Syntheses and Characterization of Dinuclear Palladium and Platinum Complexes with a Single Unsupported Bridging Group. Crystal Structure of [{C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-*o,o'*}Pd(μ-Cl)Pd{C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-*o,o'*}]BF$_4$†

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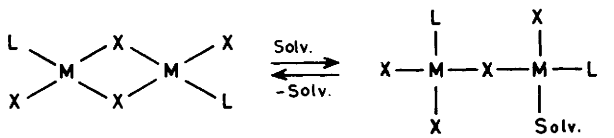
Reaction of cationic [M{C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-*o,o'*}(H$_2$O)$_n$]Y (M = Pd or Pt; *n* = 1, Y = BF$_4$; M = Pt, *n* = 0, Y = O$_3$SCF$_3$) with neutral [MX{C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-*o,o'*}] (M = Pd or Pt; X = halide or CN) gives novel homo- and hetero-dinuclear complexes possessing a single unsupported halide or cyanide bridge. The complexes have been characterized by i.r., ^{1}H n.m.r., and elemental analyses. A single-crystal *X*-ray structure determination has been carried out on the palladium species [{C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-*o,o'*}Pd(μ-Cl)Pd{C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-*o,o'*}]BF$_4$ [$a = 11.163(1)$, $b = 21.347(2)$, $c = 12.246(4)$ Å, $\beta = 91.48(2)°$, and $Z = 4$; $R = 0.042$ for 5 077 reflections]. The cation consists of two Pd{C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-*o,o'*} units sharing a single bridging chlorine atom. Both Pd^{II} centres have a slightly distorted square-planar co-ordination sphere. Each Pd atom is surrounded by a carbon atom and two mutually *trans* N atoms of the terdentate ligand and the bridging chlorine atom. Dihydride-bridged complexes [{C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-*o,o'*}M(μ-H)$_2$Pt(PPh$_3$)$_2$]BF$_4$ (M = Pd or Pt) have been prepared by using a procedure in which a reactive hydride is generated *in situ* from the reaction of a Pt^0 phosphine species and gaseous H$_2$ in the presence of [M{C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-*o,o'*}]BF$_4$(M = Pd or Pt). From ^{1}H n.m.r. these complexes are anticipated to have a geometry in which there is both a four- and a five-co-ordinate centre. The reaction of [Pt{C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-*o,o'*}]O$_3$SCF$_3$ and [Pt(O$_2$CH){C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-*o,o'*}] in benzene afforded the monohydride-bridged complex [{C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-*o,o'*}Pt(μ-H)Pt{C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-*o,o'*}]O$_3$SCF$_3$. Attempts to synthesize the palladium analogue were not successful.

Homobimetallic complexes of the type [M$_2$X$_4$L$_2$](M = Rh, Ir, Pt, or Pd; X = halogen; L = CO, PR$_3$, AsR$_3$, SbR$_3$, or SR$_2$) with halide-bridged metal centres are well known and are common precursors for the synthesis of new products.[1] Some of the reactions are believed to proceed *via* rupture of only one of the halide bridges thereby generating reactive species with a single halide bridge.[2]



Furthermore, in many redox or electron ligand transfer reactions of d^8 metal–halide complexes, halide-bridged bimetallic intermediates are proposed.[3,4] Study of such bimetallic species is of interest because their structure and chemical behaviour can give more information about the mechanism of halide-bridge cleavage reactions and halogen transfer processes. Though several compounds are known containing a single halide bridge[5,6] it was only recently that single halide-bridged bimetallic compounds without supporting ligands were reported.[7–9] A few dinuclear complexes containing an unsupported hydride bridge between two d^8 metal centres are known.[10–13]

A common feature of the above complexes[5–8,10–13] is the presence of phosphine ligands and so far, this seemed to be a condition for obtaining stable and isolable dinuclear species. However, we found that by using the monoanionic terdentate bis(amino) ligand *o,o'*-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$ (L^1), see Scheme 1, stable bimetallic species with an unsupported single atom bridge could be prepared.[14] Reaction of cationic [Pt(L^1)]$^+$ (BF$_4^-$ or O$_3$SCF$_3^-$ anion) with [PtX(L^1)] (X = Cl, Br, I, CN, or O$_2$CH) afforded the novel species [(L^1)Pt(μ-X)Pt(L^1)]$^+$ (X = Cl, Br, I, CN, or H). Recently, Rimml and Venanzi[13] reported the preparation of stable dinuclear hydrido-bridged cations [(L^2)M(μ-H)M(L^2)]PF$_6$ (M = Pt or Pd) with a monoanionic terdentate bis(phosphine) ligand, *o,o'*-(Ph$_2$PCH$_2$)$_2$C$_6$H$_3$ (L^2), which bears analogy with the L^1 system used in our study. Lavery and Nelson[9] have also reported the syntheses of dinuclear monochloro-bridged rhodium(I) complexes containing a terdentate pyridyldiaza ligand.

This paper decribes the syntheses and characterization of complexes of the type [(L^1)M(μ-X)M'(L^1)]$^+$ with discussion of their structural features on the basis of an *X*-ray crystallographic study of one representative example, *viz.* [(L^1)Pd(μ-Cl)Pd(L^1)]BF$_4$.

Experimental

General.—Reactions with [Pt(cod)$_2$] (cod = cyclo-octa-1,5-diene) were performed under a nitrogen atmosphere by using Schlenk-tube techniques and dry, freshly distilled solvents.

The ^{1}H n.m.r. spectra were recorded on Varian T60 and Bruker WM 250 spectrometers using CD$_2$Cl$_2$. Infrared spectra were recorded on a Perkin-Elmer 283 instrument in KBr pellets

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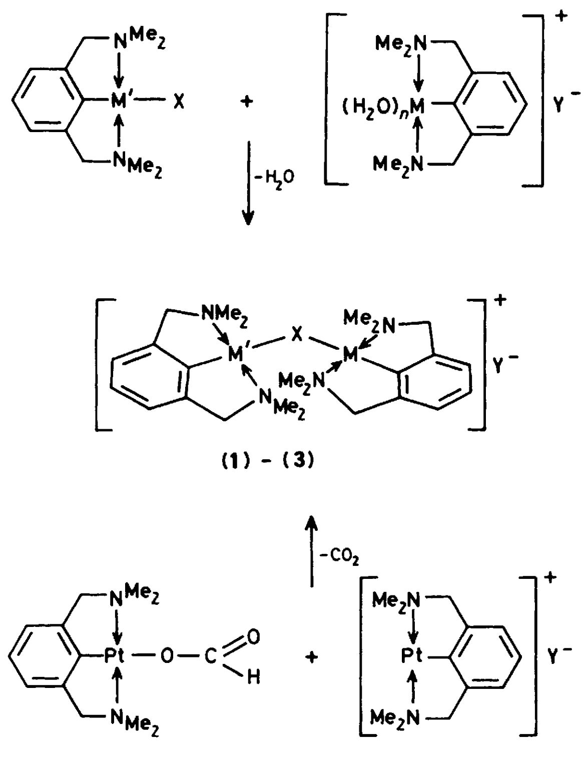
† μ-Chloro-bis[{*o,o'*-bis[(dimethylamino)methyl]phenyl-*C,N,N'*}-palladium(II)] tetrafluoroborate.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii–xx.

Table 1. Analytical data of dinuclear platinum and palladium complexes; $L^1 = C_6H_3(CH_2NMe_2)_2$-*o,o'*

	Compound	Yield (%)	Found (Calc.) (%) C	H	N	X	F
(**1a**)	$[(L^1)Pt(\mu-Cl)Pt(L^1)]BF_4$	>95	32.20	4.15	6.25	4.10	8.25
			(32.20)	(4.30)	(6.25)	(3.95)	(8.50)
(**1b**)	$[(L^1)Pt(\mu-Br)Pt(L^1)]BF_4$	>95	30.80	3.95	6.05		7.85
			(30.70)	(4.10)	(5.95)		(8.10)
(**1c**)	$[(L^1)Pt(\mu-I)Pt(L^1)]BF_4$	>95	29.30	3.85	5.70	12.95	
			(29.20)	(3.90)	(5.70)	(12.85)	
(**1d**)	$[(L^1)Pt(\mu-CN)Pt(L^1)]BF_4$	25	33.20	4.45	7.75		
			(33.90)	(3.30)	(7.90)		
(**1e**)	$[(L^1)Pt(\mu-CN)Pt(L^1)]O_3SCF_3$	87	32.85	4.00	7.35		
			(32.95)	(4.05)	(7.40)		
(**1f**)	$[(L^1)Pt(\mu-H)Pt(L^1)]BF_4$	90	33.30	4.55	6.45		
			(33.50)	(4.55)	(6.50)		
(**1g**)	$[(L^1)Pt(\mu-H)Pt(L^1)]O_3SCF_3$	>95	32.40	4.15	5.95		
			(32.55)	(4.25)	(6.05)		
(**2a**)	$[(L^1)Pd(\mu-Cl)Pd(L^1)]BF_4$	>95	39.90	5.25	7.60	5.00	
			(40.15)	(5.35)	(7.80)	(4.95)	
(**2b**)	$[(L^1)Pd(\mu-Br)Pd(L^1)]BF_4$	95	37.90	4.85	7.35	10.50	
			(37.80)	(5.05)	(7.35)	(10.50)	
(**2c**)	$[(L^1)Pd(\mu-I)Pd(L^1)]BF_4$	78	35.55	4.75	6.80	15.70	
			(35.65)	(4.75)	(6.95)	(15.70)	
(**2d**)	$[(L^1)Pd(\mu-CN)Pd(L^1)]BF_4$	61	40.95	5.35	9.15		
			(42.40)	(5.40)	(9.90)		
(3)	$[(L^1)Pt(\mu-Br)Pd(L^1)]BF_4$	93	33.20	4.40		6.50	9.55
			(33.90)	(4.50)		(6.60)	(9.40)
(**4a**)	$[(L^1)Pt(\mu-H)_2Pt(PPh_3)_2]BF_4$	55	48.26	4.80	2.30		
			(48.25)	(4.30)	(2.35)		
(**4b**)	$[(L^1)Pd(\mu-H)_2Pt(PPh_3)_2]BF_4$	45	50.20	5.05	3.10		
			(52.10)	(4.65)	(2.55)		



Scheme 1. Synthesis of the bimetallic complexes (**1**)—(**3**) [M = M' = Pt, Y = BF_4, X = Cl(**1a**), Br(**1b**), I(**1c**), CN(**1d**), Y = O_3SCF_3, X = CN(**1e**); M = M' = Pt, X = H, Y = BF_4 (**1f**) or O_3SCF_3 (**1g**); M = M' = Pd, Y = BF_4, X = Cl(**2a**), Br(**2b**), I(**2c**), CN(**2d**); M = Pt, M' = Pd, Y = BF_4, X = Br(**3**)]

or as Nujol mulls between NaCl windows. Elemental analyses were carried out by the Analytical Department of the Institute for Applied Chemistry, T.N.O., Zeist, The Netherlands (Table 1).

Compounds of formulae $[MX(L^1)]$ (M = Pt or Pd; X = Cl, Br, or I) and $[M(L^1)(H_2O)_n]Y$ (M = Pt or Pd, n = 1, Y = BF_4; M = Pt, n = 0, Y = O_3SCF_3) were prepared as previously described.[15] The preparation and characterization of the complexes $[MX(L^1)]$ (M = Pt, X = CN or O_2CH; M = Pd, X = CN) has been previously reported.[16,*]

Syntheses of $[(L^1)M(\mu-X)M(L^1)]Y$ [Y = BF_4, M = Pt, X = Cl (**1a**), Br (**1b**), I (**1c**), *or* CN (**1d**); Y = O_3SCF_3, M = Pt, X = CN (**1e**); Y = BF_4, M = Pd, X = Cl (**2a**), Br (**2b**), I (**2c**), *or* CN (**2d**)] *and* $[(L^1)Pt(\mu-Br)Pd(L^1)]BF_4$ (**3**).—The following preparation of the dinuclear palladium complex (**2b**) is representative for the method used.

A solution of $[PdBr(L^1)]$ (75 mg, 0.2 mmol) in CH_2Cl_2 (3 cm^3) and a solution of $[Pd(L^1)(H_2O)]BF_4$ (80 mg, 0.2 mmol) in CH_2Cl_2 (3 cm^3) were mixed together and stirred for 5 min. The solvent was evaporated *in vacuo* and the resulting off-white product was washed with diethyl ether (3 cm^3) and pentane (3 cm^3) and then dried *in vacuo*. Yield: 95%. Recrystallization from CH_2Cl_2–pentane afforded white crystals.

Syntheses of $[(L^1)Pt(\mu-H)Pt(L^1)]Y$ [Y = BF_4 (**1f**) *or* O_3SCF_3 (**1g**)].—The following preparation of the dinuclear platinum complex (**1g**) is representative for the method used.

The water-free complex $[Pt(L^1)]O_3SCF_3$ (276 mg, 0.5 mmol) and $[Pt(O_2CH)(L^1)]$ (222 mg, 0.5 mmol) were dissolved in

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[*] See also, D. M. Grove, G. van Koten, H. J. C. Ubbels, R. Zoet, and A. L. Spek, *J. Organomet. Chem.*, 1984, **263**, C10 for preliminary information on $[Pt(O_2CH)(L^1)]$.

Table 2. Positional parameters with e.s.d.s in parentheses for $[(L^1)Pd(\mu\text{-}Cl)Pd(L^1)]BF_4$ (**2a**)*

Atom	*x*	*y*	*z*
Pd(1)	0.212 84(3)	0.024 33(1)	0.396 84(2)
Pd(2)	0.238 44(3)	0.236 09(1)	0.426 87(3)
Cl	0.160 4(1)	0.130 24(5)	0.459 6(1)
N(1)	0.213 8(3)	−0.019 3(2)	0.551 0(3)
N(2)	0.225 0(3)	0.040 3(2)	0.228 3(3)
N(3)	0.412 6(3)	0.221 9(2)	0.489 5(4)
N(4)	0.079 1(3)	0.276 0(2)	0.363 1(3)
C(1)	0.337 3(5)	−0.015 6(2)	0.595 8(4)
C(2)	0.133 0(4)	0.008 1(2)	0.630 8(4)
C(3)	0.181 0(4)	−0.087 7(2)	0.534 3(3)
C(4)	0.220 8(3)	−0.108 7(2)	0.425 9(3)
C(5)	0.236 6(3)	−0.170 6(2)	0.390 0(4)
C(6)	0.265 6(4)	−0.181 2(2)	0.283 7(4)
C(7)	0.280 4(4)	−0.133 9(2)	0.209 7(4)
C(8)	0.267 6(4)	−0.072 1(2)	0.243 5(3)
C(9)	0.238 4(3)	−0.060 9(2)	0.350 4(3)
C(10)	0.289 4(4)	−0.014 1(2)	0.178 2(4)
C(11)	0.101 9(5)	0.042 9(3)	0.183 4(4)
C(12)	0.288 7(5)	0.099 6(2)	0.200 5(4)
C(13′)	0.469 3(5)	0.164 1(3)	0.452 5(6)
C(14′)	0.402 4(6)	0.223 5(4)	0.606 7(5)
C(15′)	0.487 9(5)	0.277 0(3)	0.453 2(6)
C(16)	0.410 4(4)	0.333 1(2)	0.439 2(5)
C(17)	0.450 0(5)	0.395 3(3)	0.438 8(5)
C(18)	0.371 1(5)	0.441 7(2)	0.410 9(4)
C(19)	0.248 2(6)	0.428 4(2)	0.386 2(4)
C(20)	0.209 8(5)	0.367 9(2)	0.390 1(4)
C(21′)	0.293 9(4)	0.320 4(2)	0.415 7(3)
C(22′)	0.076 7(5)	0.345 4(3)	0.386 5(6)
C(23′)	−0.034 2(6)	0.249 6(4)	0.408 5(7)
C(24)	0.072 3(6)	0.264 7(4)	0.242 6(5)
B	0.766 6(7)	0.135 4(3)	0.140 0(6)
F(1)	0.752 8(4)	0.176 5(2)	0.060 3(3)
F(2′)	0.855 4(6)	0.146 1(4)	0.205 0(6)
F(3′)	0.665 7(8)	0.137 1(5)	0.199 3(8)
F(4′)	0.787 7(9)	0.080 4(4)	0.094 4(8)

* Atomic sites with occupancy 0.838(2) are indicated with a prime.

benzene (10 cm^3) and the resulting mixture refluxed for 15 min. The solvent was evaporated *in vacuo* and the remaining white solid extracted with CH_2Cl_2 (5 cm^3). The CH_2Cl_2 was removed under vacuum and the resulting white product washed with diethyl ether (2 × 3 cm^3) and dried *in vacuo*.

Syntheses of $[(L^1)M(\mu\text{-}H)_2Pt(PPh_3)_2]BF_4$ [M = Pt (**4a**) *or* Pd (**4b**)].—A solution of $[Pt(cod)_2]$ (205 mg, 0.5 mmol) in toluene (10 cm^3) was mixed with PPh_3 (261 mg, 1.0 mmol) in an oxygen-free atmosphere. The resulting clear orange solution was cooled to −5 °C and added to a stirred solution of $[Pd(L^1)(H_2O)]BF_4$ in acetone (6 cm^3) while H_2 was bubbled through the solution. After 5 min the solvent was evaporated at −5 °C *in vacuo*. The light brown residue was washed with diethyl ether (5 cm^3) and recrystallized from an acetone–diethyl ether solution at −5 °C.

The light yellow platinum analogue (**4a**) was prepared by the same method using $[Pt(L^1)(H_2O)]BF_4$.

Reaction of $[PtBr(L^1)]$ *with* HBF_4.—To a solution of $[PtBr(L^1)]$ (100 mg, 0.21 mmol) in CH_2Cl_2 (3 cm^3) was added an aqueous solution of HBF_4 (35%) (1 cm^3). Slow evaporation of the solvent using a nitrogen stream afforded white crystals, which have been identified as the dinuclear product (**1b**).

Reaction of $[(L^1)Pt(\mu\text{-}Cl)Pt(L^1)]BF_4$ (**1a**) *with* LiCl.—An excess of LiCl (3 mol equiv.) was added to a solution of (**1a**) (0.05 mmol) in CD_2Cl_2. The ^1H n.m.r. spectrum of the resulting mixture showed a single new pattern which was identical to that from an authentic sample of $[PtCl(L^1)]$.

Reaction of $[Pt(L^1)(H_2O)]BF_4$ *with* KCN.—To a solution of $[Pt(L^1)(H_2O)]BF_4$ (187 mg, 0.4 mmol) in H_2O (8 cm^3) was added a seven-fold excess of KCN. Immediately a white product precipitated, which was filtered off on a glass sinter. The solid was extracted with CH_2Cl_2 (5 × 2 cm^3) and the combined filtrates dried over $MgSO_4$. The $MgSO_4$ was filtered off and the filtrate concentrated to 2 cm^3. Addition of pentane (5 cm^3) afforded white $[(L^1)Pt(\mu\text{-}CN)Pt(L^1)]BF_4$ (**1d**). Yield: 25%.

Crystal-structure Determination of $[(L^1)Pd(\mu\text{-}Cl)Pd(L^1)]BF_4$ (**2a**).—*Crystal data*. $C_{24}H_{38}BClF_4N_4Pd_2$, $M = 717.65$, monoclinic, $a = 11.163(1)$, $b = 21.347(2)$, $c = 12.246(4)$ Å, $\beta = 91.48(2)°$, $U = 2\,917(1)$ Å^3 (by least-squares refinement on diffractometer angles for 12 automatically centred reflections, $\lambda = 0.710\,69$ Å), space group $P2_1/c$, $Z = 4$, $D_c = 1.634$ g cm^{-3}, $F(000) = 1\,440$, and $\mu(Mo\text{-}K_\alpha) = 13.5$ cm^{-1}. Yellow crystal: 0.25 × 0.65 × 0.75 mm.

Data collection and processing.[17] CAD4F diffractometer, $\omega/2\theta$ scan with $\Delta\omega = (0.60 + 0.35 \tan\theta)°$, zirconium-filtered Mo-$K_\alpha$ radiation; 6 830 reflections measured ($1.1 < \theta < 35°$), 6 691 unique, giving 5 079 with $I > 2.5\sigma(I)$. Reference reflections 004. There was no indication for decay during data collection. The data set was corrected for Lorentz and polarization effects. Data set *h* 0—14, *k* 0—27, *l* 15 to −15.

Structure analysis and refinement. The structure was solved by standard Patterson and difference Fourier techniques and subsequently refined by blocked full-matrix least-squares techniques. Hydrogen atoms were introduced on calculated positions (C–H = 1.08 Å) and refined in the riding mode with one overall thermal parameter on corresponding non-hydrogen atom positions. In addition three rigid group rotation parameters for each methyl group were introduced. Preliminary refinement with anisotropic thermal parameters for the non-hydrogen atoms converged at $R = 0.058$. The difference Fourier synthesis that was calculated at this stage revealed additional unexplained densities in the neighbourhood of both the BF_4 group and L^1 ligand [the one attached to Pd(2)]. This was interpreted as disorder. The subsequently introduced disorder model (see Results and Discussion section) included two site occupation parameters, one for each of the supposed disordered groups, and two isotropic thermal parameters for the minor component. Further refinement with weights converged at $R = 0.042$ ($R' = 0.064$) for 5 077 observed reflections. Both occupation parameters appear to refine to essentially the same ratio (84:16). A final difference map showed no significant residual densities apart from some absorption artefacts near the heavy atoms. The values of the refined atomic parameters are given in Table 2 [overall thermal parameter, U_{iso}, of the hydrogen atoms = 0.097(2) Å^2].

Neutral scattering factors were taken from ref. 18 and corrected for anomalous dispersion effects.[19] Calculations were carried out on either the in-house Eclipse S/230 minicomputer with a locally modified implementation of the program SHELX 76[20] (structure determination and refinement) or on the CYBER-175 of the University of Utrecht Computer Centre with

Table 3. ^1H N.m.r. data for the complexes $[(L^1)M^1(\mu\text{-}X)M^2(L^1)]^+$ and $[(L^1)M^1(\mu\text{-}H)_2M^2(PPh_3)_2]^+$; L^1 = $C_6H_3(CH_2NMe_2)_2$-*o,o′* [a]

Compound		δ/p.p.m.					
		C_6H_3	$NCH_2(M^1)$	$NCH_2(M^2)$	$NMe_2(M^1)$	$NMe_2(M^2)$	μ-H
(1a)	$[(L^1)Pt(\mu\text{-}Cl)Pt(L^1)]BF_4$ [b]	6.9(m)	4.09	4.09	3.13	3.13	
			(46)	(46)	(37)	(37)	
(1b)	$[(L^1)Pt(\mu\text{-}Br)Pt(L^1)]BF_4$ [b]	6.9(m)	4.09	4.09	3.15	3.15	
			(46)	(46)	(38)	(38)	
(1c)	$[(L^1)Pt(\mu\text{-}I)Pt(L^1)]BF_4$ [b]	6.8(m)	4.10	4.10	3.23	3.23	
			(48)	(48)	(38)	(38)	
(1d)	$[(L^1)Pt(\mu\text{-}CN)Pt(L^1)]BF_4$	7.0(m), 6.8(m)	4.18	4.11	3.18	3.07	
			(46)	(48)	(43)	(40)	
(1e)	$[(L^1)Pt(\mu\text{-}CN)Pt(L^1)]O_3SCF_3$	6.9(m), 6.8(m)	4.20	4.12	3.19	3.09	
			(46)	(48)	(43)	(40)	
(1f)	$[(L^1)Pt(\mu\text{-}H)Pt(L^1)]BF_4$	7.0(t), 6.9(d)	4.05	4.05	3.23	3.23	−4.54
			(48)	(48)	(42)	(42)	(576)
(1g)	$[(L^1)Pt(\mu\text{-}H)Pt(L^1)]O_3SCF_3$	7.0(t), 6.9(d)	4.05	4.05	3.23	3.23	−4.54
			(48)	(48)	(42)	(42)	(576)
(2a)	$[(L^1)Pd(\mu\text{-}Cl)Pd(L^1)]BF_4$ [b]	6.8(m)	4.03	4.03	2.95	2.95	
(2b)	$[(L^1)Pd(\mu\text{-}Br)Pd(L^1)]BF_4$ [b]	6.8(m)	4.02	4.02	2.96	2.96	
(2c)	$[(L^1)Pd(\mu\text{-}I)Pd(L^1)]BF_4$ [b]	6.8(m)	4.06	4.06	3.00	3.00	
(2d)	$[(L^1)Pd(\mu\text{-}CN)Pd(L^1)]BF_4$	7.1(m), 6.9(m)	4.04	4.04	2.91	2.91	
(3)	$[(L^1)Pt(\mu\text{-}Br)Pd(L^1)]BF_4$	7.0(m), 6.9(m)	4.20	4.05	3.10	3.03	
				(48)		(38)	
(4a)	$[(L^1)Pt(\mu\text{-}H)_2Pt(PPh_3)_2]BF_4$ [c]	7.1(t), 6.9(d)	4.09		2.89		−1.86
			(46)		(35)		*d*
(4b)	$[(L^1)Pd(\mu\text{-}H)_2Pt(PPh_3)_2]BF_4$ [c]	7.0(t), 6.8(d)	4.11		2.84		−3.84
							e

[a] Measured on a Bruker WM 250 spectrometer in CD_2Cl_2 unless otherwise indicated; chemical shifts are relative to $SiMe_4$ and *J*(PtH)/Hz are given in parentheses. [b] Measured on a Varian T60 spectrometer. [c] In $[^2H_6]$ acetone. [d] δ(H) 7.45 (30 H, m, 2PPh$_3$), −1.86 [2 H, *J*(PtH) 707, *J*(HP) 117, *J*(HH) 8 Hz]; δ(P) 41.85 [2 P, *J*(PtP) 2 815 Hz]. [e] δ(H) 7.45 (30 H, m, 2PPh$_3$), −3.84 [2 H, *J*(PtH) 818, *J*(HP) 124, *J*(HH) 5 Hz]; δ(P) 33.63 [2 P, *J*(PtP) 2 594 Hz].

the programs of the EUCLID package[21] (molecular geometry and illustrations). Number of refined parameters 381, weighting scheme $w^{-1} = (\sigma^2F_o + 0.004F_o^2)/0.86$, variance (r.m.s. deviation of a reflection of unit weight) 1.41.

The two low-order reflections −102 and 200 were left out of the final refinement cycles in view of extinction effects.

Results and Discussion

Halogen and Pseudo-halogen Singly Bridged Complexes.—The neutral, square-planar platinum and palladium complexes of the terdentate ligand L^1 undergo, in acetone with silver(I) salts, like $AgBF_4$, displacement reactions which result in the formation of cationic platinum and palladium species $[M(L^1)(H_2O)]^+$ (M = Pt or Pd) with a H_2O molecule in the site *trans* to the σ M–C bond.[15,*] Displacement of this H_2O ligand by the terminal halide or cyanide ligand of a neutral complex $[MX(L^1)]$ (M = Pt or Pd; X = Cl, Br, I, or CN) then leads to the formation of new cationic, dinuclear species of stoicheiometry $[(L^1)M(\mu\text{-}X)M(L^1)]^+$ [**(1a)**—**(1e)**, **(2a)**—**(2d)**, and (3) in Scheme 1].

These reactions, which can be viewed as Lewis acid–base pairing reactions,[22] have been carried out at room temperature in CH_2Cl_2 and afford these new species as white crystalline solids upon evaporation of the solvent. An alternative route for the preparation of **(1b)** (in high yield) was found in the reaction of $[PtBr(L^1)]$ with an aqueous solution of HBF_4 (35%). All the new dinuclear species are air stable and have a good stability in CH_2Cl_2.

Addition of an excess of KCN to an aqueous solution of $[Pt(L^1)(H_2O)]BF_4$ resulted in the precipitation of a white product, which was identified as the new dinuclear species $[(L^1)Pt(\mu\text{-}CN)Pt(L^1)]BF_4$ **(1d)**. Despite earlier reports[23] dianionic products of the type $[Pt(CN)_3(L^1)]^{2-}$, in which the 'built-in' ligands $-CH_2NMe_2$ are no longer co-ordinated to the metal, were not found. Interestingly, the dinuclear palladium complex analogous to **(1d)** with a bridging cyanide group could not be prepared by this method.

The novel complexes **(1a)**—**(1e)** and **(2a)**—**(2d)** undergo reaction with metal salts like LiCl, NaI, or KBr, whereby the MXM unit is cleaved affording mixtures of neutral monomeric platinum and palladium complexes of the type $[MX(L^1)]$. These results are in line with the fact that reaction of an aqueous solution of $[M(L^1)]^+$ with an excess of KX (X = Cl, Br, I, N_3, SCN, O_2CH, *etc.*) always led to formation of neutral $[MX(L^1)]$ complexes.[15,16]

The dinuclear ionic formulation of **(1a)**—**(1e)**, **(2a)**—**(2d)**, and (3) (see Scheme 1) has been based on i.r., ^1H n.m.r., and analytical data (Tables 1 and 3) and is in accord with the observation that the complexes are only readily soluble in polar solvents (*e.g.*, CH_2Cl_2). To establish firmly the presence of a single halogen bridge in the solid state, an *X*-ray crystallographic study has been carried out on one representative example of this series, *i.e.* **(2a)**.

Description of the Crystal and Molecular Structure of $[(L^1)Pd(\mu\text{-}Cl)Pd(L^1)]BF_4$ **(2a)**.—The monoclinic unit cell con-

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[*] The kinetics of the H_2O displacement reaction from these and related cationic species is under study (A. Merbach, H. van Beek, and G. van Koten, unpublished work).

Table 4. Selected bond lengths (Å) and angles (°) for $[(L^1)Pd(\mu\text{-}Cl)Pd(L^1)]BF_4$ (**2a**)

Pd(1)–Cl	2.463(1)	Pd(2)–Cl	2.458(1)
Pd(1)–N(1)	2.105(3)	Pd(2)–N(4)	2.104(3)
Pd(1)–N(2)	2.100(4)	Pd(2)–N(3)	2.094(3)
Pd(1)–C(9)	1.929(4)	Pd(2)–C(21)	1.909(4)
Cl–Pd(1)–N(1)	97.0(1)	Cl–Pd(2)–N(4)	97.6(1)
Cl–Pd(1)–N(2)	100.3(1)	Cl–Pd(2)–N(3)	97.9(1)
Cl–Pd(1)–C(9)	174.5(1)	Cl–Pd(2)–C(21)	174.3(1)
N(1)–Pd(1)–N(2)	162.6(1)	N(3)–Pd(2)–N(4)	164.3(1)
N(1)–Pd(1)–C(9)	81.4(1)	N(3)–Pd(2)–C(21)	82.1(2)
N(2)–Pd(1)–C(9)	81.4(1)	N(4)–Pd(2)–C(21)	82.2(2)
Pd(1)–Cl–Pd(2)	134.8(1)		
Pd(1)–N(1)–C(3)–C(4)	29.5(4)	Pd(2)–N(4)–C(22)–C(20)	29.8(5)
N(1)–C(3)–C(4)–C(9)	−21.4(5)	N(4)–C(22)–C(20)–C(21)	−24.2(5)
C(3)–C(4)–C(9)–Pd(1)	1.4(5)	C(22)–C(20)–C(21)–Pd(2)	6.4(6)
C(4)–C(9)–Pd(1)–N(1)	12.9(3)	C(20)–C(21)–Pd(2)–N(4)	9.1(4)
C(9)–Pd(1)–N(1)–C(3)	−23.3(3)	C(21)–Pd(2)–N(4)–C(22)	−22.7(3)
Pd(1)–N(2)–C(10)–C(8)	28.9(4)	Pd(2)–N(3)–C(15)–C(16)	28.6(6)
N(2)–C(10)–C(8)–C(9)	−24.0(5)	N(3)–C(15)–C(16)–C(21)	−26.3(8)
C(10)–C(8)–C(9)–Pd(1)	6.4(5)	C(15)–C(16)–C(21)–Pd(2)	10.1(7)
C(8)–C(9)–Pd(1)–N(2)	8.6(3)	C(16)–C(21)–Pd(2)–N(3)	5.9(4)
C(9)–Pd(1)–N(2)–C(10)	−20.9(3)	C(21)–Pd(2)–N(3)–C(15)	−19.3(4)
Cl–Pd(1)–N(1)–C(2)	29.2(3)	Cl–Pd(2)–N(4)–C(23)	31.6(4)
Cl–Pd(1)–N(1)–C(1)	−91.6(3)	Cl–Pd(2)–N(4)–C(24)	−87.6(4)
Cl–Pd(1)–N(2)–C(12)	42.8(3)	Cl–Pd(2)–N(3)–C(13)	46.3(4)
Cl–Pd(1)–N(2)–C(11)	−77.9(3)	Cl–Pd(2)–N(3)–C(14)	−77.0(4)

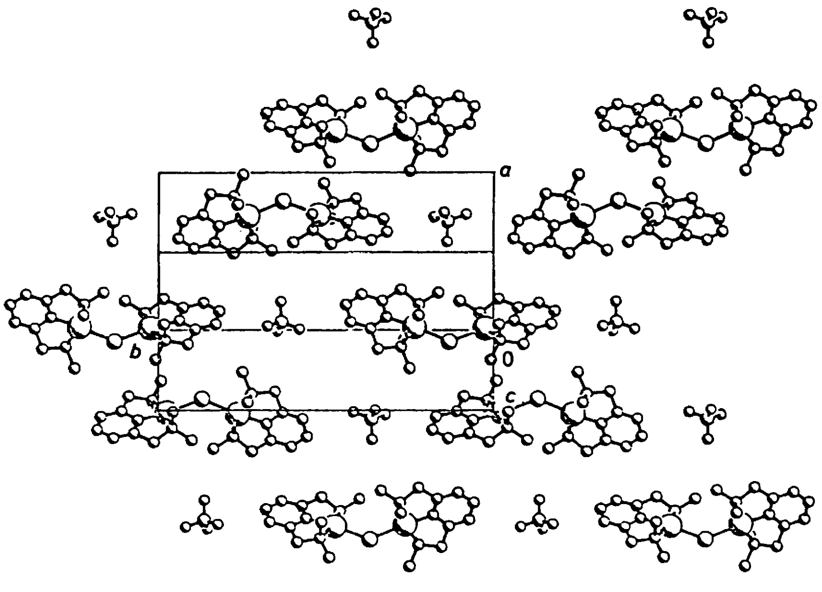


Figure 1. Crystal packing of (**2a**) as viewed perpendicular to the 102 plane

tains four cation–anion pairs. An analysis of their packing shows that the ions are essentially located in a lattice plane with Miller indices (102). Furthermore, the ion pairs are lined up along the *b* axis. The observed correlation of the two disorder parameters in one of the ligands and the BF_4 anion is interpretable in terms of steric interactions between the relevant methyl groups and F atoms. This is particularly true for those in the neighbourhood of N(4). The two disordered forms of L^1 on Pd(2) are mirror-plane related with respect to the co-ordination plane of Pd(2) and mainly differ in the position of the carbon atoms bonded to the N atoms and the sign of the five-membered chelate ring pucker.

Figure 1 shows the crystal packing and Figure 2 gives the ORTEP drawing as well as the adopted numbering scheme (ref. 14 provides an alternative complementary view of the molecular structure). The molecule (84% abundant) exhibits a non-crystallographic two-fold axis of symmetry. Relevant interatomic bond distances and angles are listed in Table 4.

The cation consists of two *trans*-(L^1)Pd units sharing a single bridging chlorine atom. Both Pd^{II} centres have a slightly distorted square-planar co-ordination sphere, *e.g.* N(1)–Pd(1)–N(2) 162.6(1) and C(9)–Pd(1)–Cl 174.5(1)° as a result of the small N–Pd–C(*ipso*) bite angles of the benzylamino ligands of 81.4(1) and 82.1(2)°, respectively. The chelating five-

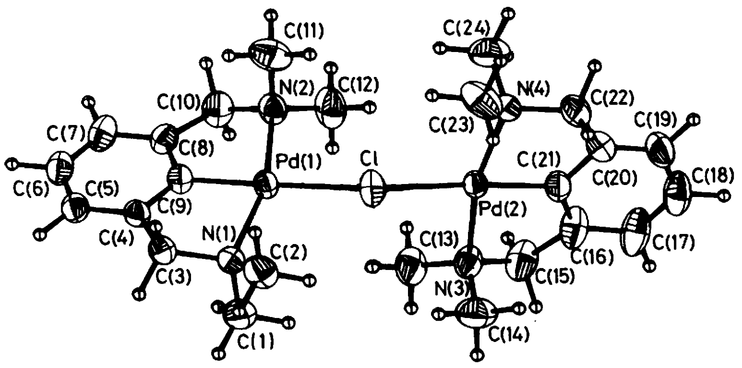


Figure 2. ORTEP drawing of $[(L^1)Pd(\mu\text{-}Cl)Pd(L^1)]BF_4$ (**2a**) with numbering scheme (40% probability). The hydrogen atoms are represented by artificially small spheres. The BF_4^- anion is shown in Figure 1

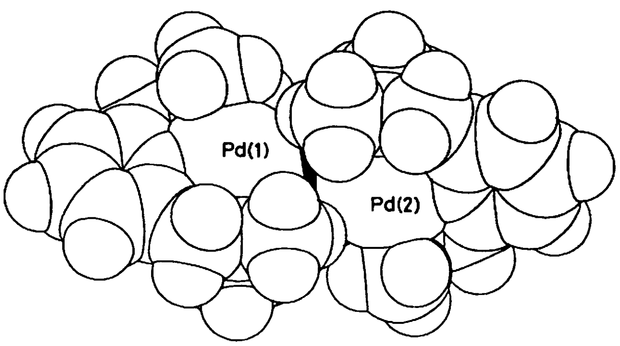


Figure 3. Cation of (**2a**) shown as space-filling model rotated 180° about the Pd–Pd vector relative to Figure 2

membered rings are puckered in opposite directions as may be seen quantitatively from the torsion angles (Table 4) and least-squares planes (supplementary data). The two virtually equivalent co-ordination planes are orientated almost perpendicularly to each other [88.5(2)°] as calculated from the least-squares planes of the carbon atoms of the two aryl moieties. The Pd(1)–Cl–Pd(2) angle of 134.8(1)° is a dominant structural feature which, taken together with the fairly long Pd–Cl distances of 2.463(1) and 2.458(1) Å, respectively, gives rise to a Pd–Pd separation of 4.544(2) Å. This value is much larger than that found in complexes with a distinct Pd–Pd bond; *e.g.* in $[Pd_2(Ph_2PCH_2PPh_2)_2Br_2]$[24] the separation is only 2.699(5) Å. Bridging halogen atoms should form bonds with a M–X–M bond angle at or near 90°. In this situation the bridging halide atom can make optimal use of its *p* orbital. This is reflected by the single bridge angles in the compounds $[(CO)_2ClRh(\mu\text{-}Cl)Rh(CO)\{C_6H_5P[OC(CH_3)_2CH_2]_2NH\}]$, Rh–Cl–Rh 89.4°,[8] and diphenyliodonium nitrate, C–I–C 92°.[25] When steric effects come into play this bond angle may deviate considerably as is shown by the complexes $[\{Fe(\eta^5\text{-}C_5H_5)(CO)_2\}_2I]BF_4$, Fe–I–Fe 110.8°,[7] and $[Pd_2(Ph_2PCH_2PPh_2)_2I(CH_3)(\mu\text{-}I)]BF_4$, Pd–I–Pd 67.0°.[5] Likewise the large deviation of the Pd–Cl–Pd angle from 90° in (**2a**) may be steric in origin, see Figure 3.

Spectroscopic Measurements.—The i.r. spectra of (**1a**)—(**1g**), (**2a**)—(**2d**), and (**3**) show broad absorption bands in the region 1 000—1 200 cm^{-1}, belonging to $\nu(BF_4)$ or $\nu(SO)$.[26] Bands due to MXM (X = halide) absorptions were obscured by ligand absorption bands and could not be identified. The i.r. spectra of the cyanide complexes (**1d**), (**1e**), and (**2d**) all showed one specific ν(CN) at 2 135 (Pt) or 2 143 cm^{-1} (Pd). These values are in agreement with those found in other complexes known to contain a M(μ-CN)M unit, *cf.* $[(NH_3)_5Co(\mu\text{-}CN)Co(CN)_5]\cdot H_2O$ [ν(CN) at 2 180 cm^{-1}].[27] Platinum compounds with a single bridging CN group are rare. Characterized examples include $[(PEt_3)_2HPt(\mu\text{-}CN)MCl_2]$ (M = Mn, Fe, Co, Ni, or Zn),[28] $[(PEt_3)_2HPt(\mu\text{-}CN)PtH(PEt_3)_2]PF_6$,[29] and $[(PhCH_2NH_2)(NH_2CH_2C_6H_4)Pt(\mu\text{-}CN)Pt(C_6H_4CH_2NH_2)(NH_2CH_2Ph)]BF_4$ [ν(CN) at 2 145 cm^{-1}].[30] These species, as well as (**1d**), (**1e**), and (**2d**) reported here, are all believed to have an essentially linear M–CN–M skeleton. It is generally found that ν(CN) for M(μ-CN)M species are 20—50 cm^{-1} higher than ν(CN) of corresponding complexes with a terminal M–CN group,[31] and the values for mononuclear $[M(CN)(L^1)]$ of 2 093 and 2 115 cm^{-1} for M = Pt and Pd, respectively[16] are in line with this observation.

The dinuclear nature of $[(L^1)M(\mu\text{-}X)M(L^1)]^+$ (X = Cl, Br, or I) in solution cannot be directly deduced from the ^1H n.m.r. spectra (see Table 3). For the halide bridged complex (**1a**) (Figure 4) the aryl protons were found as a multiplet at 6.9 p.p.m. The CH_2 and NMe_2 protons show sharp signals at 4.09 and 3.13 p.p.m., respectively, with both peaks possessing ^{195}Pt satellites of *J*(PtH) = 46 and 37 Hz, respectively. These values are typical for Pt species with two *trans* N-co-ordinated CH_2NMe_2 groups.[32]

A similar molecular geometry for (**1a**) in solution as has been found for the analogue (**2a**) in the solid (see above) would imply a number of non-equivalent CH_2NMe_2 groupings as well as diastereotopic CH_2 and NMe_2 groups. Solution ^1H n.m.r. spectra at 298 and 239 K, however, show singlet CH_2 and CH_3 resonances which imply that a fluxional process renders the CH_2NMe_2 groups as well as the prochiral CH_2 and NMe_2 groupings equivalent. A likely process involves rotation around the metal–halogen axes combined with intermolecular exchange *via* bridge cleavage reactions. A similar conclusion holds for the solution behaviour of the compounds (**1b**), (**1c**) and (**2a**)—(**2c**) (Table 3).

The occurrence of intermolecular exchange was supported by the observation that the ^1H n.m.r. spectrum of a mixture of equivalent amounts of $[PtCl(L^1)]$ and dinuclear (**1a**) showed only *one* pattern of singlet CH_2 and CH_3 signals at room temperature. At 239 K these signals decoalesced into those of $[PtCl(L^1)]$ and (**1a**).

It must be noted that direct evidence for the presence of a halide bridge in (**3**), where Br bridges between Pt and Pd, could be obtained from the ^1H n.m.r. data. Here the ^1H n.m.r. spectrum showed inequivalent CH_2NMe_2 groupings due to the different metals present in this species.

Metal inequivalency, though of different type, is also reflected in the ^1H n.m.r. spectra of the bridged dinuclear platinum cyanide complexes (**1d**) and (**1e**) which show signals for two distinct L^1 ligands. The chemical shifts [with *J*(PtH)] of the

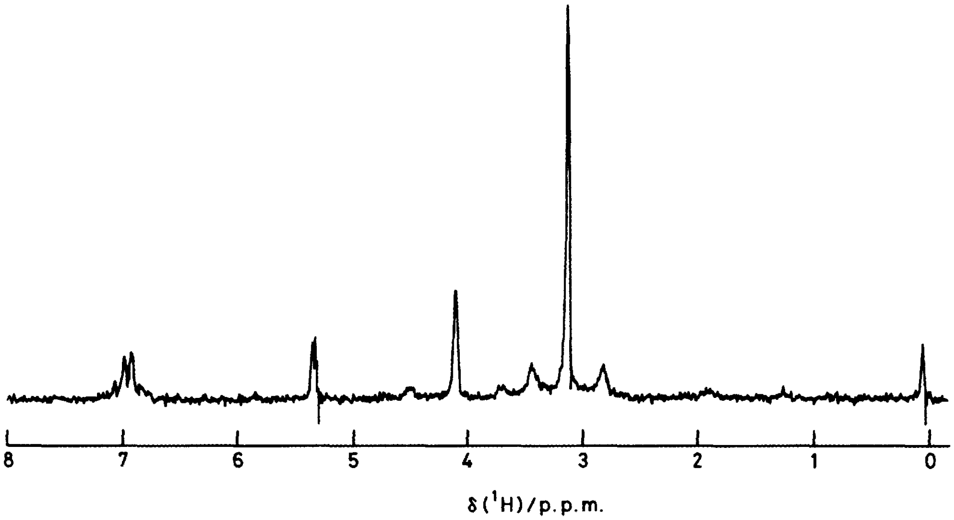
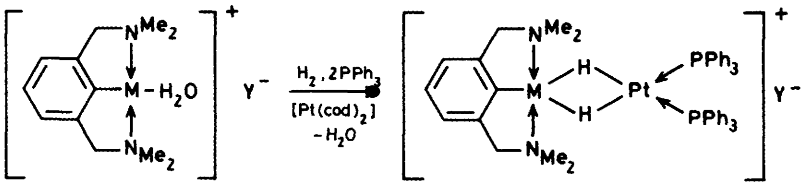


Figure 4. 60-MHz ^1H n.m.r. spectrum of $[(L^1)Pt(\mu\text{-}Cl)Pt(L^1)]BF_4$ **(1a)**



Scheme 2. Synthesis of the bimetallic dihydride complexes: M = Pt, Y = BF_4 **(4a)**, M = Pd, Y = BF_4 **(4b)**

CH_2 and NMe_2 units in the $(L^1)Pt(CN)$ moiety appear at 4.18 (46) and 3.18 p.p.m. (43 Hz), respectively, while the corresponding resonances from the N-bonded $(CN)Pt(L^1)$ moiety are at 4.11 (48) and 3.07 p.p.m. (40 Hz). This assignment is based on the characteristic shifts and couplings in $[PtN_3(L^1)]$ with a N-bonded ligand and $[PtPh(L^1)]$ with a C-bonded ligand.*

Mono- and Di-hydrido Bridged Complexes.—Attempts to synthesize mononuclear platinum(II) hydrido species by reaction of $[PtBr(L^1)]$ with metal hydrides $LiAlH_4$ and NaH failed. Instead the reaction of $[Pt(L^1)]O_3SCF_3$ and $[Pt(O_2CH)(L^1)]$ in benzene at 50 °C led to the formation of the hydrido bridged complex $[(L^1)Pt(\mu\text{-}H)Pt(L^1)]O_3SCF_3$, **(1g)**, in almost quantitative yield, see Scheme 1. This white product is air-stable and very soluble in CH_2Cl_2. Reaction of **(1g)** with CO afforded green platinum carbonyl products without the terdentate ligand and no species resulting from CO insertion into the Pt–H–Pt bridge were found.

The ^1H n.m.r. (250 MHz, CD_2Cl_2) spectrum of **(1g)** showed signals due to the protons of the terdentate ligand system, *i.e.* an AB_2 pattern for the aryl protons, $\delta(H_A)$ 7.0 (2 H, t, $2C_6H_3$) and $\delta(H_B)$ 6.9 [4 H, d, $2C_6H_3$, $^3J(AB)$ 8 Hz], and two singlets with platinum satellites for the CH_2 and NMe_2 units, see Table 3.

In the hydride region one hydride resonance was observed at −4.54 p.p.m. with $J(PtH)$ = 576 Hz. The weak outer peaks of the expected quintet were not distinguishable from the noise. The value can be compared with those of other binuclear complexes of platinum with bridging hydride groups, *viz.* $[Pt_2H_3(Ph_2PCH_2PPh_2)_2]Cl$ (−5.86 p.p.m., 540 Hz)[33] and $[(PEt_3)_2HPt(\mu\text{-}H)PtPh(PEt_3)_2]PF_6$ (−9.46 p.p.m., 500 Hz).[10]

Complex **(1g)**, containing N-donor ligands, is structurally related to $[(PEt_3)_2HPt(\mu\text{-}H)PtPh(PEt_3)_2]^+$,[10] which contains a Pt–H–Pt bridging unit. Venanzi and co-workers[13,34] have set up a formal scheme for the formation of such hydrido bridged complexes comprising the reaction of a hydride acceptor with a hydride donor. In **(1g)** the *in situ* generated mononuclear hydride complex $[PtH(L^1)]$ acts as a ligand and is bonded to a co-ordinatively unsaturated, cationic complex $[Pt(L^1)]^+$.[13,34]

Attempts to synthesize the palladium analogue of **(1g)** by a route analogous to that shown in Scheme 1 were not successful owing to premature decomposition of the palladium hydride donor complex $[Pd(O_2CH)(L^1)]$. Recently, Rimml and Venanzi[13] reported the analogous platinum and palladium complexes $[(L^2)M(\mu\text{-}H)M(L^2)]^+$ [M = Pt or Pd, L^2 = *o,o'*-$(Ph_2PCH_2)_2C_6H_3$]. They also found that the bimetallic species had a much higher stability than the mononuclear species $[PdH(L^2)]$ which decomposed in solution.[13] From these results it is clear that the stability of the M–H–M unit depends not only on the rigidity of the terdentate ligand system but also on the nature of the donor atoms and metal centres.

It is also possible to synthesize dihydrido bridged complexes according to the route shown in Scheme 2. In this case a reactive platinum dihydride species is generated *in situ* from the reaction of $[Pt(cod)_2]$, two equivalents of PPh_3, and H_2, in the presence of one equiv. of $[M(L^1)(H_2O)]^+$. The latter cationic species reacts with the dihydridoplatinum(II) intermediate, $PtH_2(PPh_3)_2$, affording the dinuclear complexes $[(L^1)M(\mu\text{-}H)_2Pt(PPh_3)_2]^+$ [M = Pt **(4a)** (light yellow) or Pd **(4b)** light brown].

Complex **(4b)** decomposes slowly in the solid state at room temperature. The $^{31}P\text{-}\{^1H\}$ n.m.r. spectra of both **(4a)** and **(4b)** (Table 3) show a single ^{31}P resonance (with Pt satellites) indicating that the two phosphine ligands are chemically equivalent.

This simplicity contrasts with the hydride region of the ^1H n.m.r. spectra (250 MHz, $[^2H_6]$acetone) of both **(4a)** and **(4b)**

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* For a series of mononuclear $[PtX(L^1)]$ compounds we observed that the values of $J(PtH)$ of the NMe_2 groups are in the ranges 39—40 Hz (N-bonded ligand) and 43—45 Hz (C-bonded ligand), see ref. 16.

which show a complicated multiplet structure centred at −1.86 and −3.84 p.p.m., respectively. This multiplet structure arises from coupling of the hydride protons with both ^{31}P and ^{195}Pt nuclei. Analysis of these patterns yielded the coupling constants reported in Table 3 which are consistent with a molecular structure as shown for **(4a)** and **(4b)** in Scheme 2 with magnetically equivalent ^{31}P atoms. Both **(4a)** and **(4b)** showed a similar pattern for the protons of the terdentate ligand system; singlet resonances for the CH_2 and NMe_2 protons and an AB_2 pattern for the aryl protons, see Table 3.

Similar structures, containing two bridging hydrides between two Pt atoms have also been reported for the related tertiary phosphine species $[(PR_3)_2Pt(\mu\text{-}H)_2Pt(PR_3)_2H]^+$ (R = Ph, cyclo-C_6H_{11}, or Et).[35] Refs. 35*b* and *c* deal in detail with the analysis of the complex ^{1}H n.m.r. hydride signals and postulate various mechanisms to account for fluxional behaviour and crystallographic distortions found in some of these species. However, the ^{1}H and ^{31}P spectra of **(4a)** and **(4b)** provided no evidence for fluxional processes and hence no evidence for the isomeric species $[(L^1)M(\mu\text{-}H)Pt(PPh_3)_2H]^+$.

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