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SYNTHESES AND STRUCTURAL ASPECTS OF RIGID ARYL-PALLADIUM(II) AND -PLATINUM(II) COMPLEXES. X-RAY CRYSTAL STRUCTURE OF *o,o′*-BIS[(DIMETHYLAMINO)METHYL]PHENYL-PLATINUM(II) BROMIDE

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Summary

The tridentate monoanionic ligand *o,o′*-$(Me_2NCH_2)_2C_6H_3$ (NCN′) has been used to synthesize novel aryl-palladium(II) and -platinum(II) complexes [PtR(NCN′)] and [MX(NCN′)] (M = Pt, Pd). Three synthetic procedures are described, namely: (i) reaction of the cationic complex $[M(NCN')(H_2O)]^+$ with KX or NaX to give [MX(NCN′)] (X = Cl, I, O_2CH, NCS, NO_2, NO_3); (ii) displacement reactions using AgX with [MBr(NCN′)] to give [MX(NCN′)] (X = CN, O_3SCF_3, O_2CMe, O_2CCF_3) and (iii) transmetallation reactions of $[PtBr\{C_6H_3(CH_2NMe_2)_2$-*o,o′*}] with organolithium to give $[PtR\{C_6H_3(CH_2NMe_2)_2$-*o,o′*}] (R = Ph, *o*-, *m*-, *p*-tolyl, C≡CPh, C≡C-*p*-tolyl). All the complexes have been characterized by elemental analysis, and IR, ^1H and ^{13}C NMR spectroscopy.

An X-ray diffraction study has shown that $[PtBr\{C_6H_3(CH_2NMe_2)_2$-*o,o′*}] (**2**) has a square-planar structure, in which the tridentate ligand is bonded via C(*ipso*) (Pt–C 1.90(1) Å), and two mutually *trans*-N donor atoms (Pt–N(1) 2.07(1), Pt–N(2) 2.09(1) Å). The fourth site *trans* to C(*ipso*) is occupied by bromine (Pt–Br 2.526(2) Å). The two chelate rings (N–Pt–C(*ipso*) 82.9(5) and 81.5(5)°) are distinctly puckered, with the two NMe_2 groups on opposite sides of the aryl plane. The Pt–C bond in **2** is shorter than analogous bonds in other arylplatinum(II) complexes, as a result of (i) the rigid structure of the tridentate ligand and (ii) the presence of two hard N donor atoms *trans* to one another across the platinum centre.

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Introduction

There is much interest in the coordination properties of tridentate monoanionic ligands which have substituents containing donor groups such as PR_2, NR_2 or SR in both positions *ortho* to *C*(*ipso*) [1] (see Fig. 1), and in metal complexes derived from such ligands. Since these *ortho*-substituents are bonded to a rigid aryl group the ligand coordinated to the metal has a specific arrangement in which the two donor atoms are located *trans* to one another across the metal, with the aryl ring, the two donor atoms, and the metal centre situated in one plane. In many cases new types of (rigid) organometallic complexes have been generated by regioselective metallation of the free protonated ligands (i.e., the *meta*-disubstituted arenes) at the carbon atom *ortho* to both substituents [1].

However, for the compound m-$(Me_2NCH_2)_2C_6H_4$, which we selected for study, direct metallation is not selective. For example metallation of m-$(Me_2NCH_2)_2C_6H_4$ with n-BuLi gave inseparable mixtures of isomers, viz. $[Li\{C_6H_3(CH_2NMe_2)_2$-$o,o'\}]$ (86%) and $[Li\{C_6H_3(CH_2NMe_2)_2$-$o,p'\}]$ (14%) [2,3]. Similarly, Trofimenko et al. have found that palladation of the closely related ethyl analogue m-$(Et_2NCH_2)_2C_6H_4$ with $PdCl_4^{2-}$ afforded a mixture of palladium compounds [1f].

In order to obtain exclusively o,o'-$(Me_2NCH_2)_2C_6H_3$-metal complexes for our studies we devised a suitable route involving lithiation of the bromo derivative o,o'-$(Me_2NCH_2)_2C_6H_3Br$, followed by a transmetallation reaction with the appropriate metal halide. By this method we have obtained many metal complexes involving Sn [2], Ni [4], Pd, Pt [5], Fe [6], Co, Rh and Ir [7].

The d^8 metal complexes of Ni, Pd and Pt have a square-planar structure in which the o,o'-$(Me_2NCH_2)_2C_6H_3$ monoanion (frequently denoted throughout this paper as NCN′) is bonded as a tridentate ligand. Accordingly the remaining potential coordination sites at the metal are well-defined: i.e. (i) one position *trans* to C(*ipso*) and (ii) two positions *cis* to C(*ipso*) in a plane perpendicular to that of the ligand. During our earlier studies it appeared that the coordination of the *trans* positioned NMe_2 amino ligands enhances the basicity of the d^8 metal centres to such an extent that these complexes show entirely different reactivity from that of the analogous complexes containing PR_2 donor groups. Examples of this special reactivity are (i) the formation of stable hetero-dinuclear complexes [Pt-

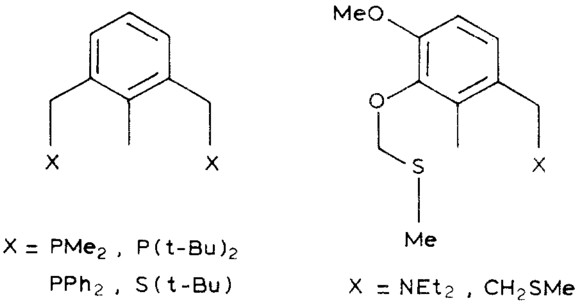

Fig. 1. Representative o,o'-disubstituted monoanionic aryl ligands with various combinations of donor atoms.

$\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}\{\mu\text{-}(p\text{-tol})NYNR\}HgBrCl]$ (Y = CH, N) [8,9], (ii) the oxidative addition leading to the unusual arenoniumplatinum(II) complex $[Pt(o\text{-tolyl})\{MeC_6H_3(CH_2NMe_2)_2\text{-}o,o'\}]I$ [10], (iii) the coordination of SO_2 to Pt^{II} leading to $[PtBr\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}(\eta^1\text{-}SO_2)]$ [11], and (iv) the formation of remarkably stable organonickel(III) compounds, e.g. $[NiX_2\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}]$ (X = halogen, pseudo-halogen) [12], by oxidation of $[NiX\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}]$ with halogens, Cu^{II} salts or by substitution.

In this paper we describe the synthesis and characterization of a new series of complexes obtained by replacement of the ligand X *trans* to C(*ipso*) in palladium and platinum complexes $[MX\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}]$ by various organic one electron ligands. Some of these complexes were, in fact, previously used as starting materials for the preparation of species mentioned above. In order to gain insight into the effects that the special orientation of the aryl ring to the coordination plane may have on the nature of the metal–C(*ipso*) bonding, as well as on the reactivity of the metal centre in these new complexes, the ^{13}C NMR spectra of the (diorgano)platinum(II) compounds $[PtR\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}]$ (with R = aryl and C≡C-aryl) have been studied. The results are discussed in the light of earlier observations on analogous nickel complexes [4] as well as the ultraviolet photo-electron spectra of the series $[MX\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}]$ with M = Ni, Pd, Pt and X = Cl, Br, I [13]. Finally, the complex $[PtBr\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}]$ (which in many respects can be regarded as the parent species for many of the other complexes made) has been the subject of an X-ray structural analysis.

Experimental

Reactions involving lithium reagents were performed under dry nitrogen using Schlenk tube techniques, and freshly-distilled, rigorously dried solvents. ^1H NMR spectra were recorded on Varian T60 and Bruker WM 250 spectrometers. The ^{13}C NMR spectra were recorded on a Bruker WM 250 spectrometer usually with noise modulated proton decoupling. Infrared spectra of samples either as Nujol mulls, KBr pellets or C_6H_6 solutions were measured on Perkin–Elmer 283 and Nicolet 7199B FT IR spectrophotometers. Elemental analyses were carried out at the Institute for Applied Chemistry, TNO, Zeist (The Netherlands). Most reagents were obtained commercially and were used without further purification. *cis*-$PtCl_2(SEt_2)_2$ was prepared as described by Kaufmann et al. [14]. The preparations of $[MX\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}]$ (M = Pt, X = Cl (**1**), Br (**2**), I (**3**), O_2CCH_3 (**4**); M = Pd, X = Cl (**5**), Br (**6**), I (**7**)) and $[M\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}(H_2O)]BF_4$ (M = Pt (**8**), Pd (**9**)) and of $[Pt(C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}]O_3SCF_3$ (**10**) have been described previously [5].

Procedures

The following routes (**A**–**C**; see Scheme 1) are representative of the method used for the preparation of the various organoplatinum(II) complexes. The analytical data, synthetic method, and yield are given in each case in Table 1.

Route A. Synthesis of $[Pt(NO_3)\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}]$. To a stirred solution of the cationic aquo complex $[Pt(C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}(H_2O)]BF_4$ (123 mg, 0.25

TABLE 1

PROCEDURES, YIELD, AND ANALYTICAL DATA FOR THE VARIOUS ORGANOPLATINUM(II) AND ORGANOPALLADIUM(II) COMPLEXES [a]

Compound	Method	Yield (%)	Analyses (Found (calcd.) (%))				
			C	H	N	X	
$[Pd\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}O_3SCF_3]\cdot H_2O$ (**11**)	A	60	34.05 (34.95)	4.29 (4.29)	6.13 (6.27)		
$[Pt(NO_2)\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}]$ (**12**)	A	32	32.56 (33.33)	4.35 (4.43)	9.28 (9.71)		
$[Pt(NO_3)\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}]$ (**13**)	A	68	31.90 (32.14)	4.34 (4.27)	9.09 (9.37)		
$[Pt(N_3)\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}]$ (**14**)	A	63	33.18 (33.62)	4.42 (4.47)	15.93 (16.33)		
$[Pt(NCS)\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}]$ (**15**)	A	98	34.68 (35.13)	4.30 (4.31)	9.35 (9.46)	6.97 (7.20)	(X = S)
$[Pt(CN)\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}]$ (**16**)	B	15	36.49 (37.86)	4.60 (4.64)	9.76 (10.18)		
$[Pt(O_2CCF_3)\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}]$ (**17**)	B	70	33.33 (33.67)	3.76 (3.83)	5.14 (5.61)	10.87 (11.41)	(X = F)
$[Pt(O_2CH)\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}]$ (**18**)	A	82	36.30 (36.19)	4.70 (4.67)	6.44 (6.50)	7.67 (7.42)	(X = O)
$[Pt(C_6H_5)\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}]$ (**19**)	C	50	46.61 (46.65)	5.22 (5.22)	5.85 (6.04)		
$[Pt(o\text{-tolyl})\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}]$ (**20**)	C	70	47.39 (47.49)	5.55 (5.49)	5.76 (5.87)		
$[Pt(m\text{-tolyl})\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}]$ (**21**)	C	31	48.89 (47.79)	5.69 (5.49)	5.61 (5.87)		
$[Pt(p\text{-tolyl})\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}]$ (**22**)	C	77	48.60 (47.79)	5.53 (5.49)	5.78 (5.87)		
$[Pt(C{\equiv}CC_6H_5)\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}]$ (**23**)	C	58	49.08 (49.27)	5.03 (4.96)	5.60 (5.75)		
$[Pt(C{\equiv}C\text{-}p\text{-tolyl})\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}]$ (**24**)	C	43	49.03 (50.29)	5.22 (5.23)	5.24 (5.59)		
$[Pd(N_3)\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}]$ (**25**)	A	98	42.26 (42.42)	5.64 (5.64)	20.09 (20.62)		
$[Pd(O_2CMe)\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}]\cdot 0.75H_2O$ (**26**)	B	85	45.44 (45.46)	6.35 (6.41)	7.53 (7.57)	11.54 (11.90)	(X = O)
$[Pd(O_2CFF_3)\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}]$ (**27**)	B	78	40.73 (40.94)	4.60 (4.66)		13.67 (13.88)	(X = F)

[a] Analytical data for **1–10** have appeared previously.

mmol) in H_2O (10 ml) was added a tenfold excess of KNO_3 (252 mg). This resulted in the separation of a white solid. After 20 min stirring the solid was filtered off and dissolved in CH_2Cl_2, and the solution was dried over $MgSO_4$ then filtered. The filtrate was concentrated to 2 ml, and pentane (10 ml) was then added to give white crystals of $[Pt(NO_3)\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}]$ (**13**). Yield 68%.

*Route **B**. Synthesis of* $[Pt(O_2CCF_3)\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}]$. One equivalent of AgO_2CCF_3 (55 mg) was added to a solution of $[PtBr\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}]$ (116 mg, 0.25 mmol) in acetone (5 ml) and the mixture was stirred overnight. The precipitate of AgBr was then filtered off and the filtrate was evaporated in vacuo. The residue was dissolved in CH_2Cl_2 (5 ml) and the solution filtered through Celite. Addition of pentane to the filtrate produced a white precipitate, which was filtered off, dried in vacuo, and identified as [Pt(O_2CCF_3){$C_6H_3(CH_2NMe_2)_2$-*o,o'*}] (**17**). Yield 70%.

Route C. Synthesis of [Pt($C{\equiv}CC_6H_5$){$C_6H_3(CH_2NMe_2)_2$-o,o'}]. A solution of lithium phenylacetylide (3.8 mmol in 2.5 ml of diethyl ether) was added to a suspension of [PtBr{$C_6H_3(CH_2NMe_2)_2$-*o,o'*}] (932 mg, 2 mmol) in dry diethyl ether (5 ml) at 223 K. The mixture was stirred at room temperature for 20 min; the white precipitate was filtered off, washed with cold pentane (5 ml), and extracted with benzene (10 ml). Concentration of the extract to 2 ml followed by addition of pentane gave a white solid, which was recrystallized from CH_2Cl_2/pentane to give white, crystalline [Pt($C{\equiv}CC_6H_5$){$C_6H_3(CH_2NMe_2)_2$-*o,o'*}] (**23**). Yield 58%.

Reaction of [PdBr{$C_6H_3(CH_2NMe_2)_2$-o,o'}] with LiC≡C-p-tolyl

A solution of lithium *p*-tolylacetylide (0.3 mmol in 2 ml of diethyl ether) was added to a suspension of [PdBr{$C_6H_3(CH_2NMe_2)_2$-*o,o'*}] (0.3 mmol) in dry diethyl ether (5 ml) at 223 K. The mixture was stirred for 20 min then warmed to room temperature, when the colour of the solution darkened. The precipitated palladium metal was filtered off, and the organic products isolated by evaporation of the filtrate in vacuo. One of the organic products was identified by ^1H NMR spectroscopy as the coupling product *o,o'*-$(Me_2NCH_2)_2C_6H_3C{\equiv}C$-*p*-tolyl; ^1H NMR ($CDCl_3$: δ (ppm)), 7.30 (m, aryl, 7H); 3.67 (s, CH_2, 4H); 2.30 (s, NMe_2, 12H); 2.35 (s, CH_3, 3H).

Synthesis of [Pd(o-tolyl){$C_6H_3(CH_2NMe_2)_2$-o,o'}]

A solution of *o*-tolyllithium (0.29 mmol in 2 ml of diethyl ether) was added to a suspension of [PdBr{$C_6H_3(CH_2NMe_2)_2$-*o,o'*}] (0.4 mmol) in dry diethyl ether at 188 K. The mixture was stirred for 20 min then warmed to room temperature. The grey precipitate was filtered off, washed with cold pentane (5 ml), and extracted with benzene (10 ml). Concentration of the extract followed by addition of pentane gave a grey precipitate. Recrystallization from CH_2Cl_2/pentane gave a grey product, which was identified by ^1H NMR spectroscopy as [Pd(*o*-tolyl){$C_6H_3(CH_2NMe_2)_2$-*o,o'*}]; ^1H NMR (C_6D_6; δ (ppm)), 7.32 (m, aryl, 7H); 3.52 (s, CH_2, 4H); 2.32 (s, NMe_2, 12H); 2.17 (CH_3, 3H). Attempts to purify the product further were unsuccessful.

Determination of the crystal structure of [PtBr{$C_6H_3(CH_2NMe_2)_2$-o,o'}]

Crystals of the title compound ($C_{12}H_{19}BrN_2Pt$) are monoclinic, space group $P2_1/c$, $Z = 4$, a 12.630(7), b 9.846(4), c 11.742(3) Å, β 110.61(2)°, V 1366.7(9) Å, D(calcd) 2.27 g cm^{-3} and $F(000) = 872$ electrons. A total of 1314 reflections with intensities above the $2.5\sigma(I)$ limit were measured on a Nonius CAD 4 diffractometer using graphite-monochromated Mo-K_α radiation *.

The positions of Pt and Br were derived from an E^2-Patterson synthesis and the remaining non-hydrogen atoms were found from subsequent ΔF-syntheses. After isotropic block-diagonal least-squares refinement an empirical absorption correction was applied [15]. Subsequent anisotropic refinement converged to $R = 0.028$ ($R_w = 0.044$). A weighting scheme $w = (5.18 + F_0 + 0.055F_0^2)^{-1}$ was applied. The anoma-

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* Lists of thermal parameters and structural factors are available from the authors.

TABLE 2

ATOMIC COORDINATES FOR $[PtBr\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}]$

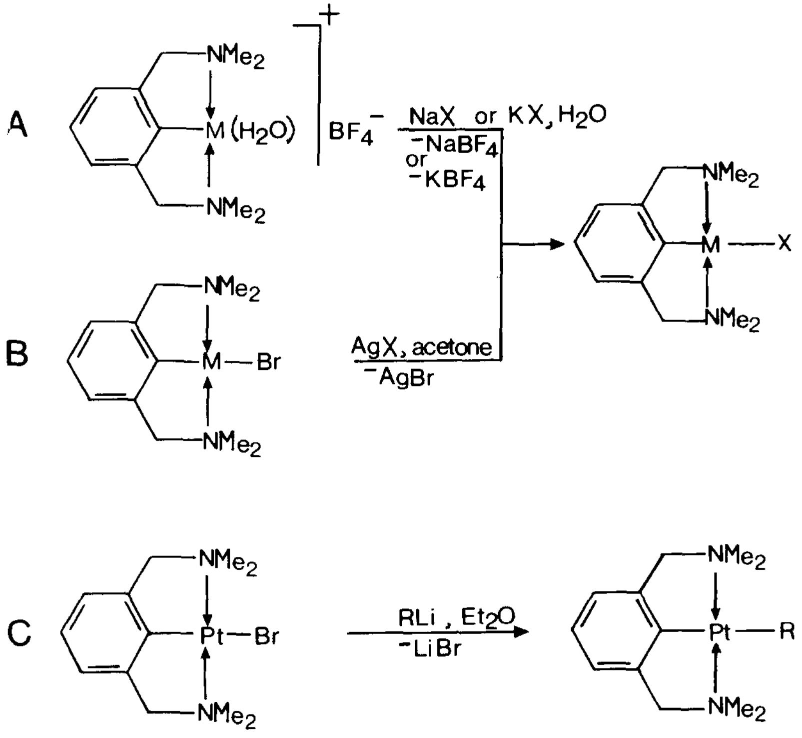
Atom	x	y	z
Pt	0.19877(5)	0.48784(5)	−0.05940(4)
Br	0.0412(2)	0.4781(2)	−0.2642(1)
N(1)	0.151(1)	0.324(1)	0.022(1)
N(2)	0.280(1)	0.659(1)	−0.095(1)
C(1)	0.316(1)	0.504(1)	0.095(1)
C(2)	0.307(1)	0.427(1)	0.193(1)
C(3)	0.391(1)	0.435(2)	0.303(1)
C(4)	0.484(1)	0.517(2)	0.319(1)
C(5)	0.496(1)	0.594(2)	0.228(1)
C(6)	0.411(1)	0.587(1)	0.109(1)
C(7)	0.203(1)	0.348(1)	0.165(1)
C(8)	0.404(1)	0.657(2)	−0.010(1)
C(9)	0.206(2)	0.196(2)	−0.002(1)
C(10)	0.029(1)	0.292(2)	−0.012(1)
C(11)	0.278(1)	0.669(2)	−0.222(1)
C(12)	0.224(2)	0.781(2)	−0.070(1)
H(3)	0.39(1)	0.37(1)	0.39(1)
H(4)	0.44(1)	0.02(1)	0.10(1)
H(5)	0.55(2)	0.66(2)	0.24(2)
H(71)	0.21(2)	0.25(2)	0.21(1)
H(72)	0.14(2)	0.40(2)	0.16(2)
H(81)	0.43(2)	0.75(2)	−0.01(1)
H(82)	0.45(2)	0.58(2)	−0.06(2)
H(91)	0.19(2)	0.19(2)	−0.08(2)
H(92)	0.28(2)	0.21(2)	0.03(2)
H(93)	0.17(1)	0.13(2)	0.04(1)
H(101)	−0.01(2)	0.36(2)	0.00(1)
H(102)	−0.02(2)	0.27(2)	−0.09(1)
H(103)	0.03(2)	0.23(2)	0.02(1)
H(111)	0.34(2)	0.59(2)	−0.21(2)
H(112)	0.20(2)	0.67(2)	−0.28(2)
H(113)	0.31(2)	0.74(2)	−0.22(2)
H(121)	0.13(2)	0.78(2)	−0.14(2)
H(122)	0.23(2)	0.80(2)	0.03(1)
H(123)	0.26(2)	0.86(2)	−0.09(2)

lous dispersion of Pt and Br was taken into account and an extinction correction was applied. The programs used were from XRAY 76 [16].

Results and discussion

General

The mononuclear organometallic complexes $[MBr\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}]$ (M = Pt (**2**), Pd (**6**)) were first obtained by reaction of the lithium compound o,o'-$(Me_2NCH_2)_2C_6H_3Li$ with $[PdBr_2(COD)]$ (COD = 1,5-cyclooctadiene) and *cis*-$[PtCl_2(SEt_2)_2]$ [5a]. The cationic complexes $[M\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}(H_2O)_n]Y$ (M = Pt; $n = 1$, Y = BF_4 (**8**) [5a], $n = 0$, Y = O_3SCF_3 (**10**) [10]; M = Pd; $n = 1$, Y = BF_4 ((**9**) [5a], $n = 0$, Y = O_3SCF_3 (**11**)) were then prepared by treating **2** and **6** in an acetone/H_2O mixture with $AgBF_4$ or AgO_3SCF_3.



SCHEME 1

The complexes $[MBr\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}]$ (**2**) and (**6**) were also be made by treating the appropriate corresponding cationic complexes with NaBr [5a]. The latter method (route **A** in Scheme 1) prevents contamination of the final products with other anions and is very useful for the syntheses of a series of new, neutral organopalladium(II) and platinum(II) products $[MX\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}]$ (M = Pt, Pd; X = Cl, Br, I, NO_2, N_3, O_2CH; M = Pt, X = NO_3, NCS). The success of the method relies on the insolubility of the neutral complexes in acetone/H_2O and the good solubility of the cationic complexes and KBF_4 in this solvent mixture. All these neutral complexes are white (Pt) or off-white (Pd), and are soluble in C_6H_6, CH_2Cl_2, and $CHCl_3$. The complexes are air stable, except for $[Pt(O_2CH)\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}]$, which decomposes slowly at room temperature.

A special case of route **A** is the reaction of $[M\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}(H_2O)]BF_4$ with KCN. Instead of the expected neutral compound $[Pt(CN)\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}]$, the homodinuclear, mono-bridged CN complex $[\{PtC_6H_3(CH_2NMe_2)_2\text{-}o,o'\}_2(\mu\text{-}CN)]BF_4$ was isolated. A schematic structure of this complex is shown in Fig. 2. This and related complexes with mono-atomic bridge complexes will be the subject of a forthcoming paper [17].

Another method for the synthesis of neutral palladium and platinum complexes involves halide abstraction from complexes **2** and **6** with appropriate silver(I) salts, i.e. route **B** in Scheme 1. This reaction gave the new complexes $[MX\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}]$ (M = Pd, Pt; X = O_3SCF_3, CN, O_2CMe, O_2CCF_3). This method is, however, limited to Ag^I salts which are soluble in organic solvents.

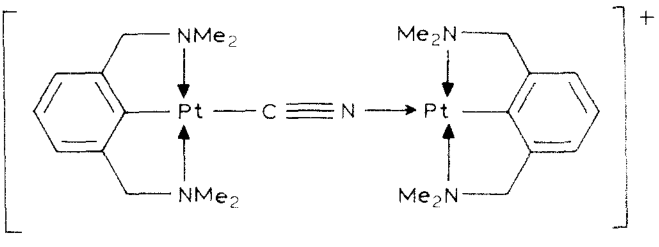


Fig. 2. Schematic structure of the $[\{Pt(C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}_2(\mu\text{-}CN)]$ cation.

The reactions of $[PtBr\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}]$ with various organolithium reagents, which are described here for the first time, leads to stable bis(organo)-platinum(II) products $[PtR\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}]$ (R = Ph, *o*-tolyl, *m*-tolyl, *p*-tolyl, C≡CPh, C≡C-*p*-tolyl), i.e. route **C** in Scheme 1. The alkyllithium reagents also reacted with **2**, but in all cases the products $[Pt(alkyl)\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}]$ decomposed readily, and attempts to isolate these mixed (aryl)(alkyl)platinum compounds were unsuccessful. All the isolated diorganoplatinum complexes are white, air stable, and readily soluble in $CHCl_3$, CH_2Cl_2 and C_6H_6.

The palladium products $[Pd(aryl)\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}]$ are not thermally stable and when route **C** is used, these compounds are accompanied by decomposition products, namely black palladium metal and organic products. In the case of $[Pd(o\text{-tolyl})\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}]$ an ^1H NMR spectrum could be recorded before the product decomposed, and this showed a similar ^1H NMR pattern to that for the corresponding $[Pt(o\text{-tolyl})\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}]$ (vide infra). The reaction of lithium *p*-tolylacetylide with $[PtBr\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}]$ gave the asymmetric coupling product $o,o'\text{-}(Me_2NCH_2)_2C_6H_3C{\equiv}C\text{-}p\text{-tolyl}$ which was identified by ^1H NMR spectroscopy.

The molecular and crystal structure of $[PtBr\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}]$ (2)

In the crystal structure of **2** four discrete molecules are present in the monoclinic unit cell. The molecular geometry and numbering scheme are shown in Fig. 3, and relevant bond distances and bond angles are given in Table 3. Each Pt^{II} centre is coordinated in a slightly distorted square-planar fashion by two N atoms, the C(*ipso*) atom of the anionic tridentate ligand system and the Br atom. The C(*ipso*)–Pt–Br bond angle is 177.4(4)°, and the two N donor atoms are in mutually *trans* positions with the N(1)–Pt–N(2) bond angle of 164.4(4)° showing an angular deviation of 15.6° from exact *trans* coordination. This distortion from the ideal square-planar arrangement is the result of the small N–Pt–C(*ipso*) bite angles in the two five-membered chelate rings of 82.9(5) and 81.5(5)°, respectively.

These chelate rings have clear puckering (see Fig. 3b) which may be described as of a 'two-fold axis' type. A characteristic feature of this puckering is the position of the two NMe_2 groups on opposite sides of the aryl plane. A similar puckering is found in octahedral complexes such as $[PtCl_3\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}]$ and $[PtI_2(p\text{-tolyl})\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}]$ [18]. In the five-coordinate square-pyramidal complexes $[M^{III}X_2\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}]$ (M = Fe, Ni and X = Cl, I) [4,6] the puckering is different, and of a mirror plane symmetry type, characterized by N donor atoms on the same side of the aryl plane away from the apical ligand.

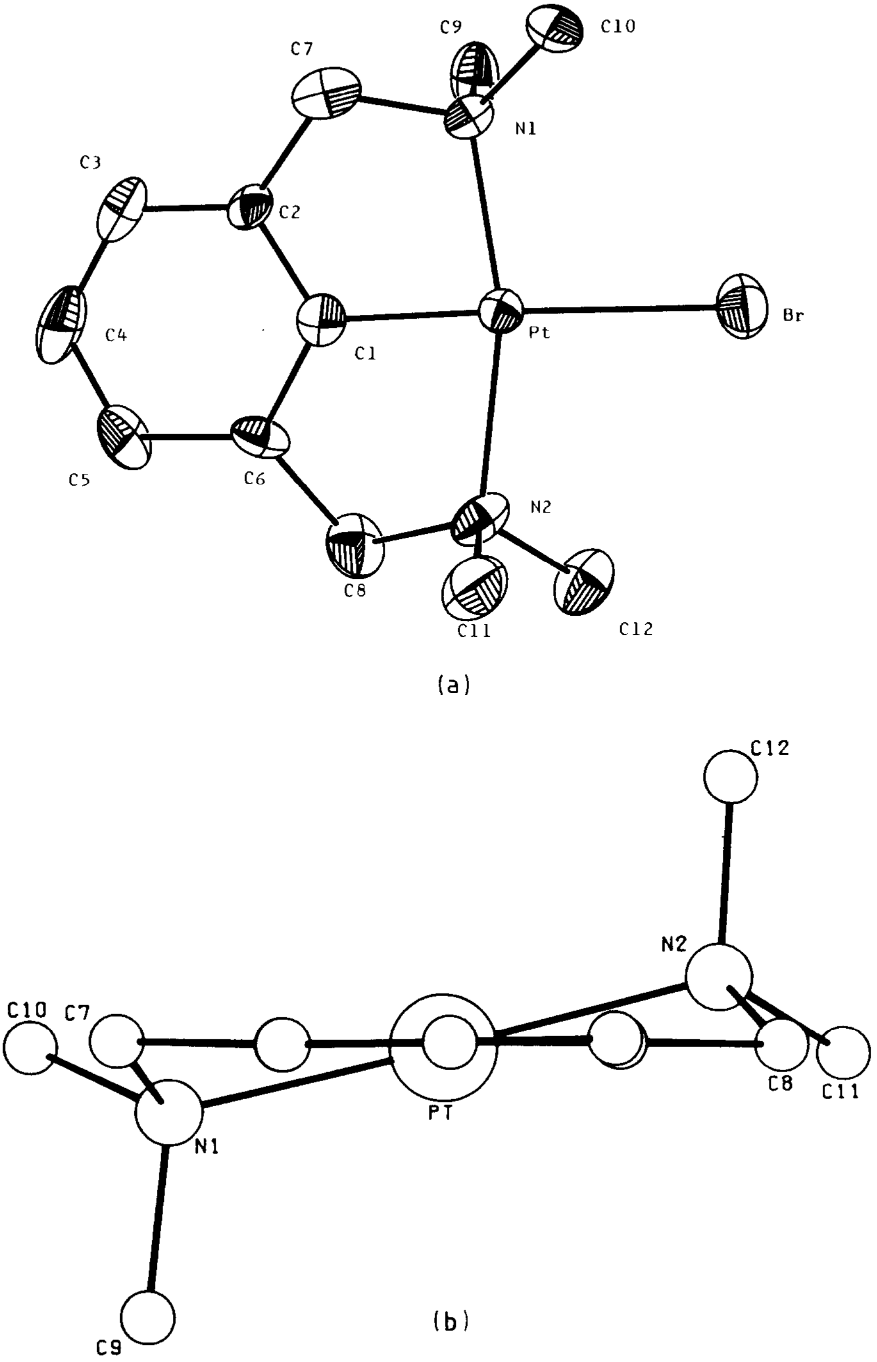


Fig. 3. (a) ORTEP drawing showing the molecular structure of [PtBr{$C_6H_3(CH_2NMe_2)_2$-*o*,*o*′}] (**2**) with the atomic numbering. Thermal ellipsoids for non-hydrogen atoms are given at the 50% probability level. (b) PLUTO drawing of the projection along the Pt–C(1) axis showing the puckering in the five-membered chelate rings of **2**.

TABLE 3

INTERATOMIC BOND DISTANCES (Å) AND ANGLES (°) OF $[PtBr(C_6H_3(CH_2NMe_2)_2$-*o,o'*)]

Pt–Br	2.526(2)	C(4)–C(5)	1.36(2)
Pt–N(1)	2.07(1)	C(5)–C(6)	1.43(2)
Pt–N(2)	2.09(1)	C(6)–C(8)	1.43(2)
Pt–C(1)	1.90(1)	C(7)–N(1)	1.58(2)
C(1)–C(2)	1.41(2)	C(8)–N(2)	1.53(2)
C(2)–C(6)	1.41(2)	C(9)–N(1)	1.52(2)
C(2)–C(3)	1.36(2)	C(10)–N(1)	1.48(2)
C(2)–C(7)	1.47(2)	C(11)–N(2)	1.48(2)
C(3)–C(4)	1.39(2)	C(12)–N(2)	1.48(2)
Br–Pt–N(1)	98.8(3)	C(8)–N(2)–C(12)	108(1)
Br–Pt–N(2)	96.8(3)	Pt–C(1)–C(2)	118.6(9)
Br–Pt–C(1)	177.4(4)	Pt–C(1)–C(6)	120(1)
N(1)–Pt–N(2)	164.4(4)	C(2)–C(1)–C(6)	121(1)
N(1)–Pt–C(1)	82.9(5)	C(1)–C(2)–C(3)	120(1)
N(2)–Pt–C(1)	81.5(5)	C(1)–C(2)–C(7)	115(1)
Pt–N(1)–C(7)	107.1(8)	C(3)–C(2)–C(7)	125(1)
Pt–N(1)–C(9)	109(1)	C(2)–C(3)–C(4)	120(1)
Pt–N(1)–C(10)	118.8(8)	C(3)–C(4)–C(5)	123(1)
C(7)–N(1)–C(9)	106(1)	C(4)–C(5)–C(6)	119(1)
C(7)–N(1)–C(10)	109(1)	C(1)–C(6)–C(5)	117(1)
C(9)–N(1)–C(10)	106(1)	C(1)–C(6)–C(8)	112(1)
Pt–N(2)–C(8)	108.3(9)	C(5)–C(6)–C(8)	130(1)
Pt–N(2)–C(11)	114.6(9)	N(1)–C(7)–C(2)	109(1)
Pt–N(2)–C(12)	108(1)	N(2)–C(8)–C(6)	109(1)
C(8)–N(2)–C(11)	110(1)		

The Pt–C bond (1.90(1) Å) in **2** is short when compared with analogous bonds in other Pt^{II}–aryl compounds, for which distances lie in the range 1.98 to 2.08 Å [19–21].

Spectroscopic measurements

Infrared spectra

The IR spectra of $[PdCl\{C_6H_3(CH_2NMe_2)_2$-*o,o'*}] and $[PtCl\{C_6H_3(CH_2NMe_2)_2$-*o,o'*}] show ν(M–Cl) values of 235 (Pd) and 262 cm^{-1} (Pt), see Table 3. These values are as expected for complexes in which the halogen is *trans* to a ligand with a strong *trans* influence [22]; cf. the values of ν(M–Cl) in [MCl(PCP′)], (PCP′) = *o,o′*-$(Bu^t_2PCH_2)_2C_6H_3$) 272 (Pd), and 283 cm^{-1} (Pt) [1a] and ν(M–Cl) in *trans*-[Pt(*o*-tolyl)Cl$(SeEt_2)_2$] 262 cm^{-1} [23]. The assignments of ν(M–Br) and ν(M–I) in Table 4 were made by comparison of the IR data with those for the analogous nickel(II) complexes [4].

The IR spectra of the cationic species **8** and **9** show broad bands in the region 900 to 1200 cm^{-1} which are characteristic of the uncoordinated BF_4 anion [24]. The number and positions of ν(SO) bands for O_3SCF_3 in the complexes **10** and **11** (see Table 4) are indicative of an oxygen-bonded anion [24].

From published IR data [25] it can be concluded that the anions X = N_3, SCN, or NO_2 in the complexes $[MX\{C_6H_3(CH_2NMe_2)_2$-*o,o'*}] are nitrogen-bonded, while the complexes in which X = O_2CMe, O_2CCF_3, or O_2CH contain single oxygen-bonded ligands. These data are in agreement with the IR data for the corresponding nickel derivatives and with the X-ray structure of [Ni-$(O_2CH)\{C_6H_3(CH_2NMe_2)_2$-*o,o'*}] which contains an oxygen-bonded formato group [4]. For [Pt$(NO_3)\{C_6H_3(CH_2NMe_2)_2$-*o,o'*}] the characteristic absorption bands of NO_3 were partly obscured by absorption bands of the tridentate ligand. However, we suggest that this anion is oxygen-bonded, as it is in the related compound [Pd$(NO_3)\{C_6H_3(CH_2PPh_2)_2$-*o,o'*}], the crystal structure of which is known [26].

The platinum(II) cyanide complex [PtCN$\{C_6H_3(CH_2NMe_2)_2$-*o,o'*}] showed one specific ν(CN) band at 2093 cm^{-1}, which points to a carbon-bonded cyanide ligand. This latter value is significantly lower than the ν(CN) value of 2135 cm^{-1} observed for the dimeric platinum complex $[\{Pt(C_6H_3(CH_2NMe_2)_2$-*o,o'*$\}_2(\mu$-CN)]$BF_4$ [17], in which the CN anion is thought to bridge linearly via carbon and nitrogen to two Pt$\{C_6H_3(CH_2NMe_2)_2$-*o,o'*} cationic moieties. Compounds with a single linear cyano bridge are well documented, and give ν(CN) values in the range 2085 to 2168 cm^{-1} [25,27,28].

^1H NMR spectra

The 60 MHz ^1H NMR spectrum of the parent aryl bromide *o,o'*-$(Me_2NCH_2)_2C_6H_3Br$ shows a multiplet pattern centred at δ 7.25 ppm for the aryl protons. The CH_2 and NMe_2 protons appear as two singlets at δ 3.48 and 2.10 ppm, respectively. This pattern of the various protons in the ligand is of particular interest because it can readily be recognized in the ^1H NMR spectra of the organometal(II) complexes.

The protons of the CH_2NMe_2 groupings, which are close to the metal, exhibit pronounced downfield shifts on coordination, whereas the aryl protons undergo upfield shifts. For example, the ^1H NMR spectrum of [PdBr$\{C_6H_3(CH_2NMe_2)_2$-*o,o'*}] shows two singlets at δ 4.00 and 2.97 ppm for the CH_2 and NMe_2 protons, respectively, while the aryl protons give a multiplet centred at δ 6.85 ppm. Rigid N donor atom coordination in these complexes is indicated by the ^1H NMR spectra of the platinum(II) complexes; in these spectra the signals of the CH_2 protons and the protons of the NMe groups show sharp ^{195}Pt ($I = 1/2$, 34% abundance) satellites with substantial $J(^{195}Pt, {}^1H)$ couplings. For example, signals are found at δ 4.02 (CH_2) and 3.13 (NMe_2), with $J(^{195}Pt, {}^1H)$ of 46 and 38 Hz, respectively. Similar changes in the chemical shifts of the ligand are observed for the other complexes whose NMR data are given in Table 4. In the case of the halide complexes **1**, **2**, and **3** there is an evident trend in the chemical shift of the NMe_2 protons, the order of increasing δ values being Cl < Br < I.

The coordination of the CH_2NMe_2 groups to the metal in [MX$\{C_6H_3(CH_2NMe_2)_2$-*o,o'*}] (vide supra) blocks the pyramidal inversion process, which takes place at the uncoordinated nitrogen atoms. As a result prochiral nitrogen centres with a stable tetrahedral configuration are created, and these may or may not coincide with a molecular plane of symmetry depending on the overall symmetry of the complex determined by the X group. Accordingly the protons of both the CH_2 and NMe_2 groups can be either enantiotopic or diastereotopic. In the latter case the coordination plane of the molecule is not a molecular plane of symmetry, and hence contains prochiral carbon centres which are characterized by inequivalent chemical shifts and magnetic couplings of the CH_2 protons in the CH_2NMe_2 arms [9].

(*Continued on p. 415*)

TABLE 4

^{1}H NMR [a] AND IR [b] DATA FOR THE ORGANOPALLADIUM(II) AND ORGANOPLATINUM(II) COMPLEXES

Compound	^{1}H NMR						IR	
	δ(NCN ligand)			δ(R group)			ν(cm^{-1})	Assignment
	C_6H_3	CH_2	NMe_2	*ortho*-H	aryl	other		
o,o'-$(Me_2NCH_2)_2C_6H_3Br$	7.25	3.84	2.10					
$[PtCl\{C_6H_3(CH_2NMe_2)_2$-*o,o'*$\}]$ (**1**)	6.80	4.00 (46)	3.07 (38)				292	Pt–Cl
$[PtBr\{C_6H_3(CH_2NMe_2)_2$-*o,o'*$\}]$ (**2**)	6.85	4.02 (46)	3.13 (38)				172	Pt–Br
$[PtI\{C_6H_3(CH_2NMe_2)_2$-*o,o'*$\}]$ (**3**)	6.90	4.00 (46)	3.17 (40)				133	Pt–I
$[Pt(O_2CMe)\{C_6H_3(CH_2NMe_2)_2$-*o,o'*$\}]\cdot H_2O$ (**4**)	6.80	4.00 (50)	3.03 (38)			2.06 (CH_3)	1578,1410	CO_2
$[PdCl\{C_6H_3(CH_2NMe_2)_2$-*o,o'*$\}]$ (**5**)	6.80	3.98	2.93				235	Pd–Cl
$[PdBr\{C_6H_3(CH_2NMe_2)_2$-*o,o'*$\}]$ (**6**)	6.85	4.00	2.97				160	Pd–Br
$[PdI\{C_6H_3(CH_2NMe_2)_2$-*o,o'*$\}]$ (**7**)	6.90	4.00	3.03				126	Pd–I
$[Pt\{C_6H_3(CH_2NMe_2)_2$-*o,o'*$\}(H_2O)]BF_4$ (**8**)	6.90	4.15 (50)	2.97 (38)				900–1100	BF_4
$[Pd\{C_6H_3(CH_2NMe_2)_2$-*o,o'*$\}(H_2O)]BF_4$ (**9**)	6.85	4.17	2.87				900–1100	BF_4
$[Pt\{C_6H_3(CH_2NMe_2)_2$-*o,o'*$\}O_3SCF_3]$ (**10**)	6.80	4.20 (50)	3.06 (38)				1250–1160 1020	O_3SCF_3
$[Pd\{C_6H_3(CH_2NMe_2)_2$-*o,o'*$\}O_3SCF_3]\cdot H_2O$ (**11**)	6.85	3.97	2.92				1246–1170 1040	O_3SCF_3
$[Pt(NO_2)\{C_6H_3(CH_2NMe_2)_2$-*o,o'*$\}]$ (**12**)	6.78	4.05 (49)	3.03 (40)				1339,1325 807	NO_2
$[Pt(NO_3)\{C_6H_3(CH_2NMe_2)_2$-*o,o'*$\}]$ (**13**)	6.77	3.97 (50)	2.97 (38)					
$[Pt(N_3)\{C_6H_3(CH_2NMe_2)_2$-*o,o'*$\}]$ (**14**)	6.77	3.99 (47)	3.00 (40)				2041	N_3

[Pt(NCS){$C_6H_3(CH_2NMe_2)_2$-*o,o'*}] (**15**)	6.87	4.02 (4)		3.03 (40)					2096,472	NCS
[Pt(CN){$C_6H_3(CH_2NMe_2)_2$-*o,o*}] (**16**)	6.83	4.06 (44)		3.16 (42)					2093	CN
[Pt(O_2CCF_3){$C_6H_3(CH_2NMe_2)_2$-*o,o'*}] (**17**)	6.83	4.02 (48)		3.01 (38)						
[Pt(O_2CH){$C_6H_3(CH_2NMe_2)_2$-*o,o'*}] [d] (**18**)	6.65	3.23 (49)		2.60 (39)				9.78 (O_2CH)	1608,1596 1313	CO_2
[Pt(C_6H_5){$C_6H_3(CH_2NMe_2)_2$-*o,o'*}] (**19**)	6.90	4.14 (43)		2.93 (45)		7.71 (28)	7.1m			
[Pt(*o*-tolyl){$C_6H_3(CH_2NMe_2)_2$-*o,o'*}] (**20**)	6.90	4.21 (44)	4.13 (44)	2.93 (45)	2.95 (45)	7.67 (28)	7.1m	2.82 (CH_3) (6)		
[Pt(*m*-tolyl){$C_6H_3(CH_2NMe_2)_2$-*o,o'*}] (**21**)	6.90	4.14 (44)		2.93 (44)		7.50 (28)	7.1m	2.31 (CH_3)		
[Pt(*p*-tolyl){$C_6H_3(CH_2NMe_2)_2$-*o,o'*}] (**22**)	6.90	4.16 (43)		2.95 (43)		7.64 [e] (28)	7.1m [e]	2.33 (CH_3		
[Pt(C≡CC_6H_5){$C_6H_3(CH_2NMe_2)_2$-*o,o'*}] (**23**)	6.90	4.10 (44)		3.20 (43)			7.2		2040	C≡C
[Pt(C≡C-*p*-tolyl){$C_6H_3(CH_2NMe_2)_2$-*o,o'*}] (**24**)	6.90	4.09 (44)		3.19 (43)			7.2m	2.26 (CH_3)		
[Pd(N_3){$C_6H_3(CH_2NMe_2)_2$-*o,o'*}] (**25**)	6.80	3.98		2.90					2044	N_3
[Pd(O_2CMe){$C_6H_3(CH_2NMe_2)_2$-*o,o'*}]·0.7H_2O [c] (**26**)	6.83	4.00		2.82				1.77 (O_2CMe)		
[Pd(O_2CCF_3){$C_6H_3(CH_2NMe_2)_2$-*o,o'*}] (**27**)	6.85	4.05		2.83						

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[a] Recorded in $CDCl_3$ unless otherwise stated; $\delta(^1H)$ in ppm, m = multiplet, $J(^{195}Pt,^1H)$ in Hz between parentheses. [b] Measured as KBr pellets: **4**, **8–29**; as Nujol mull: **1–3**; as C_6H_6 solution: **5–7**. [c] Recorded in acetone-d_6. [d] Recorded in C_6D_6. [e] AB pattern $^3J(H,H)$ 7 Hz.

TABLE 5

^{13}C NMR DATA OF [PtX{$C_6H_3(CH_2NMe_2)_2$-*o*,*o*′}] (X = Cl, Br) AND [PtR{$C_6H_3(CH_2NMe_2)_2$-*o*,*o*′}] (R = Ph, *o*-, *m*-, *p*-tolyl, C≡C_6H_5, C≡C-*p*-tolyl) [a,b]

No.	Group *trans* to C(1)	δ(NCN′ ligand)						δ(R group)						
		C(1)	C(2)	C(3)	C(4)	CH_2	NCH_3	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	CH_3
1	Cl	144.5 (1002)	142.7 (77)	118.6 (35)	122.6	77.1 (65)	53.7							
2	Br	145.7 (1003)	142.7 (77)	118.7 (36)	122.8	76.8 (67)	54.5							
19	Ph	171.8 (587)	145.1 (54)	118.1 (15)	122.8	81.1 (31)	54.9	183.9 (780)	139.2	126.5 (41)	121.0	126.5 (41)	139.2	
20	*o*-tolyl	172.1 (584)	145.1 (54)	118.2 (15)	122.4	81.1 (32)	54.8 54.1	182.6 (796)	145.2	123.5 (40)	121.0	127.4 (32)	138.7	25.5 (40)
21	*m*-tolyl	172.0 (58)	145.1 (54)	118.1 (16)	122.4	81.1 (30)	54.9	183.7 (780)	140.1	134.8 (40)	121.8	126.4 (42)	136.1	21.8
22	*p*-tolyl	172.0 (587)	145.1 (54)	118.1 (16)	122.4	81.1 (30)	54.9	179.2 (785)	138.9	127.4 (42)	129.6	127.4 (42)	138.9	20.9
23	C≡CC_6H_5	166.7 (–)	146.1 (56)	118.7	123.3	80.0 (43)	56.0	137.3 (–)	131.6	127.9 ( )	124.7	127.9	131.5	[c]
24	C≡C-*p*-tolyl	166.8 (–)	146.1 (58)	118.6	123.3	80.1 (43)	56.0	135.3 (–)	131.5	128.6 (–)	134.2	128.6	131.5	21.3 [d]

[a] Recorded in $CDCl_3$; δ(^{13}C) in ppm relative to TMS; $J(^{195}Pt,^{13}C)$ (Hz) between parentheses. [b] The values of $J(^{195}Pt,^{13}C(4))$ of the NCN′ ligand were generally less than 7 Hz; the satellites were generally not sufficiently resolved to permit definite assignment. [c] R = $C_\alpha \equiv C_\beta C_6H_5$; δ($C_\alpha$) 129.0, δ($C_\beta$) 107.8 ppm. [d] R = $C_\alpha \equiv C_\beta$(*p*-tolyl); δ(C_α) 125.8, δ(C_β) 107.7 ppm.

The ^1H NMR spectrum of [Pt(*o*-tolyl){$C_6H_3(CH_2NMe_2)_2$-*o*,*o*′}] (**20**) (measured at 308 K) showed an AB pattern at δ 4.23 and 4.21 ppm for the CH_2 protons, with $J(^{195}Pt, ^1H)$ and $J(^1H, ^1H)$ of 44 and 13 Hz, respectively. The protons of the NMe_2 groups were found as two singlets at δ 2.93 and 2.95 ppm, with $J(^{195}Pt, ^1H)$ of 45 Hz. These data indicate that the coordination plane in **20** is no longer a molecular plane of symmetry, and this is consistent with a structure in which the *o*-tolyl group is locked in a position perpendicular to the coordination plane of the complex. Further support for this structure comes from the downfield chemical shifts of the *ortho* methyl groups of the *o*-tolyl ligand. The signal from these methyl protons appears as a singlet at δ 2.82 ppm, ($J(^{195}Pt, ^1H)$ 8 Hz), cf. δ(Me) of toluene 2.32. Similar chemical shifts are encountered for other *o*-tolyl complexes in which *ortho* methyl groups are in close proximity to a metal, e.g. in *trans*(*o*-tolyl)(trichlorovinyl)bis(triethylphosphine)nickel(II) δ 2.88 [29], [$NiBr$(*o*-tolyl)$(PMePh_2)_2$] 2.68 [30], and in [$PtI(MeC_6H_3(CH_2NMe_2)_2$-*o*,*o*′}$(H_2O)]BF_4$ δ 3.13 ppm [5]. Another significant downfield shift was observed for the *ortho* proton of the *o*-tolyl ligand in **20**. This proton gives a doublet at 7.67 ppm with $J(^{195}Pt, ^1H)$ of 28 Hz, while the remaining aryl protons give a multiplet at 6.90 ppm. The ^1H NMR shift data for [Pd(*o*-tolyl){$C_6H_3(CH_2NMe_2)_2$-*o*,*o*′}] are similar, though in contrast to the platinum case the NMe_2 protons give one broad singlet.

The ^1H NMR (C_6D_6) spectrum of [$Pt(O_2CH)${$C_6H_3(CH_2NMe_2)_2$-*o*,*o*′}] showed a well-defined pattern for the NCN′ ligand, viz. δ(C_6H_3) 6.65 (m), δ(CH_2) 3.23 (s) ppm with $J(^{195}Pt, ^1H)$ 49 Hz and δ(NMe) 2.60 (s) with $J(^{195}Pt, ^1H)$ 39 Hz. In addition a signal was found at low field δ 9.78 ppm with $J(^{195}Pt, ^1H)$ 52 Hz, which is consistent with the presence of a M–O–C(H)=O grouping. These data, which are consistent with those found for the analogous nickel compound [4], support the earlier conclusion (see discussion of the IR spectra) that the O_2CH group is oxygen-bonded as O–C(=O)H to the platinum centre.

^{13}C NMR

The ^{13}C NMR data (62.89 MHz, $CDCl_3$) PtX{$C_6H_3(CH_2NMe_2)_2$-*o*,*o*′}] (X = Cl, Br) and PtR{$C_6H_3(CH_2NMe_2)_2$-*o*,*o*′}] (R = aryl or C≡CR) are given in Table 5. The ^{13}C resonances of the platinum complexes at high field could be assigned to the carbon atoms of the CH_2NMe_2 substituents. For compound **2** the CH_2 carbon atoms appeared as a singlet at δ 76.8, and the NMe_2 carbon also as a singlet at δ 54.5. This pattern is consistent with a C_2 symmetry for the molecule. The ^{13}C NMR spectrum of [Pt(*o*-tolyl){$C_6H_3(CH_2NMe_2)_2$-*o*,*o*′}], however, showed two signals for the NMe_2 carbon atoms at δ 54.8 and 54.1 ppm, which indicates a non-equivalence of the methyl groups. This can be accounted for in terms of a structure for [Pt(*o*-tolyl){$C_6H_3(CH_2NMe_2)_2$-*o*,*o*′}] involving restricted rotation of the *o*-tolyl group around its Pt–C(*ipso*) bond, which results in a non-equivalence of the space above and below the Pt-coordination plane (see also discussion of the ^1H NMR spectrum).

The assignment of the remaining part of the ^{13}C NMR spectra of **1**, **2** and **19–24** was made by comparison of the data with those for the related aryl- and acetylide-platinum(II) complexes [31,32]. The *ortho* and C(*ipso*) carbon atoms in the tridentate ligand could be distinguished from the *meta* and *para* carbon atoms on the basis of their relative intensities. Further support for the assignments comes from the magnitude of the $J(^{195}Pt, ^{13}C)$ coupling constants, see Table 5. In the case of the *para* carbon, the values of $J(^{195}\text{Pt}, ^{13}\text{C})$ were too small to be measured accurately. For **19–22** we could not unambiguously assign the signals of the two C(*ipso*) atoms, but constancy of one signal (~ 172 ppm with $J(^{195}\text{Pt}, ^{13}\text{C})$ ~ 585 Hz) strongly suggests that that this is associated with the invariant tridentate ligand, and it has been so assigned in Table 5.

The ^{13}C NMR data reveal that the ligand *trans* to the aryl moiety of the tridentate ligand has a relatively large influence on its ^{13}C(*ipso*) chemical shift, the values of δ ranging from 144.5 to 172 ppm. The shieldings of the *ortho*, *meta* and *para* carbons of the aryl moiety change within much smaller ranges (viz., δ 142.7–145.1 (*ortho*), 118.6–118.1 (*meta*), 122.6–122.4 ppm (*para*)). Similar sensitivity to the *trans* X group is found when the $J(^{195}\text{Pt}, ^{13}\text{C})$ coupling constants of the tridentate ligand signals are compared. The $J(^{195}\text{Pt}, ^{13}\text{C})$ of C(*ipso*) spans the range 587–1002 Hz, whereas for the *ortho*, *meta* and *para* carbon atoms there are much smaller ranges of 54–77 Hz ($^2J(^{195}\text{Pt}, ^{13}\text{C})$) and 16–35 Hz ($^3J(^{195}\text{Pt}, ^{13}\text{C})$), respectively. Such a *trans* influence on the ^{13}C chemical shifts has been observed for other arylplatinum and methylplatinum complexes [32].

The value of $J(^{195}\text{Pt}, ^{13}\text{C})$ of 1000 Hz found for $[\text{PtX}\{\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-}o,o'\}]$ (X = Br, Cl) is relatively high (cf. this coupling in *trans*-$[\text{Pt(Aryl)(As(Me)}_3)_2\text{Cl}]$ of 858 Hz [31]). This suggests the presence of an aryl–platinum π interaction, which may contribute to the Pt–C bonding. Support for this view comes from the ultraviolet photoelectron spectra of a series of $[\text{MX}\{\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-}o,o'\}]$ complexes (M = Ni, Pd, Pt; X = Cl, Br, I) [13]. It was observed that there is a strong interaction between the π levels on the phenyl part of the tridentate ligand and metal *d*-orbitals. The fact that the plane of the aryl ring and the metal coordination plane are close to coplanar is important, because this allows mixing of the filled Pt-d_{xz} with the empty $\pi^\star$ orbitals on the aryl ring. Recently, a value of $J(^{195}\text{Pt}, ^{13}\text{C}(ipso))$ of 1174.5 Hz [20] was reported for the rigid square-planar complex *cis*-bis(2-phenylpyridine)platinum(II). It is noteworthy that in this complex the plane of the aryl ring is also coplanar with the platinum coordination plane.

For the *trans*-diorganoplatinum(II) complexes **19–22** values of $J(^{195}\text{Pt}, ^{13}\text{C}(ipso))$ are much lower. This may be the result of the stronger *trans* influence of the second aryl group compared with those of the halide ligands in **1** and **2**.

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