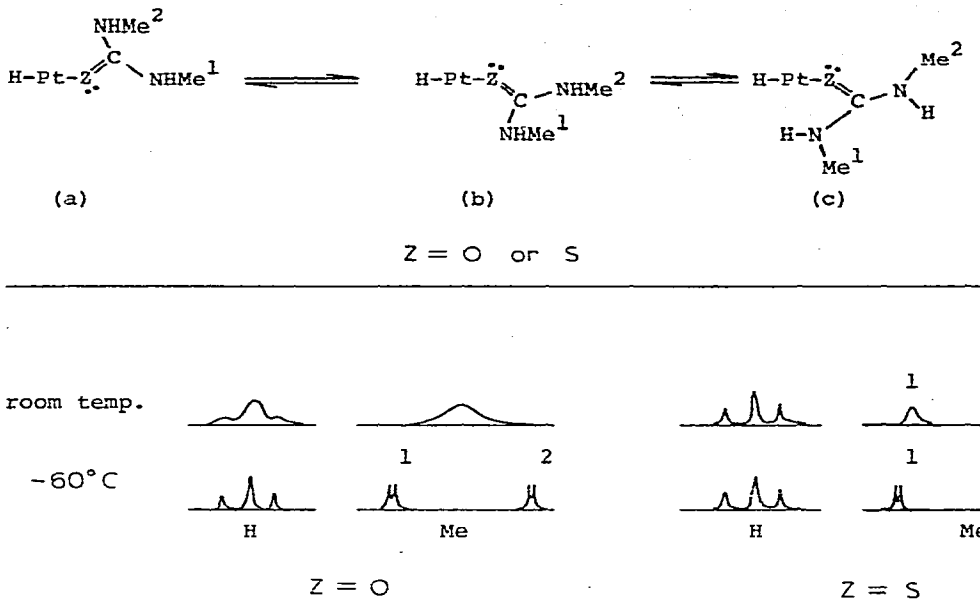

Fig. 2. The temperature dependence of the ^{1}H NMR spectrum of *trans*-PtH[ZC(NHMe)$_2$](PBz$_3$)$_2$BPh$_4$ (Z = O or S), and a proposed model of the reorientation processes. In the upper row, the two dots near the Z atom represent a lone pair.

temperature. This separation is slightly increased in cooling to —60°C, and each methyl signal is now split by a NH proton, but the line shape of the hydridic proton signal is not temperature-dependent.

For both complexes, the ^{1}H NMR spectra due to the benzyl groups do not show any distinctive change from —60 to 30°C.

From these results, we can build up a reasonable hypothesis concerning the stereochemical non-rigidity of these ligands in platinum hydrides. The reorientation process is schematically proposed in Fig. 2a—c, in which two Pt—P bonds are almost vertical to the given figures and omitted for clarity. At —60°C, the rate of any reorientation is slow enough for a pair of doublets due to methyl groups to be observed, and the ^{1}H NMR spectra for the two complexes can be equivalent to a sterically constrained stationary conformation (Fig. 2c). The two types of methyl groups in this conformation are tentatively assigned as shown by numbers (1 and 2) in Fig. 2. On the other hand, at room temperature, it appears that both ligands execute a rapid reorientation on the pivot of the Z-atom (Z = O or S) in such a manner as the swing of the pendulum (Fig. 2a ⇌ Fig. 2b), together with limited rotation of methyl groups around the C—N axes (Fig. 2b ⇌ Fig. 2c). For urea (Z = O), the rate of such processes is fast enough to show a very broad singlet of methyl protons and broad signals of the hydridic proton, while the rate of thiourea (Z = S) is restricted to such an extent that two broad methyl signals are observed in the presence of NH—Me coupling (^3J(NH—Me)).

The broad ^{1}H NMR spectrum of both methyl protons and the hydridic proton in the complex *trans*-PtH[OC(NHMe)$_2$](PCy$_3$)$_2$BPh$_4$ (No. 129) at room tem-

perature indicates that the molecular motion similar to that described above may also occur in the hydridocyclohexylphosphineplatinum(II) system.

As to other hydride complexes containing amides or unsymmetrical ureas (Nos. **103—111, 101**), neither the methyl signal nor the hydridic line shape shows any distinctive change with temperature. It can, therefore, be presumed that a symmetrical arrangement of methyl groups such as in *sym*-dimethylurea is favorable for the pendulum-like motion described above.

2. The mutual influence of ligands through platinum(II)

2.1. The trans-influence of a hydridic ligand

The high *trans*-influence of a hydridic ligand can be understood qualitatively for some complexes from the value of $^{195}Pt—l$ coupling constant (l representing a certain set of protons in a donor molecule L). For example, the value of ^3J(Me—Pt) on *trans*-$PtH(SMe_2)(PBz_3)_2BPh_4$ (No. 114) (SMe_2 *trans* to H^-, 25 Hz) is much less than that on *trans*-$PtCl_2(SMe_2)_2$ (SMe_2 *trans* to SMe_2, 42 Hz) and that on *cis*-$PtCl_2(SMe_2)_2$ (SMe_2 *trans* to Cl^-, 50 Hz). These differences in the values of ^3J(Me—Pt) indicate the high *trans*-influence of the coordinated hydride [6] and, consequently, the considerable weakening of platinum—sulfur bond in this particular hydride.

For the complex *trans*-PtH(3,5-lutidine)$(PBz_3)_2BPh_4$ (No. 63), the 2,6-ring protons in the coordinated lutidine are split by ^{195}Pt with a coupling constant of 23.5 Hz (lutidine *trans* to H^-), while the coupling for *trans*-$PtCl_2$(3,5-lutidine)$_2$ (lutidine *trans* to N) has a value of 35 Hz. These data indicate, at least qualitatively, the high *trans*-influence of the hydride ligand in comparison with that of the nitrogen donor.

2.2. Platinum—hydride stretching frequencies (ν(Pt—H))

Infrared spectra of a series of hydridobenzylphosphineplatinum(II) complexes have been investigated to see how the platinum-hydride frequencies change as the ligands X or L are changed, but a number of difficulties attend to measurement.

For the present compounds, it is difficult to determine precisely the wave number of ν(Pt—H) in solution, since the spectrum broadens in $CHCl_3$ or CH_2Cl_2 which are the only suitable solvents for the complexes.

The KBr method also is inappropriate for the characterization of a series of hydridoplatinum(II) complexes. For example, platinum hydrides such as urea complexes (Nos. **100—102, 129**) and amide complexes (Nos. **103—111**) react slowly with KBr in the solid state:

$$trans\text{-}PtH(OCRR')(PBz_3)_2BPh_4 + KBr \rightarrow trans\text{-}PtHBr(PBz_3)_2 + KBPh_4 + OCRR'$$

In consequence, the spectrum is complicated by both ν(C=O) from the free ketone and ν(Pt—H) from *trans*-$PtHBr(PBz_3)_2$.

Other difficulties arose even when we measured the IR spectra in nujol mulls. (i) For complexes containing oxygen donors, except No. **11** with X = NO_3, no platinum—hydride stretching band was observed, and for nitrile complexes (Nos. **45—56**), only a weak CN stretching band was observed in the range 2000—2300 cm^{-1}. (ii) A complex band due to ν(Pt—H) appeared for some compounds,

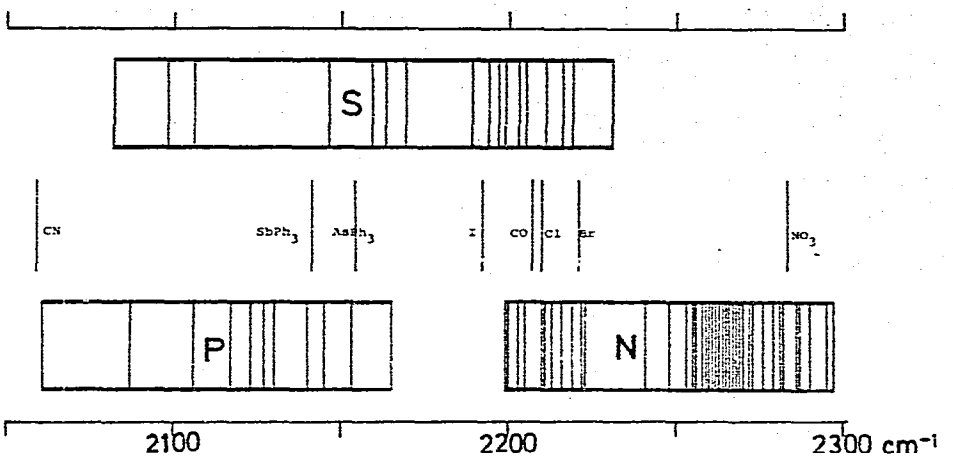

Fig. 3. Plot of ν(Pt—H) for a series of hydridobenzylphosphineplatinum(II) complexes. Each upright line corresponds to the measured value of each compound listed in Table 2.

X = SBu-t (No. 15) and L = PPh_3 (Nos. 87—89). Such a case has been reported for solid *trans*-$PtHCl(PPh_3)_2$, for which it was explained that the complexity in ν(Pt—H) results from solid state effects [31].

Thus, while at the present stage we cannot discuss in detail the inductive or mesomeric effects [32] in each compound, a general trend in the ν(Pt—H) region depending upon the kind of ligand donor atom is observed as shown in Fig. 3. It will be seen that the *trans*-influence of the donor atoms is, with decreasing order of the frequency region of ν(Pt—H), N < S < P.

2.3. Chemical shift of the hydridic proton τ(H)

For the present complexes, the hydridic chemical shifts were also classified according to the donor atoms through which ligands X or L coordinate to platinum. Each of the donor atoms N, S, O, or P has a characteristic region as plotted in Fig. 4.

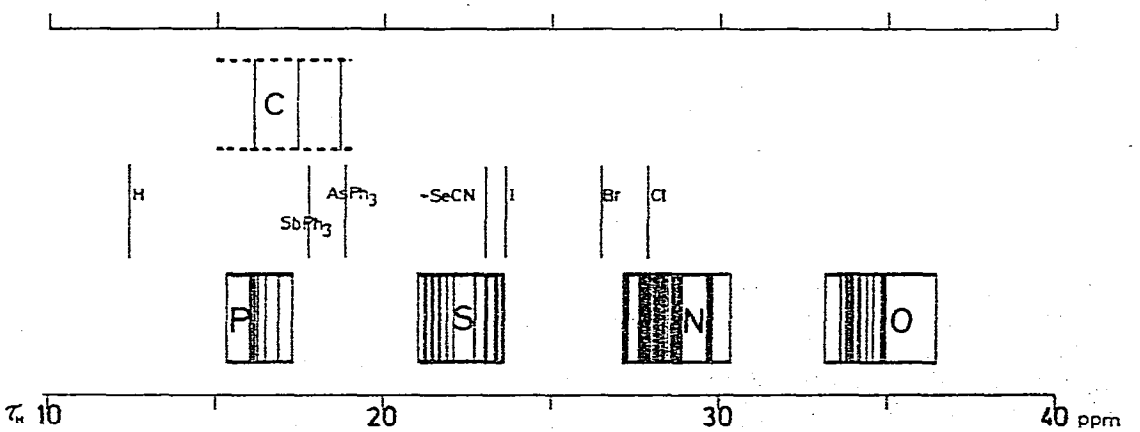

Fig. 4. Plot of τ(H) for a series of hydridobenzylphosphineplatinum(II) complexes. Each upright line represents the observed value of τ(H) for each compound listed in Table 2.

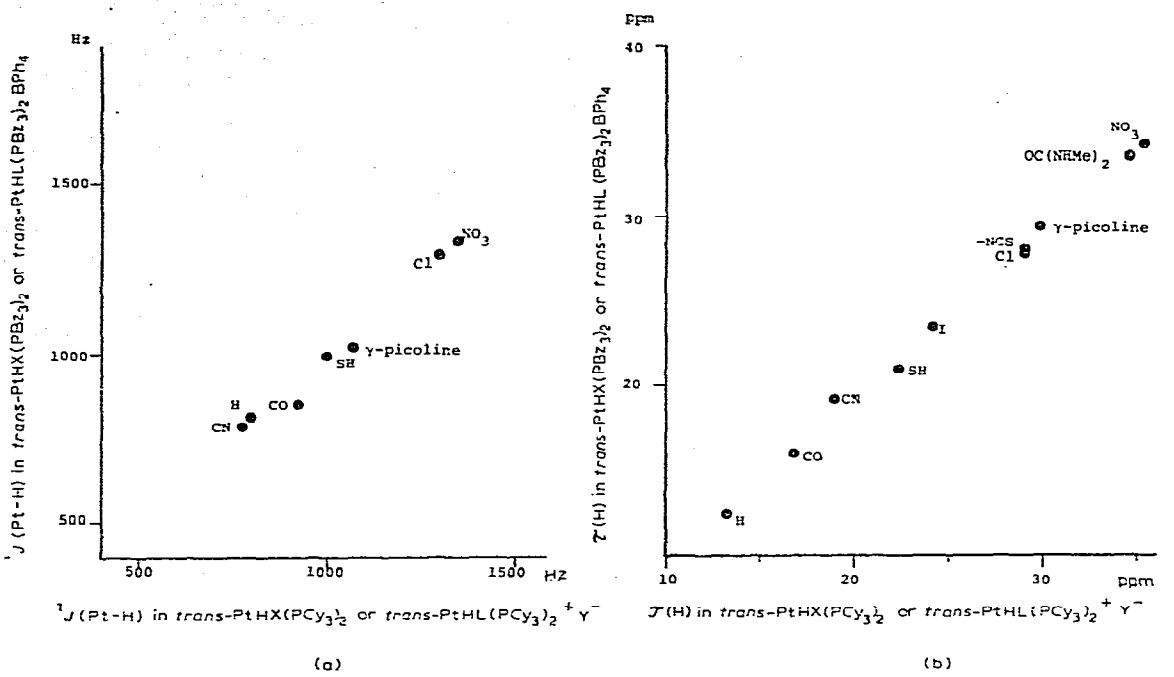

Fig. 5. Graphs of ^{1}H NMR data (from Table 2) for the hydridic protons in hydridobenzylphosphineplatinum(II) vs. those (from Table 4 and refs. 11, 19, 33) in hydridocyclohexylphosphineplatinum(II). Plot (a) is with respect to ^1J(Pt—H), and plot (b) to τ(H).

Data for carbon donors (e.g., Nos. 9, 25, 97) are as yet too limited for us to make other than an estimate as to the specific region for the chemical shifts. For NMR parameters (τ(H) and ^1J(Pt—H)), there are good linear correlations between our hydridobenzylphosphineplatinum(II) system and other hydridoalkylphosphineplatinum(II) systems, for example, as shown in Fig. 5 in the case of alkylphosphine = PCy_3. From these correlations, we deduced the specific region for carbon donors by references to isonitrile, olefin, and carbene complexes [33], as shown by the dotted lines in Fig. 4.

Changes in hydride shifts do not really indicate variations in the Pt—H bond itself but rather those at the platinum atom [6]. Consequently, variations in τ(H) values are not a good indication of the *trans*-influence. To make matters worse, anisotropic effects of aromatic rings in tribenzylphosphine may influence τ(H). In fact, such an effect was found in the ^{1}H NMR spectrum of the donor molecule (L) in the cationic hydridobenzylphosphine platinum(II) complexes; the whole spectrum of L showed an abnormal shift towards higher field upon coordination, whereas substituent groups such as methyl usually show a slight deshielding of their protons in other metal complexes. Thus, we cannot formulate a *trans*-influence series of donors (X or L) directly from the hydridic shift data.

2.4. Platinum—hydride coupling constant (^1J(Pt—H))

As shown in Fig. 6 the regions of platinum—hydride coupling constants for the three donors, nitrogen, phosphorus, and oxygen, are separated clearly from each other, but that there is an overlap of the ranges for nitrogen and sulfur donors.

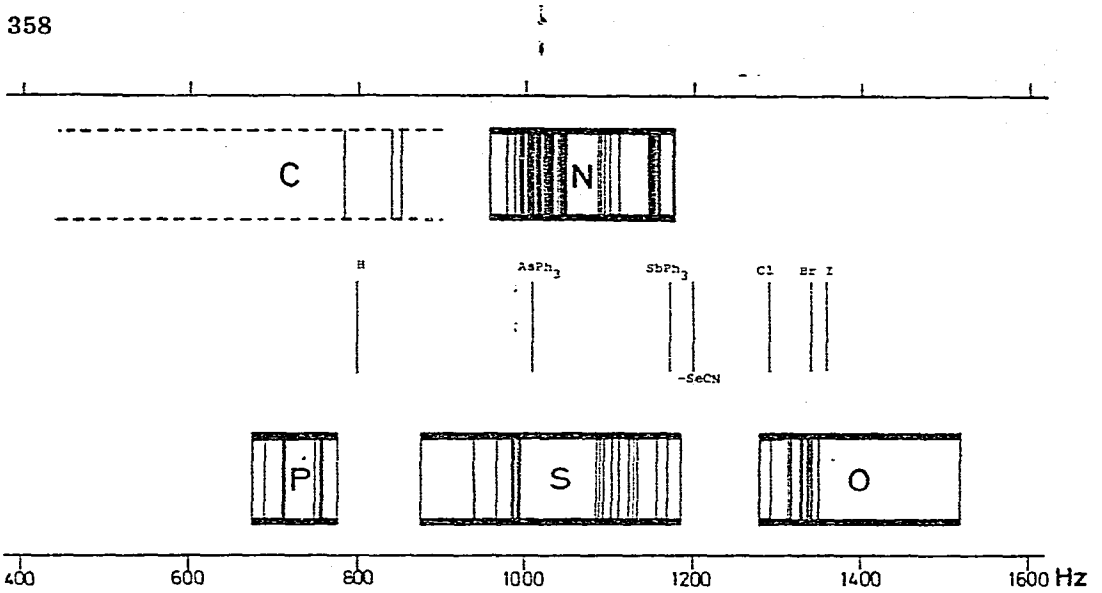

Fig. 6. Plot of ^1J(Pt—H) for a series of hydridobenzylphosphineplatinum(II) compounds. The positions of the upright lines indicate the values observed for individual compounds from Table 2.

The region characteristic of carbon donors was estimated as in section 2.3, from the data for other hydridoalkylphosphineplatinum(II) complexes.

Since increase in covalency of Pt—H bonds is at least partly responsible for any increase of the platinum—hydride coupling constant ^1J(Pt—H) [6], the values of ^1J(Pt—H) give the *trans*-influence series: O < N ≤ S < P. This order agrees with that obtained from the platinum—hydride stretching frequencies.

It is worth remarking that the values of ^1J(Pt—H) also reflect the variations of σ-influence [34] by donors X or L. Yatsimirskii proposed the model of "ligand mutual influence (LMI)" based on simple LCAO, and grouped orbitals according to their ability to transmit LMI [34]. Since the Pt—H bond consists solely of pure σ-type orbitals, *σ-trans*-influence induced by an anion X or a molecule L may be dominant in the variations of ^1J(Pt—H). Thus, it will be seen from Table 2 that the *σ-trans*-influence order is as follows: ClO_4^- < I^- < OCHNRR′ < Br^- < OCMeNRR′ < NO_3^- < $OC(NHMe)_2$ < py-*N*-oxides < Cl^- < -$SeCN^-$ < -SCN^- < $SbPh_3$ ≤ NCR ≃ $SC(NRR')_2$ ≃ SR_2 ≤ NH_2Ph ≤ pyrazoles ≤ NH_3 ≤ NH_2R (R = alkyl) ≤ $AsPh_3$ < -NO_2^- ≤ pyridines ≤ imidazoles ≤ NHRR′ ≤ SR^- < -$S(O)_2C_6H_4$-4-Me^- < CO < H^- < CN^- < PPh_3 < $P(OPh)_3$ < PPh_2Me < $P(OMe)_3$ < PBz_3 < -$P(O)RR'^-$.

2.5. Platinum—phosphorus coupling constant (^1J(Pt—P))

The ^{31}P NMR spectra of some hydridobenzylphosphineplatinum(II) complexes were measured to test the variations in ^1J(Pt—P) resulting from the changes of the ligands X or L. The values of ^1J(Pt—P) again show a trend depending upon donor atoms, and show good correlation with ^1J(Pt—P) data for some *trans*-$PtMeX(PEt_3)_2$ compounds [35] (Fig. 7). From this trend, an NMR *cis*-influence series is determined to be P > S > N > O. On the whole, the observed variations in ^1J(Pt—P) are small relative to those in ^1J(Pt—H); that is, the ligands X or L have a small *cis*-influences on the Pt—P bond in comparison with their large *trans*-influences on the Pt—H bond.

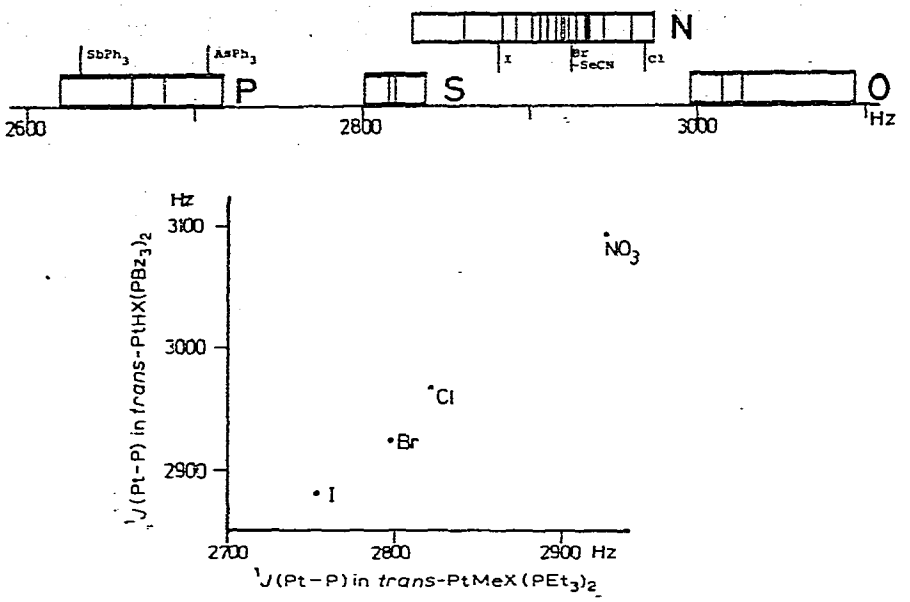

Fig. 7. Plot of ^1J(Pt—P), and a graph of ^1J(Pt—P) on *trans*-PtHX$(PBz_3)_2$ (from Table 2) vs. ^1J(Pt—P) on *trans*-PtMeX$(PEt_3)_2$ (from ref. 35).

However, it is not clear what types of molecular orbitals would determine the above order of an NMR *cis*-influence series, because changes in any variables in the Fermi contact term which dominates the coupling ^1J(Pt—P) can be equally important [6].

3. Conclusion

The foregoing lines of evidence all point to the likelihood that the strength of the Pt—H bond in a series of square-planar platinum hydrides is governed essentially by the nature of the donor atom in the *trans* position.

For a large number of hydridobenzylphosphineplatinum(II) complexes, the *trans*-influence series of donor atoms has thus been established empirically as $O < N \leqslant S < P$ from the data of ν(Pt—H) and ^1J(Pt—H). In our system, the *cis*-influences of ligands X or L are small relative to the *trans*-influences, as has already been pointed out by Allen and Sze for several bis(triethylphosphine)platinum(II) systems [36].

Experimental

Infrared spectra (400—4000 cm^{-1}) were recorded on a Hitachi EPI-G2 spectrophotometer. A 0.05 mm cell with NaCl windows was used for solutions. ^1H NMR spectra were recorded on a JEOL-PS 100 or a Hitachi R-24 instrument at 100 MHz or 60 MHz, respectively, and ^{31}P NMR spectra were recorded with a Hitachi R-20B instrument operating at 24.3 MHz with proton noise decoupling. Conductivity measurements were made in nitromethane using a Radiometer Inc., CDM-2D instrument. All reagents were supplied by Wako Pure Chemicals Industries, Ltd., Tokyo Kasei Kogyo Co., Ltd., or Nippon Engelhart, Ltd.

Some preparative information was briefly mentioned in a previous paper [10]. Here, we describe particularly the methods developed for the preparation of hydridobenzylphosphineplatinum(II) complexes.

Preparation of trans-$PtCl_2(PBz_3)_2$

The entire preparation was done under nitrogen. A dispersion of $PtCl_2(SMe_2)_2$ (11.5 g) in benzene (200 ml) containing PBz_3 (20.0 g) was refluxed until it became homogeneous (ca. 30 min.). It was evaporated under vacuum to half volume, and methanol (100 ml) added. The pale yellow product (21.1 g) crystallized on standing. ^{1}H NMR in CH_2Cl_2: τ 6.62 ppm (triplet of triplets, 12 H, CH_2, $^3J(CH_2—Pt)$ 20.5 Hz; $^3J(CH_2—P) + {}^5J(CH_2—P)$ 4.0 Hz), τ 2.7 ppm (sextet, 30 H, Ph). ^{31}P NMR in CH_2Cl_2: ^1J(Pt—P) 2462 Hz; δ —5.8. Anal. Found: C, 57.7; H, 5.1; Cl, 8.5. $C_{42}H_{42}P_2Cl_2Pt$ calcd.: C, 57.7; H, 4.8; Cl, 8.1%.

The *trans*-form of the product was confirmed by the triplet methylene protons due to virtual coupling, and by the value of ^1J(Pt—P).

Preparation of trans-$PtHCl(PBz_3)_2$ (No. 1)

An ethanol solution (100 ml) of $NaBH_4$ (0.2 g) was added dropwise under argon to a solution of *trans*-$PtCl_2(PBz_3)_2$ (2.1 g) in tetrahydrofuran (200 ml). Gas was evolved almost instantly and the color of the solution gradually changed from yellow to pale yellow. After the reaction was essentially complete (ca. 2 hours), the solution evaporated to dryness and the residue extracted with benzene (100 ml). This solution was treated with hydrochloric acid (10^{-2} *M*). After evolution of gas ceased, the benzene layer was separated and reduced to one-third of the volume. On addition of hexane (50 ml), white crystals separated. These were recrystallized from dichloromethane/diethyl ether to give 1.8 g of pure product.

Other hydride complexes (Nos. 2, 3, 10, 11) were prepared by the same method using hydrobromic, hydroiodic, nitric, or perchloric acids as required.

Preparation of trans-$PtH[(MeO)_2P(O)](PBz_3)_2$ (No. 21)

A dichloromethane solution containing both *trans*-$PtHCl(PBz_3)_2$ (No. 1, 0.94 g) and $P(OMe)_3$ (1.7 g) was stirred for 50 hours. White needles (0.65 g) formed on addition of hexane. Complex No. 23 was prepared similarly from *trans*-$PtHCl(PBz_3)_2$ and $PPh(OMe)_2$.

Preparation of $PtH(SnCl_3)(PBz_3)_2$ (No. 7)

An ethanol solution (20 ml) of $SnCl_2$ (0.15 g) was added dropwise to a benzene solution (80 ml) containing *trans*-$PtHCl(PBz_3)_2$ (0.8 g). The white precipitate was recrystallized from chloroform to give 0.8 g of the product.

Preparation of neutral hydridoplatinum(II) (Nos. 2—6, 8—20) by metatheses

A typical method will be described:

With NaSMe. An aqueous, 20% solution (0.5 ml) of NaSMe was added dropwise to the mixed solvent of benzene (50 ml)/ethanol (30 ml) containing *trans*-$PtHCl(PBz_3)_2$ (1.2 g). The solvent was removed under vacuum and the residue was extracted with 60 ml of benzene. The extract was concentrated to half its volume and 100 ml of hexane added. The white crystalline solid which formed

on standing was recrystallized from dichloromethane/diethyl ether to give 1.0 g of *trans*-$PtH(SMe)(PBz_3)_2$.

Preparation of $PtH(PBz_3)_2BPh_4 \cdot nCH_2Cl_2$ *(*$n = \frac{1}{4}$ *or* $\frac{1}{2}$*) (No. 25)*

An ethanol solution (20 ml) containing $NaBPh_4$ (0.62 g) was added to benzene (20 ml) in which the complex, *trans*-$PtH(NO_3)(PBz_3)_2$ (No. 11, 1.1 g), was dispersed. After stirring for 30 minutes, the precipitate was filtered and recrystallized from dichloromethane/diethyl ether. The product was dried at 50°C for 24 hours (0.001 mmHg) to give 0.72 g of $PtH(PBz_3)_2BPh_4 \cdot \frac{1}{4}CH_2Cl_2$.

Preparation of trans-$PtH(urea)(PBz_3)_2BPh_4$ *(No. 100)*

The complex, $PtH(PBz_3)_2BPh_4 \cdot \frac{1}{2}CH_2Cl_2$ (No. 25, 4.7 g), was dissolved in dichloromethane (50 ml) and a 50 v/v water/ethanol solution containing urea (0.4 g) was added with stirring. After the solvent was evaporated to dryness under vacuum, the residue was extracted with dichloromethane (50 ml). On addition of 100 ml of the hexane to the dichloromethane solution, 4.5 g of a white solid crystallized.

The three cationic hydridoplatinum(II) complexes (Nos. 45, 46, 72) were prepared similarly from $PtH(PBz_3)_2BPh_4 \cdot \frac{1}{2}CH_2Cl_2$ and L (L = NCMe, $NCCH_2Ph$, or benzimidazole).

Preparation of trans-$PtH(PPh_3)(PBz_3)_2(tosyl)$ *(No. 89)*

A benzene solution containing dihydridoplatinum(II) species (ca. 0.002 *M*), prepared by the same manner as for *trans*-$PtHCl(PBz_3)_2$ (No. 1), was treated both with an aqueous solution containing *p*-toluenesulfonic acid monohydrate (0.46 g) and with a benzene solution (15 ml) containing PPh_3 (0.7 g). The benzene layer was separated and evaporated to half the volume. The solid precipitating upon addition of hexane (100 ml) was washed successively with cold water, ethanol, and diethyl ether. Recrystallization from dichloromethane/diethyl ether gave 2.3 g of product.

Similarly a cationic hydridoplatinum(II) complex, *trans*-$PtH(PPh_3)(PBz_3)_2ClO_4$ (No. 88), was obtained by the use of perchloric acid in place of *p*-toluenesulfonic acid.

Preparation of cationic hydridoplatinum(II) (Nos. 26—44, 47—71, 73—99, 101—123*) by the reaction of trans-*$PtHX(PBz_3)_2$ *(*$X = Cl$ *or* NO_3*) with a donor molecule*

With sym-dimethylurea. The ligand, $OC(NHMe)_2$ (0.11 g) was added to a mixed solvent of benzene (20 ml)/ethanol (20 ml) in which hydridonitratoplatinum(II) (No. 11, 1.1 g) and $NaBPh_4$ (0.44 g) were dissolved. After about 10 minutes, a white crystalline solid formed and recrystallized from dichloromethane/diethyl ether. The product, *trans*-$PtH[OC(NHMe)_2](PBz_3)_2BPh_4$ (No. 102, 1.2 g), was dried under vacuum (0.001 mmHg) at 70°C for 17 hours.

With methylisothiocyanate and ethanol. Methyl isothiocyanate (0.58 g) was dissolved in a mixed solvent of benzene (20 ml)/ethanol (10 ml) containing *trans*-$PtH(NO_3)(PBz_3)_2$ (No. 11, 0.62 g) and $NaBPh_4$ (0.26 g). After stirring for 24 hours, the precipitate was filtered and recrystallized from dichloromethane/diethyl ether to give 0.54 g of *trans*-$PtH[SC(OEt)NHMe](PBz_3)_2BPh_4$ (No. 123).

Preparation of trans-PtHCl(PCy_3)$_2$ (No. 124)

Several methods for preparation of hydridochlorobis(tricyclohexylphosphine)platinum(II) have already been reported [11,19,33]. We outline a new method. The complex, *trans*-PtHCl(PBz_3)$_2$ (9.6 g) and PCy_3 (6.5 g) were dissolved into benzene (80 ml) and the solution dried under vacuum. After washing with diethyl ether (200 ml), the residue was recrystallized from dichloromethane/diethyl ether to give 6.3 g of the product. The entire procedure was performed in a dry, nitrogen atmosphere.

Some other hydridocyclohexylphosphineplatinum(II) complexes (Nos. 125—129) have been prepared by similar methods as described above in the preparation of a series of hydridobenzylphosphineplatinum(II) complexes.

Acknowledgement

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