The Role of Transition Metal Atoms as Hydrogen Bond Acceptors: A Neutron Diffraction Study of $[NPr^n_4]_2[PtCl_4]\cdot$*cis*-$[PtCl_2(NH_2Me)_2]$ at 20 K[‡]

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Single-crystal neutron diffraction has allowed accurate characterisation of N–H ··· Pt and N–H ··· Cl interactions linking the two square-planar platinum(II) units which comprise the dianion of $[NPr^n_4]_2[PtCl_4]\cdot$*cis*-$[PtCl_2(NH_2Me)_2]$ **1**: Pt ··· H 2.262(11) Å, N–H ··· Pt 167.1(9)°; Cl ··· H 2.318(12) Å, N–H ··· Cl 151.0(12)°. An extensive network of C–H ··· Cl hydrogen bonding between the cation and anion species is also revealed, and provides valuable information on what is one of the least well characterised types of hydrogen bond. A weak C–H ··· Pt interaction between one cation unit and the anion is also observed. In the light of this and particularly the stronger intra-anion N–H ··· Pt interaction, a new type of three-centre four-electron hydrogen bridge, involving a transition-metal atom, is proposed. Further supporting evidence is drawn from a re-evaluation of spectroscopic data for similar interactions previously reported. This type of interaction is contrasted with the more well known three-centre two-electron M–H⇀M, C–H⇀M, Si–H⇀M and B–H⇀M interactions and compared with conventional four-electron hydrogen bonds. Compound **1** is triclinic, space group $P\bar{1}$ (no. 2), $Z = 2$, with $a = 10.680(4)$, $b = 11.926(2)$, $c = 15.350(15)$ Å, $\alpha = 93.88(4)$, $\beta = 100.57(5)$ and $\gamma = 96.58(4)$° at 20 K. Final $R(F^2) = 0.124$, $S = 1.136$ for 5244 F^2 values ($F_o^2 > 0.0$).

For many years there has been considerable interest in interactions between hydrogen and transition metal atoms, not least because of the role of such interactions in many important transition-metal-catalysed reactions.[1] A fascinating aspect of this area of chemistry is the great diversity of such interactions. A number of different transition metal hydride bonding modes have been identified,[2] notably terminal, μ and μ_3 bridging, as well as μ_6 interstitial modes. A variety of three-centre two-electron (3c–2e) hydrogen-bridge interactions are also known, either between two metal atoms[2] (M–H⇀M′) or between metal and non-metal atoms, for example B–H⇀M,[2,3] Si–H⇀M[2,4] and the now widely studied agostic C–H⇀M[5] interactions. In addition, recent attention has been focused on the ability of dihydrogen to act as ligand in an η^2 co-ordination mode.[6] These latter interactions are important as models for intermediate stages in such reactions as C–H or H–H bond activation at a metal centre.

In a previous communication[7] we raised the possibility that electron-rich transition metal atoms, like electron-rich non-metals such as oxygen and nitrogen, may act as hydrogen bond acceptors. Here we present a detailed description of the structure of the unusual diplatinum salt $[NPr^n_4]_2[PtCl_4]\cdot$*cis*-$[PtCl_2(NH_2Me)_2]$ **1** which led us to this conclusion. A comparison with a number of compounds found in the literature, and which can be interpreted as incorporating N–H ··· M or C–H ··· M hydrogen bond type interactions, also will be presented. Spectroscopic evidence, in the form of ^1H NMR data from these compounds, supports our conclusion, and will be discussed. Analogous ^1H NMR data for **1** could not be obtained primarily due to signal broadening and possible dynamic effects causing averaging of the signals. Hydrogen bonding is a pervasive and much studied[8] form of interaction in organic chemistry and biochemistry, and is known to play an important role in both structure and reactivity. However, whilst proton-transfer reactions involving transition metals continue to be an area of great interest,[9] the possible incorporation of transition metals in hydrogen bonding interactions has, to our knowledge, received no attention. Some implications of transition metals in such a role will be discussed.

In addition to providing new insight into the role of transition metals in their interaction with hydrogen atoms, the neutron diffraction results reported here present a good opportunity to study another type of hydrogen bonding for which there is little accurate structural information, namely C–H ··· Cl hydrogen bonding. An extensive network of such interactions, of varying strengths, was found to link the cation and dianion units in compound **1**.

Experimental

As reported in our previous communication,[7] the product **1** resulted from the reaction of methylamine with $[NPr^n_4]_2[PtCl_6]$ in *N*,*N*-dimethylformamide; ^{195}Pt NMR data[7] concur with the observed structure. Large, air-stable, orange crystals of **1** were more conveniently obtained from a solution of $[PtCl_2(NH_2Me)_2]$ and $[NPr^n_4]_2[PtCl_4]$ in CH_2Cl_2. An irregularly shaped single crystal of approximately pentagonal cross-section and volume 3.52 mm^3 was selected for neutron data collection. The crystal was mounted on a hollow aluminium pin, sealed in an aluminium canister under a helium atmosphere and placed in a closed-cycle helium refrigerator (Air Products DISPLEX model CS-202). This in turn was mounted on the *H6S* four-circle diffractometer at the High Flux Beam Reactor, Brookhaven National Laboratory. After establishing

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[‡] Bis(tetra-*n*-propylammonium) tetrachloroplatinate(II)–dichlorobis-(methylamine)platinum(II) (1/1).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Table 1 Neutron data collection and refinement parameters for compound **1**

Crystal sample	
Faces [distance from origin (mm)]	$(\bar{1}01)$ [0.0], $(10\bar{1})$ [1.34], $(\bar{1}\bar{2}\bar{1})$ [0.0], $(01\bar{2})$ [0.0], $(0\bar{1}2)$ [1.84], (212) [2.04], $(02\bar{1})$ [1.24]
Volume/mm^3	3.52
Absorption coefficient,[a] μ/cm^{-1}	3.22
Transmission coefficients	0.617–0.712
Crystal data	
Symmetry	Triclinic
Space group	$P\bar{1}$ (no. 2)
Lattice constants[b] (Å)	$a = 10.680(4)$, $b = 11.926(2)$, $c = 15.350(15)$
(°)	$\alpha = 93.88(4)$, $\beta = 100.57(5)$, $\gamma = 96.58(4)$
U/Å^3	1901(2)
D_c/g cm^{-3}	1.813
Diffraction measurements	
T/K	20.0(5)
λ/Å	1.159 33(8)
$\sin\theta/\lambda$ limit (Å^{-1})	0.57
Number of observations	
total	6194
independent	5766
used in refinement (n) ($F^2 > 0.0$)	5244
Refinement	
Number of variables (v)	786
Extinction parameter (g[c])	2.1(2)
Indices of fit[d]	
$R(F^2)$	0.124
$R(F^2)$ $[F^2 > 3\sigma(F^2)]$	0.079
$R'(F^2)$	0.111
S	1.136

[a] Evaluated from mass absorption coefficients (μ/ρ) taken from ref. 10 for non-hydrogen atoms and as determined by Koetzle and McMullan[11] for hydrogen atoms. [b] Determined from least-squares fit of $\sin^2\theta$ values for 32 reflections with $0.32 < \sin\theta/\lambda < 0.44$ Å^{-1}. [c] Isotropic $g \times 10^3$ for type I crystal with Lorentzian mosaic distribution, according to the formalism of Becker and Coppens.[12] [d] $R(F^2) = \Sigma|F_o^2 - F_c^2|/\Sigma F_o^2$; $R'(F^2) = [\Sigma w|F_o^2 - F_c^2|^2/\Sigma(wF_o^2)^2]^{\frac{1}{2}}$; $S = [\Sigma w|F_o^2 - F_c^2|^2/(n - v)]^{\frac{1}{2}}$.

the lattice symmetry and unit-cell parameters (see Table 1), intensity data were measured[13,14] by ω–2θ step scans for one hemisphere of reciprocal space, using a Ge (220) monochromated neutron beam of wavelength 1.159 33(8) Å (based on prior calibration for a KBr crystal, $a_0 = 6.6000$ Å at 298 K). A 75-step scan of fixed width, $\Delta 2\theta = 3.0°$, was used in the range $0 < 2\theta \leqslant 60°$. Scan widths were calculated according to $\Delta 2\theta = 1.08\ (1 + 3.34 \tan\theta)$ for $60 < 2\theta \leqslant 82°$, using variable step sizes and 60–90 steps per scan. Counting times (*ca.* 1.8 s per step) were determined by monitoring the incident beam; no significant crystal or instrument instability was observed based on the intensities of three reflections remeasured after every 200 data. The sample temperature (calibration with respect to the magnetic phase transition of FeF_2 at 78.4 K)[15] was maintained at 20.0(5) K during the experiment using a germanium-resistance thermometer. Experimental details are summarised in Table 1.

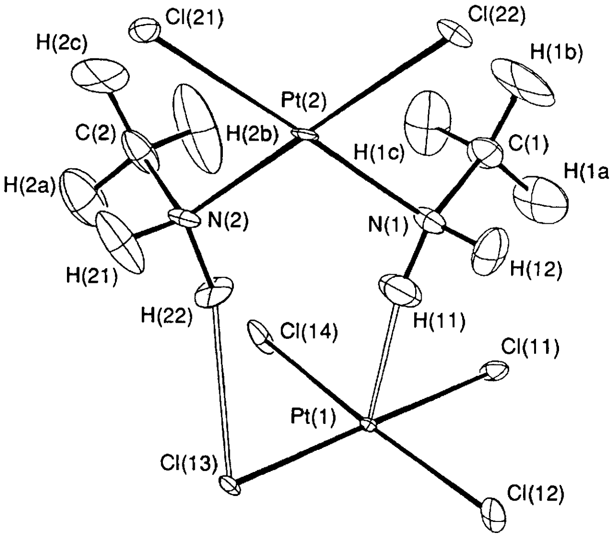

Fig. 1 The molecular structure of the $[PtCl_4]$·*cis*-$[PtCl_2(NH_2Me)_2]^{2-}$ anion of **1**, from the neutron diffraction study. All atoms are represented by 50% probability ellipsoids[20]

The initial refinement model was based on non-hydrogen atomic coordinates from a preliminary room-temperature X-ray diffraction study. Hydrogen atom positions were obtained by Fourier difference synthesis, and initial refinements of positional and displacement parameters* were conducted by differential Fourier synthesis.[16] Disorder is present in one NPr^n_4 cation, for which two orientations are approximately related by two-fold rotation of each propyl group about its N···C(Me) vector. This required the construction of a seven-site rigid group to describe each of the four methyl groups, *i.e.* two sets of partial-occupancy hydrogen atom sites and a common carbon atom site of full occupancy. Refinement of these rigid groups and the determination of the occupancy factors for the two components of the disordered cation was achieved using the blocked-cascade least-squares algorithm and parameter constraints of the SHELXTL package.[17] The occupancy factors obtained [0.533(2) and 0.467(2)] were then held constant together with positional and displacement parameters for the disordered methyl hydrogen atoms in final cycles of refinement, which were conducted by full-matrix least squares.[18] Positional parameters for all other atoms, including those of the disordered cation, were refined together with anisotropic displacement parameters for all atoms of the ordered groups and the central nitrogen atom of the disordered cation. Isotropic displacement parameters were refined for all remaining atoms of the disordered cation and an isotropic extinction parameter was also incorporated (see Table 1). The function $\Sigma w|F_o^2 - F_c^2|^2$ was minimised for 5244 F^2 values ($F_o^2 > 0.0$) using a weighting scheme $w = [\sigma^2(F_o^2) + 0.0036(F_o^2)^2 + 0.81]^{-1}$, and refinements converged to $R(F^2) = 0.124$, $S = 1.136$. In the final difference density map, the largest positive and negative features had magnitudes of 19% of a typical carbon atom and 28% of a typical hydrogen atom respectively. Both were located in the region of the C(20)–H(20a–f) disordered methyl group and reflect the difficulty in adequately modelling the nuclear density in this region. Neutron scattering lengths used in the refinement (H, −0.374; C, 0.6648; N, 0.940; Cl, 0.958 and Pt, 0.950 × 10^{-12} cm) were taken from ref. 19. Details of the final refinement are summarised in Table 1.

Additional material available from the Cambridge Crystallographic Data Centre comprises remaining bond lengths and angles.

Results and Discussion

The molecular structure and mean atomic displacements are

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* With the exception of disordered methyl hydrogen atoms in one cation unit, for which peaks were too close to permit refinement at this data resolution, *i.e.*, H···H′ ≈ 0.33 Å, *cf.* resolution of $\sin\theta/\lambda < 0.57$ Å^{-1} ($d_{min} = 0.88$ Å).

Table 2 Fractional coordinates[a] (× 10^4) and atomic displacement parameters[a,b] (× 10^3 Å^2) for compound **1**

Atom	X/a	Y/b	Z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
(*i*) [PtCl$_4$]·*cis*-[PtCl$_2$(NH$_2$Me)$_2$] Dianion									
Pt(1)	3 764(3)	808(2)	2 356(2)	9(1)	5(1)	7(1)	−1(1)	1(1)	−1(1)
Pt(2)	1 358(3)	3 796(2)	2 492(2)	12(1)	6(1)	14(1)	2(1)	2(1)	−6(1)
Cl(11)	4 670(3)	534(2)	3 786(2)	23(2)	8(1)	18(2)	1(1)	−7(1)	−1(1)
Cl(12)	1 993(3)	−456(3)	2 425(2)	20(2)	24(2)	10(1)	−2(1)	−4(1)	1(1)
Cl(13)	2 841(3)	1 086(2)	914(2)	32(2)	8(1)	8(1)	4(1)	7(1)	0(1)
Cl(14)	5 641(3)	2 155(3)	2 310(2)	31(2)	32(2)	22(2)	−26(2)	17(2)	−13(1)
Cl(21)	714(3)	5 283(2)	1 699(2)	13(2)	8(1)	24(2)	0(1)	1(1)	−2(1)
Cl(22)	−141(3)	3 901(2)	3 391(2)	13(2)	17(2)	15(2)	4(1)	4(1)	−6(1)
N(1)	1 951(4)	2 482(3)	3 170(2)	15(2)	16(2)	17(2)	5(2)	2(1)	−3(1)
N(2)	2 665(3)	3 680(3)	1 676(3)	22(2)	11(2)	26(2)	2(1)	9(2)	−8(1)
C(1)	2 729(6)	2 789(5)	4 078(3)	30(3)	19(3)	21(3)	1(3)	−3(2)	−4(2)
C(2)	3 790(5)	4 534(5)	1 883(4)	17(3)	40(4)	25(3)	−10(2)	4(3)	−10(2)
H(11)	2 448(10)	1 981(8)	2 819(7)	41(6)	25(5)	34(5)	11(5)	9(5)	−5(4)
H(12)	1 169(10)	1 955(8)	3 223(7)	23(5)	23(5)	55(7)	−12(5)	−2(5)	9(4)
H(21)	2 186(10)	3 762(11)	1 045(8)	27(6)	76(8)	28(6)	1(5)	8(5)	−6(5)
H(22)	2 967(13)	2 880(9)	1 634(10)	89(9)	10(5)	101(10)	24(5)	71(8)	13(5)
H(1a)	3 002(12)	2 064(11)	4 383(8)	58(7)	45(7)	41(6)	23(6)	−13(5)	3(6)
H(1b)	2 169(14)	3 236(11)	4 461(7)	94(10)	66(8)	15(5)	34(8)	1(6)	−15(5)
H(1c)	3 589(12)	3 359(11)	4 055(8)	42(7)	60(8)	55(7)	−32(7)	−23(6)	7(6)
H(2a)	4 443(11)	4 437(11)	1 410(9)	31(6)	69(8)	60(8)	−10(5)	19(6)	−4(6)
H(2b)	4 336(12)	4 496(16)	2 527(9)	33(7)	146(15)	36(7)	−20(8)	−17(6)	22(8)
H(2c)	3 476(13)	5 390(11)	1 852(10)	69(8)	21(7)	91(10)	−26(6)	23(7)	−32(6)
(*ii*) Ordered NPr$^n_4$ cation **I**									
N(3)	7 739(3)	2 388(2)	274(2)	11(1)	6(1)	13(1)	−3(1)	2(1)	−2(1)
C(3)	8 221(4)	2 065(3)	1 205(3)	15(2)	7(2)	10(2)	−1(2)	−1(2)	−3(2)
C(4)	8 588(5)	868(4)	1 262(3)	17(3)	13(2)	13(2)	3(2)	1(2)	0(2)
C(5)	8 648(5)	558(4)	2 211(3)	22(3)	14(3)	13(2)	−1(2)	−4(2)	2(2)
C(6)	6 397(4)	1 749(4)	−62(3)	12(2)	12(3)	7(2)	−1(2)	6(2)	−1(2)
C(7)	5 679(4)	2 056(4)	−934(3)	12(2)	15(3)	14(2)	−2(2)	4(2)	5(2)
C(8)	4 374(4)	1 316(4)	−1 179(3)	11(2)	14(3)	16(3)	−2(2)	−1(2)	1(2)
C(9)	7 710(4)	3 664(3)	318(3)	13(3)	7(2)	15(3)	−2(2)	6(2)	−1(2)
C(10)	6 810(5)	4 110(4)	880(4)	19(3)	7(2)	28(3)	1(2)	13(2)	−1(2)
C(11)	6 881(5)	5 396(4)	832(4)	18(3)	9(2)	25(3)	0(2)	7(2)	−1(2)
C(12)	8 592(4)	2 079(4)	−361(3)	14(2)	9(3)	7(2)	3(2)	0(2)	−2(2)
C(13)	10 010(4)	2 549(4)	−90(3)	12(2)	9(3)	11(3)	−1(2)	4(2)	−3(2)
C(14)	10 718(4)	2 100(4)	−789(3)	10(3)	8(3)	17(3)	−2(2)	2(2)	0(2)
H(3a)	7 450(9)	2 170(7)	1 586(6)	30(5)	27(5)	17(4)	1(4)	6(4)	1(3)
H(3b)	9 062(8)	2 701(7)	1 501(5)	16(5)	27(5)	21(4)	−5(4)	−1(4)	−7(4)
H(4a)	7 887(10)	260(7)	811(6)	46(6)	15(4)	14(4)	1(4)	−9(4)	−1(4)
H(4b)	9 536(9)	807(8)	1 074(6)	24(5)	33(5)	34(5)	6(4)	9(4)	10(4)
H(5a)	9 027(12)	−254(9)	2 298(7)	88(9)	24(6)	29(5)	21(6)	9(5)	9(4)
H(5b)	7 732(12)	497(9)	2 392(7)	44(7)	52(7)	32(6)	−3(5)	23(5)	8(5)
H(5c)	9 297(11)	1 195(9)	2 687(7)	52(7)	32(6)	33(5)	−13(5)	−9(5)	−14(5)
H(6a)	5 857(8)	1 871(7)	482(5)	29(5)	33(5)	12(4)	3(4)	15(4)	−5(3)
H(6b)	6 512(9)	848(8)	−126(6)	30(5)	12(5)	31(5)	0(4)	−1(4)	0(4)
H(7a)	5 538(9)	2 971(9)	−899(7)	30(5)	25(6)	45(6)	−2(4)	−8(4)	10(4)
H(7b)	6 217(9)	1 921(10)	−1 464(6)	25(5)	72(7)	21(5)	9(5)	14(4)	14(5)
H(8a)	4 506(10)	425(8)	−1 291(7)	47(6)	11(5)	45(6)	−3(4)	3(5)	−13(4)
H(8b)	3 785(9)	1 558(10)	−1 781(7)	24(5)	63(7)	23(5)	−7(5)	−10(4)	6(5)
H(8c)	3 828(10)	1 390(9)	−658(7)	35(6)	58(7)	28(5)	−8(5)	12(5)	−7(5)
H(9a)	7 472(9)	3 869(7)	−363(6)	31(5)	22(5)	21(6)	4(4)	−1(4)	5(4)
H(9b)	8 701(9)	4 048(7)	594(6)	22(5)	13(4)	32(5)	0(4)	3(4)	2(4)
H(10a)	7 072(11)	3 920(8)	1 564(7)	63(7)	31(5)	28(6)	8(5)	24(5)	1(4)
H(10b)	5 834(11)	3 702(8)	648(8)	35(7)	25(5)	66(7)	1(5)	28(5)	−10(5)
H(11a)	6 316(12)	5 758(9)	1 276(8)	61(7)	27(5)	54(7)	6(5)	30(6)	−11(5)
H(11b)	6 548(12)	5 609(9)	181(9)	58(7)	38(6)	38(7)	8(5)	3(6)	−1(5)
H(11c)	7 859(11)	5 792(9)	1 065(8)	30(6)	30(6)	63(7)	−12(5)	8(5)	−1(5)
H(12a)	8 485(8)	1 155(7)	−443(6)	25(5)	10(5)	29(5)	−5(3)	6(4)	−2(3)
H(12b)	8 177(8)	2 380(8)	−1 009(6)	23(5)	43(5)	11(4)	4(4)	2(4)	10(4)
H(13a)	10 403(8)	2 272(8)	564(6)	21(5)	48(6)	17(5)	2(4)	0(4)	10(4)
H(13b)	10 140(8)	3 478(8)	−26(6)	23(5)	10(5)	41(5)	−10(3)	4(4)	−8(4)
H(14a)	11 768(9)	2 363(9)	−596(6)	16(6)	54(6)	35(5)	7(4)	5(4)	−1(4)
H(14b)	10 391(9)	2 423(9)	−1 426(6)	30(5)	63(7)	17(5)	17(5)	5(4)	10(5)
H(14c)	10 548(10)	1 182(8)	−874(6)	51(6)	18(6)	36(5)	6(4)	19(5)	−5(4)
(*iii*) Disordered NPr$^n_4$ cation **IIa**[c]									
N(4)[d]	2 199(3)	7 405(2)	4 506(2)	10(1)	9(1)	9(1)	0(1)	3(1)	0(1)

Table 2 (*continued*)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	U_{130}	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	U_{130}
C(151)	1 043(7)	7 245(7)	3 726(5)	12(12)	C(211)	3 385(8)	7 735(7)	4 145(5)	12(2)^e
H(15a)	1 139(16)	8 018(14)	3 386(11)	26(4)^e	H(21a)	3 297(15)	8 573(14)	3 862(11)	26(4)^e
H(15b)	1 157(16)	6 536(14)	3 280(11)	26(4)^e	H(21b)	4 197(17)	7 916(14)	4 756(11)	22(3)^e
C(161)	−272(8)	7 033(7)	3 990(5)	15(2)^e	C(221)	3 701(7)	6 910(6)	3 452(5)	8(2)^e
H(16a)	−384(16)	7 705(14)	4 459(11)	26(4)	H(22a)	2 983(18)	6 866(15)	2 818(12)	33(4)^e
H(16b)	−382(16)	6 226(14)	4 318(11)	28(4)	H(22b)	3 686(17)	6 061(15)	3 637(12)	33(4)^e
C(17)^d	−1 283(4)	6 931(3)	3 143(3)	15(1)^e	C(23)^d	5 060(4)	7 447(4)	3 268(3)	16(1)^e
H(17a)	−1 203	7 713	2 819	27^f	H(23a)	5 796	7 445	3 863	27^f
H(17b)	−2 233	6 772	3 308	27^f	H(23b)	5 003	8 317	3 103	27^f
H(17c)	−1 139	6 227	2 695	27^f	H(23c)	5 305	6 951	2 717	27^f
C(181)	2 264(8)	6 275(7)	4 915(5)	12(2)^e	C(241)	2 069(7)	8 300(6)	5 210(5)	11(2)^e
H(18a)	2 003(15)	5 605(13)	4 396(11)	24(4)^e	H(24a)	1 271(16)	7 971(14)	5 528(11)	24(3)^e
H(18b)	1 462(17)	6 199(15)	5 293(11)	31(4)^e	H(24b)	2 954(15)	8 367(13)	5 731(10)	24(4)^e
C(191)	3 510(8)	6 164(7)	5 536(5)	15(2)^e	C(251)	1 912(8)	9 453(7)	4 902(5)	15(2)^e
H(19a)	4 272(16)	6 068(14)	5 122(11)	26(4)^e	H(25a)	1 068(15)	9 434(13)	4 344(10)	22(3)^e
H(19b)	3 837(18)	6 940(16)	5 982(15)	23(4)^e	H(25b)	2 741(17)	9 799(15)	4 627(12)	30(4)^e
C(20)^d	3 442(5)	5 162(4)	6 017(3)	28(1)^e	C(26)^d	1 825(4)	10 316(4)	5 645(3)	20(1)^e
H(20b)	2 807	5 258	6 495	27^f	H(26a)	1 002	10 037	5 941	27^f
H(20b)	4 392	5 059	6 365	27^f	H(26b)	1 690	11 127	5 370	27^f
H(20c)	3 048	4 442	5 549	27^f	H(26c)	2 698	10 416	6 145	27^f
(*iv*) Disordered NPr^n_4 cation **IIb**^{g}									
C(152)	841(8)	6 928(7)	4 173(6)	10(2)^e	C(212)	2 969(8)	7 243(7)	3 765(6)	8(2)^e
H(15d)	348(19)	6 967(17)	4 752(13)	30(4)^e	H(21d)	2 718(19)	7 876(17)	3 276(13)	29(4)^e
H(15e)	793(18)	6 006(16)	3 946(12)	25(4)^e	H(21e)	2 648(18)	6 396(16)	3 426(12)	25(4)^e
C(162)	83(8)	7 494(7)	3 405(6)	12(2)^e	C(222)	4 420(8)	7 426(7)	4 079(6)	12(2)^e
H(16d)	108(17)	8 389(15)	3 618(12)	22(4)^e	H(22d)	4 727(20)	8 172(16)	4 531(13)	25(4)^e
H(16e)	545(17)	7 455(15)	2 824(12)	23(4)^e	H(22e)	4 709(19)	6 723(17)	4 444(13)	30(4)^e
H(17d)	−1 290	6 044	2 910	27^f	H(23d)	4 837	8 184	2 915	27^f
H(17e)	−1 791	7 363	2 611	27^f	H(23e)	4 707	6 677	2 828	27^f
H(17f)	−1 755	6 975	3 714	27^f	H(23f)	6 097	7 499	3 488	27^f
C(182)	2 763(8)	6 849(7)	5 315(6)	11(2)^e	C(242)	2 343(8)	8 697(7)	4 744(6)	9(2)^e
H(18d)	3 685(16)	7 298(16)	5 598(13)	18(4)^e	H(24d)	2 024(19)	9 073(17)	4 152(13)	28(4)^e
H(18e)	2 187(17)	7 041(15)	5 844(12)	22(4)^e	H(24e)	3 342(18)	8 985(16)	4 967(13)	27(4)^e
C(192)	2 756(8)	5 581(7)	5 164(6)	10(2)^e	C(252)	1 646(9)	9 055(7)	5 484(6)	14(2)^e
H(19d)	3 117(20)	5 336(17)	4 564(14)	32(5)^e	H(25d)	648(20)	8 718(17)	5 320(14)	33(5)^e
H(19e)	1 763(18)	5 128(15)	5 074(12)	25(4)^e	H(25e)	2 086(19)	8 728(17)	6 111(13)	30(4)^e
H(20d)	4 458	5 461	6 121	27^f	H(26d)	1 448	10 681	5 028	27^f
H(20e)	3 287	4 240	5 961	27^f	H(26e)	2 839	10 626	5 856	27^f
H(20f)	3 043	5 490	6 576	27^f	H(26f)	1 301	10 566	6 156	27^f

[a] Estimated standard deviations in the last significant digit are given in parentheses, unless the parameter was not refined in final cycles. [b] The anisotropic temperature factor exponent has the form: $-2\pi^2(h^2a^{*2}U_{11} + \cdots + 2klb^*c^*U_{23})$. [c] Orientation **a** of the disordered cation **II**; occupancy of these sites is 0.533 unless otherwise stated. [d] Occupancy of this site is 1.0, *i.e.* this site is common to both orientations of the disordered cation. [e] Isotropic displacement parameter, U_{iso}. [f] Fixed isotropic displacement parameter. [g] Orientation **b** of the disordered cation **II**; occupancy of these sites is 0.467.

depicted in Fig. 1; atomic positional and displacement parameters are listed in Table 2 and selected interatomic distances and angles in Table 3.

The compound $[NPr^n_4]_2[PtCl_4]$·*cis*-$[PtCl_2(NH_2Me)_2]$ consists of four molecular units, two of which, $[PtCl_4]^{2-}$ and *cis*-$[PtCl_2(NH_2Me)_2]$, form a dianionic species held together by short intermolecular N–H ··· Pt and N–H ··· Cl interactions. The two NPr^n_4 cations, one of which is subject to two-fold disorder as previously indicated, exhibit no unusual intramolecular features. However, their orientation results in a network of intermolecular cation–anion contacts indicative primarily of C–H ··· Cl hydrogen bonding. Hereafter, the two NPr^n_4 ions will be referred to as cation **I** (which is ordered) and cation **II** (which is disordered), the latter having two orientations, **a** (53.3% occupancy) and **b** (46.7% occupancy).

Primary co-ordination at each platinum centre is square-planar, as anticipated, with in-plane angles close to 90°. The most interesting, and indeed remarkable, features of this structure are the short hydrogen contacts, H(11) ··· Pt(1) 2.262(11) and H(22) ··· Cl(13) 2.318(12) Å, which connect the two platinum species. The N(2)–H(22) ··· Cl(13) linkage is readily identified as a hydrogen bond interaction, having dimensions comparable with other Pt–N–H ··· Cl–Pt hydrogen bonds inferred from X-ray diffraction [N ··· Cl 3.270(5) Å in **1**, 3.30 Å in 'cisplatin' *cis*-$[PtCl_2(NH_3)_2]$,[21] 3.31 Å in the 2:1 cisplatin·18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) adduct[22]]. However, it is not as straightforward to define the nature of the N(1)–H(11) ··· Pt(1) linkage. The N(1)–H(11) vector lies above the central Pt atom of the $PtCl_4$ plane, inclined at 79.5° to that plane. With an N(1)–H(11) ··· Pt(1) angle of 167.1(9)°, the geometry of this linkage resembles that of typical three-centre four-electron (3c–4e) hydrogen bonds, which tend towards linearity.* Indeed it lies closer to linearity than the conventional N(2)–H(22) ··· Cl(13) hydrogen bond [151.0(12)°]. On initial inspection one might have assumed the N–H ··· Pt bond to be analogous to agostic C–H ⇀ M bridges, or other 3c–2e bonds such as B–H ⇀ M and M–H ⇀ M. However, in contrast to the situation observed here, 3c-2e interactions exhibit a markedly bent geometry[5] (as anticipated on energetic grounds for such bonds), typically having angles of 90–130°. To our knowledge there has been no discussion in the literature of the possibility that transition-

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* Whilst linearity of 3c–4e interactions is favoured on enthalpic grounds, entropic considerations lead to an overall energetic preference for a configuration which is slightly bent (*e.g.* 160–170° is typical of intermolecular N–H ··· O[23] and O–H ··· O[24] hydrogen bonds).

Table 3 Selected interatomic distances (Å) and angles (°) for compound **1** *

(*i*) $[PtCl_4]\cdot cis\text{-}[PtCl_2(NH_2Me)_2]$ Dianion

Pt(1)–Cl(11)	2.291(5)	Pt(1)–Cl(12)	2.303(4)	N(1)–C(1)	1.484(6)	N(1)–H(11)	1.032(11)
Pt(1)–Cl(13)	2.314(4)	Pt(1)–Cl(4)	2.294(5)	N(1)–H(12)	1.005(11)	N(2)–C(2)	1.456(7)
Pt(1) ••• H(11)	2.262(11)	Pt(1) ••• N(1)	3.276(5)	N(2)–H(21)	1.025(13)	N(2)–H(22)	1.043(12)
Pt(2)–Cl(21)	2.315(4)	Pt(2)–Cl(22)	2.305(4)	C(1)–H(1a)	1.055(14)	C(1)–H(1b)	1.070(14)
Pt(2)–N(1)	2.037(5)	Pt(2)–N(2)	2.050(5)	C(1)–H(1c)	1.086(14)	C(2)–H(2a)	1.105(14)
Pt(2) ••• H(3b)	2.768(9)	Pt(2) ••• C(3)	3.850(6)	C(2)–H(2b)	1.058(15)	C(2)–H(2c)	1.112(14)
Cl(13) ••• H(22)	2.318(12)	Cl(13) ••• N(2)	3.270(5)				
Cl(11)–Pt(1)–Cl(12)	90.4(2)	Cl(11)–Pt(1)–Cl(13)	179.7(2)	H(11)–N(1)–H(12)	103.4(9)	Pt(2)–N(2)–C(2)	115.3(3)
Cl(11)–Pt(1)–Cl(14)	89.9(2)	Cl(11)–Pt(1)–H(11)	92.4(3)	Pt(2)–N(2)–H(21)	106.3(7)	Pt(2)–N(2)–H(22)	112.9(8)
Cl(12)–Pt(1)–Cl(13)	89.4(2)	Cl(12)–Pt(1)–Cl(14)	176.5(2)	C(2)–N(2)–H(21)	108.3(8)	C(2)–N(2)–H(22)	108.9(8)
Cl(12)–Pt(1)–H(11)	78.7(3)	Cl(13)–Pt(1)–Cl(14)	90.2(2)	H(21)–N(2)–H(22)	104.4(11)	N(1)–C(1)–H(1a)	111.4(8)
Cl(13)–Pt(1)–H(11)	87.4(3)	Cl(14)–Pt(1)–H(11)	97.9(3)	N(1)–C(1)–H(1b)	108.0(8)	N(1)–C(1)–H(1c)	110.6(8)
Cl(21)–Pt(2)–Cl(22)	93.9(2)	Cl(21)–Pt(2)–N(1)	178.7(2)	H(1a)–C(1)–H(1b)	110.7(10)	H(1a)–C(1)–H(1c)	108.8(11)
Cl(21)–Pt(2)–N(2)	86.2(2)	Cl(22)–Pt(2)–N(1)	87.4(2)	H(1b)–C(1)–H(1c)	107.3(11)	N(2)–C(2)–H(2a)	111.7(8)
Cl(22)–Pt(2)–N(2)	178.9(2)	N(1)–Pt(2)–N(2)	92.6(2)	N(2)–C(2)–H(2b)	112.5(10)	N(2)–C(2)–H(2c)	109.2(8)
Pt(1)–Cl(13)–H(22)	78.4(4)	Pt(2)–N(1)–C(1)	116.1(3)	H(2a)–C(2)–H(2b)	106.8(11)	H(2a)–C(2)–H(2c)	108.6(11)
Pt(2)–N(1)–H(11)	112.3(6)	Pt(2)–N(1)–H(12)	108.1(7)	H(2b)–C(2)–H(2c)	107.9(13)	Pt(1) ••• H(11)–N(1)	167.1(9)
C(1)–N(1)–H(11)	108.2(7)	C(1)–N(1)–H(12)	107.9(7)	Cl(13) ••• H(22)–N(2)	151.0(12)	Pt(2) ••• H(3b)–C(3)	164.4(7)

(*ii*) Ordered $NPr^n{}_4$ cation **I**; range in square brackets

N–C(av.)	1.519(8) [1.508(5)–1.525(5)]	C–N–C(av.)	109.5(16) [108.0(3)–112.0(3)]
C–C(av.)	1.523(9) [1.506(6)–1.534(6)]	N–C–C(av.)	116.0(6) [115.3(4)–116.5(3)]
C–H(av.), methylene	1.099(12) [1.081(11)–1.117(11)]	C–C–C(av.)	108.7(5) [108.3(4)–109.4(4)]
C–H(av.), methyl	1.086(15) [1.055(14)–1.108(11)]	H–C–H(av.), methylene	107.2(8) [105.8(10)–108.1(7)]
		H–C–H(av.), methyl	107.9(10) [106.0(10)–109.4(10)]

(*iii*) Disordered $NPr^n{}_4$ cation **IIa** and **IIb**; range in square brackets

N–C(av.)	1.516(23) [1.496(9)–1.538(8)]	C–N–C(av.)	109.5(18) [105.4(5)–111.9(4)]
C–C(av.)	1.515(25) [1.448(9)–1.560(9)]	N–C–C(av.)	115.6(10) [114.4(6)–117.1(6)]
C–H(av.), methylene	1.099(23) [1.059(22)–1.144(19)]	C–C–C(av.)	109.7(28) [105.0(5)–113.2(6)]
C–H(av.), methyl	1.089(4) [1.083–1.094]	H–C–H(av.), methylene	106.3(17) [102.0(15)–108.8(17)]
		H–C–H(av.), methyl	109.6(3) [109.0–110.1]

* Estimated standard deviations (e.s.d.s) in the least significant digit are given in parentheses, with the exception of distances involving the disordered methyl hydrogen atoms of cation **II** whose positions were not refined in the final cycles. They are derived directly from the variances of refined parameters, except for averaged dimensions which are derived from the distribution of observed values, using the formula $\Sigma_{i=1}^{n}(d_i - \bar{d})^2/n(n-1)$.

metal atoms can act as hydrogen bond acceptors,* as is suggested by the N–H ••• Pt interaction in compound **1**. The following discussion raises the question of hydrogen bonding, in the context of the N(1)–H(11) ••• Pt(1) interaction, as well as the apparently analogous, but weaker, C–H ••• Pt interaction between cation **I** and the other platinum centre [H(3b) ••• Pt(2) 2.768(9) Å; C(3)–H(3b) ••• Pt(2) 164.4(7)°], and a number of other N–H ••• M and C–H ••• M interactions previously reported in the literature.

Z–H ••• M *Interactions* (Z = N or C, M = d^8 *transition metal centre*).—The description of the N(1)–H(11) ••• Pt(1) linkage as a two- or four-electron interaction invokes, in the four-electron description, the involvement of the filled Pt $5d_{z^2}$ orbital and, in the two-electron description, participation of the empty Pt $6p_z$ orbital. As we have previously noted,[7] both orbitals are of appropriate symmetry to interact with the N–H group (in a σ manner), and hence both may participate in a composite interaction. However, available experimental evidence suggests that a three-centre four-electron description is most appropriate, or at least that the major component of the interaction is of this nature.

Crystallographic evidence comes from the near linearity of the N–H ••• Pt linkage, while the likelihood of an electrostatic component to the interaction is evident from the acidic nature of H(11), being bonded to nitrogen. Such an argument also follows for the much weaker C(3)–H(3b) ••• Pt(2) interaction. In that case, as the donor is a less polar C–H group, one would anticipate a weaker interaction, though it has been shown[26] that the electron-withdrawing inductive effect of an adjacent nitrogen atom enhances the ability of C_α–H groups to participate in hydrogen bonding. The adjacent N(3) atom, particularly in view of its formal positive charge, should have such an effect on the C(3)–H(3b) group. As noted above, ^1H NMR data for the amine protons in compound **1** could not be obtained. Signals for these protons are not observed due to broadening by unresolved coupling to nitrogen. From spectra run in CH_2Cl_2 solvent, a resonance corresponding to the methyl protons of the amine was observed at δ 2.64. Coupling of these protons to the amine hydrogens [^3J(H–H) 6.3 Hz] and to platinum [^3J(Pt–H) 48.8 Hz] were also resolved. No coupling between the platinum atom of the $[PtCl_4]^{2-}$ unit and the amine hydrogens is observed. However, spectroscopic evidence available from a number of compounds with similar C–H ••• M and N–H ••• M interactions (see below) is consistent with the crystallographic evidence and qualitative electronic arguments suggesting that the interactions described here are 3c–4e in nature.

In the light of this discussion the nature of a number of transition metal–hydrogen contacts already noted in the literature warrants reconsideration. In particular, Roundhill and co-workers[27] have reported the complex $cis\text{-}[Pt\{o\text{-}Ph_2PC_6H_4NC(O)C_6H_4\}\{o\text{-}Ph_2PC_6H_4NHC(O)Ph\}]$ **2** in which an intramolecular N–H ••• Pt interaction is indicated

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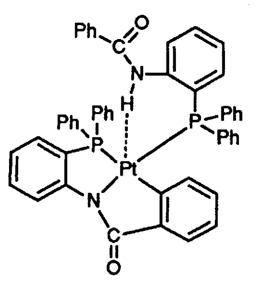
* With the exception of our previous communication[7] and the suggestion by Cecconi *et al.*[25] that electrostatic forces are probably important in the approximately linear N–H ••• Ni interaction observed in $[Ni(CO)\{NH(CH_2CH_2PPh_2)_3\}]BPh_4$. Such interactions are also implicit in the discussion by Creutz and Sutin[9a] of proton exchange between transition metal centres.



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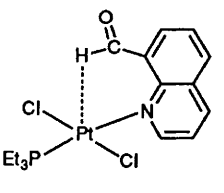

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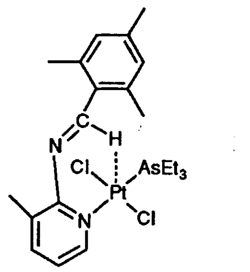

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from the X-ray diffraction study [Pt···H 2.318(22),* Pt···N 3.24 Å, *cf.* Pt···N 3.276(5) Å in **1**]. They term the interaction 'agostic,' which implies 3c–2e bonding, though as in compound **1** the N–H group lies above the square plane of the platinum(II) complex facilitating the involvement of the filled Pt $5d_{z^2}$ orbital. In addition, ^1H NMR studies in $CDCl_3$ indicate a *downfield* shift of the resonance assigned to the interacting hydrogen (δ 11.0), with respect to both the free ligand (δ 8.7) and the monodentate ligand (δ 9.0). This contrasts[5] with ^1H NMR data for agostic (3c–2e) C–H⇀M interactions, which show the bridging hydrogen atoms to be hydridic in nature, typically resonating *upfield* of $SiMe_4$. The only structurally characterised platinum complex exhibiting a definitively agostic interaction, $[Pt(C_7H_{11})(Bu^t{}_2PCH_2CH_2PBu^t{}_2)]BPh_4$,[28] shows a proton resonance at δ −1.05. On the other hand, a *downfield shift* of the ^1H NMR resonance, as found for **2**, *is* characteristic of participation in hydrogen bonding.[29] The spectroscopic evidence therefore supports assignment of this interaction as 3c–4e in nature.

Albinati, Pregosin and co-workers[30] have reported a number of compounds which exhibit intramolecular C–H···M (M = Pt^{II} or Pd^{II}) interactions. In each case the C–H groups are directed approximately normal to a metal square plane as well as being adjacent to functional groups with an electron-withdrawing inductive effect. Complexes **3**[30a] and **4**[30b] have been structurally characterised by X-ray crystallographic studies. Whilst it is necessary to be cautious in the interpretation of refined hydrogen atom parameters in these structures, it is apparent that a significant Pt···H interaction is present in both cases [Pt···H 2.6(1) Å in **3**, with C–H 0.9(2) Å; Pt···H 2.43(8) Å in **4**,† with C–H 1.02(8) Å]. Again ^1H NMR studies show *downfield* shifts for the resonance of the interacting proton, relative to the free ligand. Magnitudes of these shifts are *ca.* 1.5–2.0 ppm for **3** and related complexes in which the PEt_3 ligand is substituted by other tertiary phosphines or arsines. Smaller shifts, *ca.* 0.25–0.35 ppm are noted for **4** and related complexes in which $AsEt_3$ is substituted by PEt_3 and/or Pt by Pd and/or the mesityl substituent is replaced by other aryl groups. Albinati, Pregosin and co-workers[30] also point out that, in contrast to typical agostic interactions, no reduction in $J(^{13}C-^1H)$ value occurs due to interaction of the C–H group with the transition metal. However, in the IR spectrum there is a small decrease of 134 cm^{-1} in ν(C–H) for **3** relative to the uncomplexed ligand. In the examples described so far [**2**–**4**, and derivatives (measurement not obtained for **1**)], it is also noted that the $^{195}Pt-^1H$ coupling is small, *ca.* 5–20 Hz. The significance of these values will be addressed later in the discussion.

Whilst the evidence presented above supports the existence of hydrogen bond-like 3c–4e interactions with transition metals, some caution should be exercised in interpreting the ^1H NMR results noted here. It has long been known that the paramagnetic anisotropy of the metal ion in square-planar d^8 complexes causes a deshielding effect of nuclei which lie above the square plane.[31] This effect is invoked by Lippard and co-workers,[32] Vrieze and co-workers[33] and Riess and co-workers[34] in accounting for downfield shifts in ^1H NMR signals for hydrogen atoms involved in interactions analogous to those described above for compounds **2**–**4**. In their study of *cis*-$[Pt(NH_3)_2L_2Cl]^+$ and *cis*-$[Pt(NH_3)_2L_2]^{2+}$ (L = 9-aminoacridine) Lippard and co-workers correctly note[32] that the intramolecular C–H···Pt interactions which they observe are *not* agostic in nature. However, they further propose that the proximity of these hydrogen atoms to the platinum centres is merely a result of steric requirements, and that the Pt···H interaction may be repulsive rather than attractive. However, whilst the paramagnetic anisotropy effect may contribute substantially to the downfield shifts noted for hydrogen atoms involved in Z–H···M interactions (M = Pd or Pt) described above, this does not preclude the 3c–4e description of these interactions proposed here. Most of the downfield shifts observed for the compounds discussed here are quite large (1–3.5 ppm), and we believe are unlikely to be wholly due to the d^8 metal paramagnetic anisotropy effect. Furthermore, our discussion of these interactions as 3c–4e hydrogen bonds is supported by other evidence, most notably the geometric and spectroscopic differences between these and 3c–2e agostic interactions. The assertion of an electrostatic component to the 3c–4e interactions is also supported by the protonic nature of the hydrogen atoms involved. This is reinforced by the tendency for their ^1H NMR shifts to be substantially downfield of $SiMe_4$, both in the presence of the Z–H···M interaction and, where spectra have been recorded, in its absence.

d^8 Square-planar complexes in which a ligand C–H or N–H group is positioned above the plane and directed approximately towards the central metal atom, whilst not being abundant, are not rare in the literature. Examples are known in which the metal is Pt^{II},[7,32,33,35] Pd^{II},[34,36] Ni^{II},[31b,37] and Rh^I.[38,39] In most cases an X-ray diffraction study indicates the presence of the short M···H contact, though this is frequently inferred from a poorly refined or calculated hydrogen position (assuming idealised hybridisation and C–H or N–H distance). Most of the interactions referred to here are intramolecular. Indeed we are aware of only one report of an intermolecular interaction with a d^8-metal centre, other than that for **1**, namely $[NBu^n{}_4]_2[Pd\{C_6H_4C(Me)NNHPh\text{-}C,N\}Br(Cl)]$.[36f] The C–H···Pd interaction in this compound involves the α-C–H group of a tetraalkylammonium cation, as is the case for **1**.

With regards to the importance of 3c–4e hydrogen-bridge interactions in hydrogen-transfer or other reactions, two recent reports[9c,38] deserve particular attention. Tani and co-workers[38] have structurally and spectroscopically characterised a square-planar rhodium(I) complex, $[Rh\{Fe[\eta^5\text{-}C_5H_4(2\text{-}C_5H_4N)](\eta^5\text{-}C_5H_4PPh_2)\}(cod)]PF_6$ (cod = cycloocta-1,5-diene) which has a C–H···Rh interaction typical of the 3c–4e interactions described above. In addition they also report the iridium 'analogue,' which is an octahedral iridium(III) complex, having undergone oxidative addition of C–H with respect to the rhodium complex. This suggests that, like agostic interactions,

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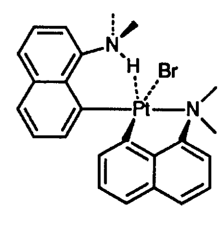
* Using the coordinates given in the paper, the Pt···H separation is calculated at 2.46 Å.

† The *y* coordinate of the hydrogen atom, referred to as H(C6) in the paper,[30b] should be 0.2278 not −0.2278 as given. In addition, this hydrogen atom is referred to as being bound to C(6), whereas it is in fact bound to C(7′).



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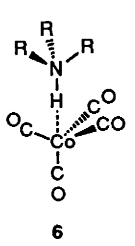
3c–4e C–H···M interactions can also lead to oxidative addition of C–H at a transition metal centre, despite the formal electronic differences between the 3c–2e and 3c–4e cases. More recently van Koten and co-workers[9c] have reported the structure and spectroscopic characterisation of $[Pt\{C_{10}H_6(NMe_2)\text{-}8\text{-}C',N\}\{C_{10}H_6(NHMe_2)\text{-}8\text{-}C'\}Br]$ **5**. This complex contains an intramolecular N–H···Pt interaction similar to that in **2**, and related to the intermolecular interaction in **1**. The ^1H NMR resonance due to the bridging hydrogen atom is shifted further downfield, at δ 16, than any of the species discussed above. In addition, this proton is coupled to the central platinum atom with a coupling constant of 180 Hz, which far exceeds those values observed for **2**–**4** at < 20 Hz, and even exceeds that of 136 Hz for the only reported agostic C–H ⇀ Pt interaction, in $[Pt(C_7H_{11})(Bu^t{}_2PC_2H_4PBu^t{}_2)]^+$.[28] Such results suggest that the ^{195}Pt–^1H coupling constant is sensitive more to the Pt–H separation than the type of interaction (3c–4e *vs.* 3c–2e). Hence, unlike the ^1H NMR chemical shift, this coupling constant is not an observation which can be used to distinguish between 3c–2e and 3c–4e Z–H–Pt interactions. Remarkably, when the preparation of **5** is conducted in aprotic solvents (*e.g.* CH_2Cl_2 or C_6H_6 rather than CH_2Cl_2–MeOH), the product obtained is the platinum(IV) hydride $[Pt\{C_{10}H_6(NMe_2)\text{-}8\text{-}C',N\}_2H(Br)]$, a tautomer of **5**. Like the aforementioned work of Tani and co-workers, the isolation of these products suggests that metal-centred oxidative addition, in this case of an N–H bond, may be attainable *via* a 3c–4e hydrogen-bridge interaction.

Interactions with d^{10} Metal Centres.—From the discussion of 3c–4e interactions involving square-planar d^8 metal centres, it is clear that it would be desirable to find examples of compounds which exhibit this type of interaction without also exhibiting a large paramagnetic anisotropy effect which makes difficult the interpretation of ^1H NMR data for the key hydrogen atoms. More favourable examples in this regard are to be found among complexes involving d^{10} metal centres. Three publications in this area warrant particular attention. Calderazzo *et al.*[40] have shown that addition of trimethylamine or triethylamine to $[CoH(CO)_4]$ yields adducts $R_3NH^+ \cdots [(OC)_3Co(CO)]^-$ **6** in which the trialkylammonium N–H group is oriented approximately toward the Co atom to give a near linear N–H···Co contact, as determined by X-ray crystallographic studies. For the triethylamine adduct, H···Co 2.85(7) Å with a N–H···Co angle of 180° was obtained, though a neutron diffraction study would be required to investigate the possibility of a disordered hydrogen position with concomitant deviation from linearity in the angle subtended at the hydrogen site(s). Creutz and Sutin [9a] suggest that these adduct orientations could be a result of interaction between the ammonium N–H and the carbonyl ligands. However, we believe that the linearity of the N–H···Co contacts is more indicative of 3c–4e interaction involving filled metal orbitals. Spectroscopic evidence is less definitive than in the d^8 examples given above. However, ^1H NMR shifts for the nitrogen-bound atoms are indicative of their being protonic rather than hydridic in nature [δ 9.1 (R = Me) 8.1 (Et)].



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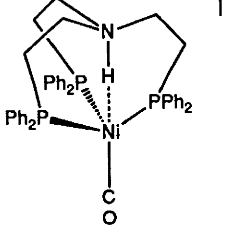
The second notable example is a related nickel(0) complex $[Ni(CO)\{NH(CH_2CH_2PPh_2)_3\}]BPh_4$[25] **7** which has been characterised by an X-ray diffraction study as its tetrahydrofuran solvate. An approximately linear N–H···Ni interaction is present, though imprecisely determined [171(6)°]. In this case, unlike **6**, such a geometry is virtually necessitated by the polydentate phosphine ligand, as is a very short Ni···H contact [1.95(9) Å, *cf.* Co···H 2.85(7) Å in **6** (R = Et)]. A broad singlet (1 H) at δ 14.55 noted in the ^1H NMR spectrum is attributed to the unique nitrogen-bound hydrogen atom; no signal upfield of $SiMe_4$ is observed. This evidence, as for the cobalt adducts described above, is consistent with the formulation of a 3c–4e N–H···M interaction. In addition extended-Hückel molecular orbital (EHMO) calculations on $H_3NH^+ \cdots Ni(PH_3)_3(CO)$, a model complex for **7**, indicate[25] a partial positive charge associated with the hydrogen atom directed towards Ni, and involvement of the filled Ni d_{z^2} orbital in the N–H···Ni interaction. These authors also infer from their calculations that electrostatic forces are important in this interaction.



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A more ambiguous example in which short C–H···M contacts might be described as 3c–4e in nature is the study by Otsuka *et al.* of linear bis(tertiary phosphine)-palladium(0) and -platinum(0) complexes.[41] X-Ray diffraction studies of $[M(PPhBu^t{}_2)_2]$ **8**, in which the ligand hydrogen atom positions were located and refined, show short intramolecular M···H contacts of 2.70(10), 2.83(10) (M = Pd) and 2.77(12), 2.83(11) Å (M = Pt). Corresponding C–H···M angles lie in the range 123–133°. The evidence concerning the nature of the C–H···M interactions in **8** is inconclusive. The fact that the metal d shell is filled supports the invocation of a four-electron interaction. However, it is clear that the hydrogen atoms involved will not be particularly acidic, in contrast to the other examples presented here. The large deviation from linearity of these interactions is more reminiscent of 3c–2e agostic interaction, though *intra*molecular hydrogen bonds frequently also show such large deviations due to steric or conformational requirements.[23] Spectroscopic evidence is also uninformative in this case, perhaps primarily because of the fact that these are clearly very weak interactions, and may even result from packing requirements of the molecules in the crystal lattice.

Intermolecular C–H···Cl *Hydrogen Bonding.*—The potential of a C–H group to act as a proton donor in a hydrogen bond has been assumed in the preceding discussion. Whilst this has been a subject of much debate, there is considerable evidence to support the formulation of C–H···X (X = O, N, Cl or S) hydrogen bonds in many systems. Such evidence arises from spectroscopic studies,[8c,42,43] quantum-mechanical calculations,[44] and from crystallographic studies using

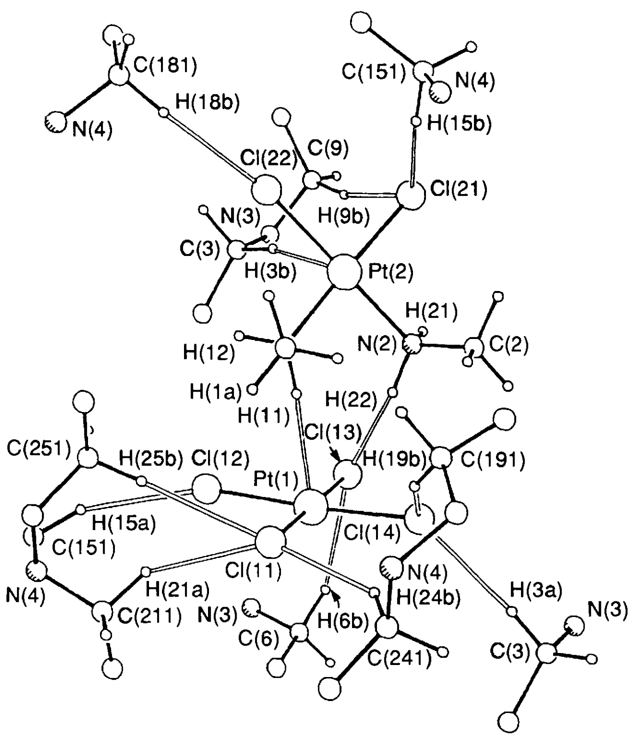

Fig. 2 View showing C–H ··· Cl hydrogen bonds (Cl ··· H < 2.75 Å) between the anion and cations **I** and **IIa** in compound **1**. The N–H ··· Pt, C–H ··· Pt and N–H ··· Cl hydrogen bonds are also indicated for completeness

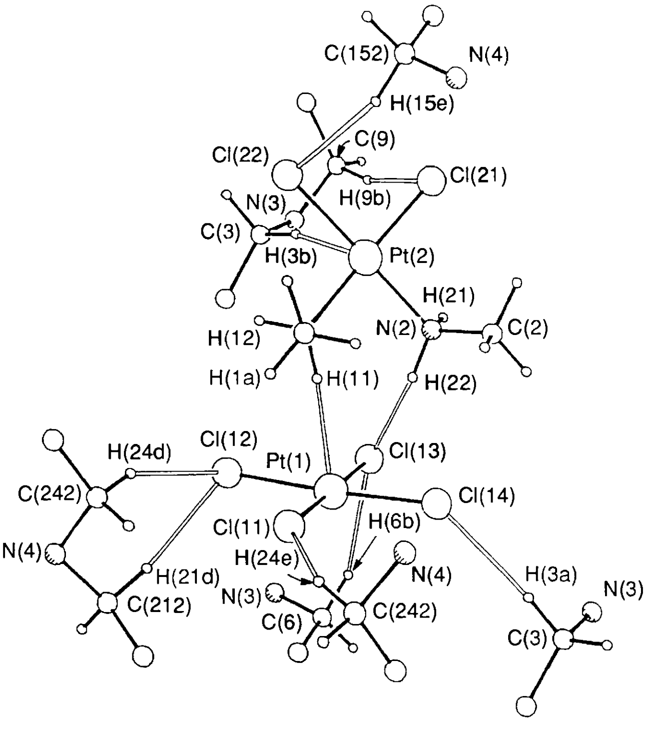

Fig. 3 View analogous to Fig. 2, showing C–H ··· Cl hydrogen bonds (Cl ··· H < 2.75 Å) between the anions and cations **I** and **IIb** in compound **1**

neutron diffraction.[26] In their discussion of C–H ··· X hydrogen bonding. Taylor *et al.*[26] also refer to unpublished potential-energy calculations[45] which support this conclusion.

Calculation of anion–cation short contacts in compound **1** indicates that all six chlorine atoms are involved in C–H ··· Cl hydrogen bonds. As noted earlier, a N–H ··· Cl hydrogen bond also links the two platinum units of the dianion. These interactions presumably promote the previously noted[7] solubility of the complex in CH_2Cl_2.

An indication of the strength of the cation–anion C–H ··· Cl interactions can be derived from the observed Cl ··· H separations. Using the values given by Bondi (1.20 Å for H and 1.75 Å for Cl),[46] the sum of the van der Waals radii for H and Cl is 2.95 Å, hence only contacts shorter than this value will be discussed. Figs. 2 and 3 depict the stronger interactions (Cl ··· H < 2.75 Å), the former with cation **II** in orientation **a**, the latter showing orientation **b**. Table 4 gives details of these and of weaker interactions (2.75 < Cl ··· H < 2.95 Å). Examination of the distribution of the C–H ··· Cl interactions reveals that the four shortest Cl ··· H contacts are associated with the $[PtCl_4]^{2-}$ subunit rather than $[PtCl_2(NH_2Me)_2]$. The $[PtCl_4]^{2-}$ unit participates in an average of 1.75* strong interactions (Cl ··· H < 2.75 Å) per chlorine atom compared with 1.25 per chlorine atom for the $[PtCl_2(NH_2Me)_2]$ unit. In addition all the weaker interactions, with the exception of C(182)–H(18e) ··· Cl(22), involve the $[PtCl_4]^{2-}$ subunit. Assuming a preferential localisation of the anionic charge on the $[PtCl_4]^{2-}$ unit, as formally denoted, these observations are consistent with the observations of Taylor and Kennard,[26] who note a predominance of C–H ··· Cl^- over C–H ··· Cl–R short contacts in their study of structure determinations by neutron diffraction. This suggests that the dominant force in the intermolecular C–H ··· Cl interactions of compound **1** is electrostatic attraction. Further evidence in support of this assertion arises from the predominance among these interactions of α-C–H groups of the cations, particularly among the stronger interactions. These C–H groups necessarily have the most acidic hydrogen atoms due to their proximity to the formally positive charged quaternary nitrogen atoms.

The C–H ··· Cl hydrogen bonds should be regarded as relatively weak interactions, *e.g.* by comparison with O–H ··· O bonds. This arises primarily from the fact that carbon is not very electronegative and partly because the size of the chlorine atom (*cf.* N, O, F) makes its lone-pair orbitals relatively diffuse. A manifestation of the weakness of these interactions is an ease of deformation, resulting in a wide range of C–H ··· Cl geometries. The C–H ··· Cl angles in compound **1** range from 118.1(12)† to 171.2(7)° (*cf.* Taylor and Kennard[26] 119 < C–H ··· Cl < 170°).

In their study of C–H ··· O hydrogen bonds, Taylor and Kennard[26] have observed that for strong interactions the proton generally lies within 30° of the plane of the oxygen lone pairs. In fact this preference is greater still in stronger hydrogen bonds, *e.g.* N–H ··· O=C.[23] Examination of the stronger C–H ··· Cl interactions in compound **1** reveals a large range of Pt–Cl ··· H angles, 86.7(4)–145.5(5)°, and hence little preference of orientation. This indicates less directionality of the (chlorine) lone pairs in metal-bonded chloride than, for example, those of ketonic oxygen.

Conclusion

Accurate characterisation of $[NPr^n_4]_2[PtCl_4]$·*cis*-$[PtCl_2(NH_2Me)_2]$ by low-temperature neutron diffraction has allowed the identification of a new type of transition metal–hydrogen interaction. This interaction, a three-centre four-electron hydrogen bridge, Z–H ··· M (Z = C or N; M = transition metal), is analogous to the conventional hydrogen bond and quite distinct from the well known three-centre two-electron

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* Including in this count the N(2)–H(22) ··· Cl(13) contact, and assigning half weight to interactions with a particular orientation of anion **II**.

† The 118.1° angle corresponds to the very weak C(162)–H(16e) ··· Cl(12) interaction, Cl(12) ··· H(16e) 2.940(18) Å; all other linkages have angles greater than 140°.

Table 4 C–H ··· Cl Hydrogen bond geometries for compound **1**

Interaction	Position[a]	C–H Transformation[b]	Cl ··· C (Å)	Cl ··· H (Å)	C–H (Å)	Cl ··· H–C (°)	Pt–Cl ··· H (°)
Cation **I**							
Pt(1)–Cl(14) ··· H(3a)–C(3)	α	I	3.669(6)	2.571(10)	1.107(10)	171.2(7)	133.8(3)
Pt(2)–Cl(21) ··· H(9b)–C(9)	α	II	3.747(6)	2.695(10)	1.099(10)	160.1(7)	95.9(2)
Pt(1)–Cl(13) ··· H(6b)–C(6)	α	III	3.773(5)	2.749(9)	1.096(10)	155.4(7)	96.2(2)
Pt(1)–Cl(13) ··· H(8c)–C(8)	γ	I	3.876(6)	2.833(11)	1.078(12)	162.8(8)	133.6(3)
Pt(1)–Cl(13) ··· H(12a)–C(12)	α	III	3.883(5)	2.858(9)	1.091(10)	156.5(6)	96.7(2)
Pt(1)–Cl(14) ··· H(6a)–C(6)	α	I	3.961(6)	2.917(9)	1.109(9)	157.1(6)	104.3(2)
Pt(1)–Cl(13) ··· H(4a)–C(4)	β	III	3.896(6)	2.929(9)	1.088(10)	148.3(7)	137.1(2)
Cation **IIa**							
Pt(1)–Cl(12) ··· H(15a)–C(151)	α	IV	3.659(9)	2.608(20)	1.093(18)	161.0(13)	142.5(4)
Pt(1)–Cl(11) ··· H(21a)–C(211)[c]	α	IV	3.578(9)	2.636(20)	1.123(18)	141.0(12)	96.9(4)
Pt(1)–Cl(11) ··· H(24b)–C(241)	α	V	3.615(9)	2.669(20)	1.111(18)	142.6(12)	111.8(4)
Pt(2)–Cl(22) ··· H(18b)–C(181)	α	VI	3.752(10)	2.670(18)	1.118(19)	162.7(13)	166.1(4)
Pt(2)–Cl(21) ··· H(15b)–C(151)	α	I	3.703(10)	2.697(19)	1.084(18)	154.1(13)	86.7(4)
Pt(1)–Cl(14) ··· H(19b)–C(191)	β	V	3.664(10)	2.704(19)	1.096(21)	146.1(15)	103.1(4)
Pt(1)–Cl(11) ··· H(25b)–C(251)	β	IV	3.816(10)	2.720(20)	1.100(19)	174.1(13)	107.8(4)
Pt(1)–Cl(12) ··· H(21a)–C(211)[c]	α	IV	3.729(9)	2.782(20)	1.123(18)	141.7(12)	92.7(4)
Pt(1)–Cl(11) ··· H(21b)–C(211)	α	V	3.791(10)	2.797(19)	1.144(19)	144.9(12)	131.1(4)
Pt(1)–Cl(11) ··· H(23b)–C(23)	γ	IV	3.799(5)	2.862	1.090	144.0	86.7
Cation **IIb**							
Pt(1)–Cl(11) ··· H(24e)–C(242)	α	V	3.698(9)	2.566(20)	1.067(21)	151.1(15)	145.5(5)
Pt(1)–Cl(12) ··· H(21d)–C(212)	α	IV	3.672(9)	2.569(20)	1.120(21)	168.1(15)	109.4(5)
Pt(2)–Cl(22) ··· H(15e)–C(152)	α	I	3.695(9)	2.617(19)	1.123(20)	160.7(14)	90.9(4)
Pt(1)–Cl(12) ··· H(24d)–C(242)	α	IV	3.732(10)	2.743(20)	1.059(22)	155.5(15)	109.8(4)
Pt(2)–Cl(22) ··· H(18e)–C(182)	α	VI	3.781(10)	2.824(18)	1.132(20)	142.1(13)	152.9(4)
Pt(1)–Cl(11) ··· H(22d)–C(222)	β	V	3.849(10)	2.845(20)	1.070(21)	156.3(15)	136.8(4)
Pt(1)–Cl(12) ··· H(16e)–C(162)	β	IV	3.590(9)	2.940(18)	1.097(20)	118.1(12)	157.6(4)
Pt(1)–Cl(11) ··· H(18d)–C(182)	α	V	3.903(10)	2.947(18)	1.066(20)	149.5(14)	102.6(4)

[a] Position of carbon atom relative to the central nitrogen atom of the cation. [b] Transformation applied to the original atomic coordinates to generate those of the interacting C–H group: I, x, y, z; II $-1 + x, y, z$; III $1 - x, -y, -z$; IV $x, -1 + y, z$; V $1 - x, 1 - y, 1 - z$; VI $-x, 1 - y, 1 - z$. [c] H(21a) is involved in a bifurcated hydrogen bond with Cl(11) and Cl(12).

interactions, C–H→M, Si–H→M, B–H→M and M–H→M′. Characteristic features of this type of interaction are: (*i*) the approximate linearity of the Z–H ··· M linkage (only in intermolecular cases), (*ii*) the acidity of the bridging hydrogen atom (typically adjacent to electron-withdrawing groups), indicating an electrostatic component to the interaction, (*iii*) the involvement of an electron-rich transition-metal atom with suitably oriented filled d orbitals capable of facilitating the metal atom's acceptor role, (*iv*) ^{1}H NMR chemical shift of the bridging hydrogen atom which is downfield of $SiMe_4$, *and* shifted *downfield* relative to the signal for the same hydrogen atom in a non-interacting environment (*e.g.* for the free ligand, or complexed ligand with no Z–H ··· M interaction), analogous to the well known effect in conventional hydrogen bonds.

A number of compounds previously reported in the literature have been identified as containing interactions analogous to the N(1)–H(11) ··· Pt(1) and C(3)–H(3b) ··· Pt(2) interactions observed in compound **1**. All examples noted to date involve either a d^{10} or square-planar d^8 metal centre, and in most of these compounds the interactions are *intra-* rather than intermolecular. It is from these literature examples that the spectroscopic evidence for this type of interaction is derived. An important point with regard to the aforementioned downfield shifts observed in the ^{1}H NMR spectrum is that in square-planar d^8 transition-metal complexes downfield shifts are experienced by nuclei located close to the metal centre and above the co-ordination plane, due to a magnetic anisotropy effect. However, we feel that the shifts noted in many cases are too large to be solely due to this effect and hence result in part from the hydrogen bond-like interaction. Furthermore, in the d^{10} systems, which should not show such a strong magnetic anisotropy effect, the hydrogen atoms in question also resonate substantially downfield of $SiMe_4$. Clearly further work is required to design systems for which interpretation of the ^{1}H NMR spectra is more straightforward.* Accurate structural characterisation of such species will also be of great importance, as it continues to be in the fields of conventional hydrogen bond interactions and three-centre two-electron hydrogen-bridged systems.

The implications of the involvement of transition metals in hydrogen bonding are substantial, particularly in the fields of organometallic chemistry and biochemistry. For example, as noted in the Introduction, the $[PtCl_2(NH_2Me)_2]$ component of **1** bears close resemblance to the antitumour agent[47] 'cisplatin,' and related compounds, whose binding with DNA have been the focus of attention for many years. It is conceivable that interactions such as those described here may be involved in proton-transfer reactions in some biochemical systems. The

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* *Note added at proof:* Since submission of this manuscript we have been engaged in trying to resolve further the electronic origins of the downfield shift of the ^{1}H NMR signal for the bridging hydrogens in the Z–H ··· M (Z = C or N) interactions described in this paper. In this regard, we are grateful to Professor Aage E. Hansen of the H. C. Ørsted Institue, Copenhagen, for some informative discussions on NMR shielding tensors. It is our conclusion that the paramagnetic anisotropy effect, discussed especially with regard to d^8 metal complexes, may well be the same effect as that which causes the downfield shift of protons involved in conventional hydrogen bonds. Thus, in the former case, proximity of the proton to the metal d_{z^2} orbital causes the downfield shift, whereas, in the latter case, proximity to the lone pair orbital of the hydrogen bond acceptor is responsible. This differs slightly from our initial suggestion that these were two separate effects combining in the case of the metal complexes to give a resultant downfield shift.

This modified assessment of the origins of the downfield shifts does not alter our conclusions as to the nature of the Z–H ··· M interactions. However, it suggests that observation of such a downfield shift in these types of metal complexes is not sufficient evidence in itself to indicate a 3c–4e Z–H ··· M interaction. Supporting evidence, as we have already indicated, should be examined. A more detailed discussion of these points will be reserved for a subsequent publication.

work of Tani and co-workers,[38] and van Koten and co-workers,[9c] indicates that 3c–4e Z–H $\cdots$ M interactions (Z = C or N) may play a role in some organometallic systems in the oxidative addition of Z–H bonds at metal centres.

Finally, in addition to the Z–H $\cdots$ M bonding already discussed, this structure determination allowed the accurate characterisation of a large number of the uncommon and very weak C–H $\cdots$ Cl bond. Results indicate that the C–H $\cdots$ Cl anion–cation contacts in compound **1** arise primarily due to electrostatic attraction. Additionally, the wide range of C–H $\cdots$ Cl angles observed is indicative of a weak interaction with little orientational preference in comparison to stronger hydrogen-bond acceptors, such as ketonic oxygen.

Acknowledgements

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References

1 J. P. Collman, L. S. Hegedus, J. R. Norton and R. G. Finke, *Principles and Applications of Organotransition Metal Chemistry*, University Science Books, Mill Valley, CA, 1987.
2 R. G. Teller and R. Bau, *Struct. Bonding (Berlin)*, 1981, **44**, 1.
3 B. D. James and M. H. Wallbridge, *Prog. Inorg. Chem.*, 1970, **11**, 99.
4 U. Schubert, G. Scholz, J. Müller, K. Ackermann, B. Wörle and R. F. D. Stansfield, *J. Organomet. Chem.*, 1986, **306**, 303.
5 M. Brookhart and M. L. H. Green, *J. Organomet. Chem.*, 1983, **250**, 395; M. Brookhart, M. L. H. Green and L.-L. Wong, *Prog. Inorg. Chem.*, 1988, **36**, 1.
6 G. J. Kubas, *Acc. Chem. Res.*, 1988, **21**, 120; R. H. Crabtree, *Acc. Chem. Res.*, 1990, **23**, 95.
7 L. Brammer, J. M. Charnock, P. L. Goggin, R. J. Goodfellow, T. F. Koetzle and A. G. Orpen, *J. Chem. Soc., Chem. Commun.*, 1987, 443.
8 (*a*) W. C. Hamilton and J. A. Ibers, *Hydrogen Bonding in Solids*, W. A. Benjamin, New York, 1968; (*b*) *The Hydrogen Bond*, eds. P. Schuster, G. Zundel and C. Sandorfy, North-Holland, Amsterdam, New York, Oxford, 1976; (*c*) G. C. Pimentel and A. L. McClellan, *The Hydrogen Bond*, W. H. Freeman, San Francisco, 1960; (*d*) *Hydrogen Bonding*, ed. D. Hadži, Pergamon, New York, 1959.
9 (*a*) C. Creutz and N. Sutin, *J. Am. Chem. Soc.*, 1988, **110**, 2418; (*b*) R. E. Stevens, R. D. Guettler and W. L. Gladfelter, *Inorg. Chem.*, 1990, **29**, 451; (*c*) I. C. M. Wehman-Ooyevaar, D. M. Grove, P. van der Sluis, A. L. Spek and G. van Koten, *J. Chem. Soc., Chem. Commun.*, 1990, 1367.
10 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1962, vol. 3.
11 T. F. Koetzle and R. K. McMullan, Research Memo, C-4, Brookhaven National Laboratory, New York, 1980.
12 P. J. Becker and P. Coppens, *Acta Crystallogr., Sect. A*, 1974, **30**, 129.
13 D. G. Dimmler, N. Greenlaw, M. A. Kelley, D. W. Potter, S. Rankowitz and F. W. Stubblefield, *IEEE Trans. Nucl. Sci.*, 1976, NS-23, 398.
14 R. K. McMullan, and in part, L. C. Andrews, T. F. Koetzle, F. Reidinger, R. Thomas and G. J. B. Williams, NEXDAS, Neutron and X-ray Data Acquisition System, unpublished work.
15 M. T. Hutchings, M. P. Schulhof and H. J. Guggenheim, *Phys. Rev. B*, 1972, **5**, 154.
16 R. K. McMullan, DIFSYN, A differential Fourier synthesis refinement program, 1979, unpublished work; D. W. J. Cruickshank, *Acta Crystallogr.*, 1950, **3**, 10.
17 G. M. Sheldrick, SHELXTL, An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data, revision no. 4, Nicolet Instruments Ltd., Warwick, January, 1983.
18 J.-O. Lundgren, *Crystallographic Computer Programs*, Report UUIC-B13-4-05, Institute of Chemistry, University of Uppsala, Uppsala, 1982; modified, Brookhaven National Laboratory, New York, 1983.
19 L. Koester and W. B. Yelon, in *Neutron Diffraction Newsletter*, ed. M. S. Lehmann, International Union of Crystallography (Commission for Neutron Diffraction), Chester, 1983.
20 C. K. Johnson, ORTEP II, Report ORNL-5138, Oak Ridge National Laboratory, TN, 1976.
21 G. W. H. Milburn and M. R. Truter, *J. Chem. Soc. A*, 1966, 1609.
22 D. R. Alston, J. F. Stoddart and D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 1985, 532.
23 R. Taylor, O. Kennard and W. Versichel, *Acta Crystallogr., Sect. B*, 1984, **40**, 280.
24 C. Ceccarelli, G. A. Jeffery and R. Taylor, *J. Mol. Struct.*, 1981, **70**, 255.
25 F. Cecconi, C. A. Ghilardi, P. Innocenti, C. Mealli, S. Midollini and A. Orlandini, *Inorg. Chem.*, 1984, **23**, 922.
26 R. Taylor and O. Kennard, *J. Am. Chem. Soc.*, 1982, **104**, 5063.
27 D. Hedden, D. M. Roundhill, W. C. Fultz and A. L. Rheingold, *Organometallics*, 1986, **5**, 336.
28 N. Carr, B. J. Dunne, A. G. Orpen and J. L. Spencer, *J. Chem. Soc., Chem. Commun.*, 1988, 926.
29 D. H. Williams and I. Fleming, *Spectroscopic Methods in Organic Chemistry*, McGraw-Hill, London, 1966, p. 87.
30 (*a*) A. Albinati, C. G. Anklin, F. Ganazzoli, H. Rüegg and P. S. Pregosin, *Inorg. Chem.*, 1987, **26**, 503; (*b*) A. Albinati, C. Arz and P. S. Pregosin, *Inorg. Chem.*, 1987, **26**, 508.
31 (*a*) A. D. Buckingham and J. P. Stephens, *J. Chem. Soc.*, 1964, 4583; (*b*) R. G. Miller, R. D. Stauffer, D. R. Fahey and D. R. Parnell, *J. Am. Chem. Soc.*, 1970, **92**, 1511.
32 W. I. Sundquist, D. P. Bancroft and S. J. Lippard, *J. Am. Chem. Soc.*, 1990, **112**, 1590.
33 J. F. Van Baar, K. Vrieze and D. J. Stufkens, *J. Organomet. Chem.*, 1974, **81**, 247.
34 M. Postel, M. Pfeffer and J. G. Riess, *J. Am. Chem. Soc.*, 1977, **99**, 5623.
35 D. Hottentrot and C. H. Stam, *Cryst. Struct. Commun.*, 1975, **4**, 421.
36 (*a*) D. M. Roe, P. M. Bailey, K. Moseley and P. M. Maitlis, *J. Chem. Soc., Chem. Commun.*, 1972, 1273; (*b*) K. Kan, K. Miki, Y. Kai, N. Yasuoka and N. Kasai, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 733; (*c*) B. E. Mann, P. M. Bailey and P. M. Maitlis, *J. Am. Chem. Soc.*, 1975, **97**, 1275; (*d*) L. G. Kuz'mina and Yu. T. Struchkov, *Cryst. Struct. Commun.*, 1979, **8**, 715; (*e*) G. Minghetti, M. A. Cineddu, A. L. Bandini, G. Banditelli, F. Demartin and M. Manassero, *J. Organomet. Chem.*, 1986, **315**, 387; (*f*) J. Dehand, J. Fischer, M. Pfeffer, A. Mitschler and M. Zinsius, *Inorg. Chem.*, 1976, **15**, 2675.
37 K. Kan, Y. Kai, N. Yasuoka and N. Kasai, *Bull. Chem. Soc. Jpn.*, 1977, **50**, 1051; H. Bandes, R. Goddard, P. W. Jolly, C. Krüger, R. Mynott and G. Wilke, *Z. Naturforsch., Teil B*, 1984, **39**, 1139; B. L. Barnett and C. Krüger, *J. Organomet. Chem.*, 1974, **77**, 407; H. M. Echols and D. Dennis, *Acta Crystallogr., Sect. B*, 1974, **30**, 2173.
38 T. Yoshida, K. Tani, T. Yamagata, Y. Tatsumo and T. Saito, *J. Chem. Soc., Chem. Commun.*, 1990, 292.
39 D. Valentine, jun., J. F. Blount and K. Toth, *J. Org. Chem.*, 1980, **45**, 3691.
40 F. Calderazzo, G. Fachinetti, F. Marchetti and P. F. Zanazzi, *J. Chem. Soc., Chem. Commun.*, 1981, 181.
41 S. Otsuka, T. Yoshida, M. Matsumoto and K. Nakatsu, *J. Am. Chem. Soc.*, 1976, **98**, 5850.
42 R. D. Green, *Hydrogen Bonding by C–H Groups*, Wiley Interscience, New York, 1974.
43 K. M. Harmon, I. Gennick and S. L. Madeira, *J. Chem. Phys.*, 1974, **78**, 2585.
44 P. Kollman, J. McKelvey, A. Johansson and S. Rothenberg, *J. Am. Chem. Soc.*, 1975, **97**, 955; H. Umeyama and K. Morokuma, *J. Am. Chem. Soc.*, 1977, **99**, 1316; S. Vishveshwara, *Chem. Phys. Lett.*, 1978, **59**, 26; R. Gay and G. Vanderkooi, *J. Chem. Phys.*, 1981, **75**, 2281.
45 L. Leiserowitz, personal communication to R. T. and O. K. in ref. 26.
46 A. J. Bondi, *J. Chem. Phys.*, 1964, **68**, 441.
47 *Cisplatin, Current Status and New Developments*, eds. A. W. Prestayko, S. T. Crooke and S. K. Carter, Academic Press, New York, 1980.

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