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THE ^{13}C NMR SPECTRA OF ISONITRILE COMPLEXES OF PLATINUM(II), PALLADIUM(II), OSMIUM(II) AND RUTHENIUM(II)

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Summary

^{13}C NMR chemical shifts (δ, ppm) have been obtained for the compounds *trans*-[PtX(CNR)(PEt$_3$)$_2$]$^+$ [X = Cl or Br; R = Me, t-Bu, C$_6$H$_{11}$, 4-C$_6$H$_4$R^1 (R^1 = H, Me, OMe, Cl or NO$_2$) or 2,6-C$_6$H$_3$Cl$_2$]; *cis*-[PtCl$_2$(CNR)(PEt$_3$)]; *cis*-[PtCl$_2$(CNC$_6$H$_{11}$)$_2$]; *cis*-[PdCl$_2$(4-MeOC$_6$H$_4$NC)(PEt$_3$)]; [OsCl$_2$(CNR)$_2$(PR$^2_3$)$_2$] [PR$^2_3$ = PEt$_3$, PEt$_2$Ph or P-n-Bu$_2$Ph]; [OsCl$_2$(MeNC)(PEt$_3$)$_3$]; [OsCl(MeNC)$_2$(PEt$_3$)$_3$]$^+$ and [RuCl$_2$-(PhNC)$_2$(PMe$_2$Ph)$_2$] (various isomers). Values of ^1J(Pt—C) and ^2J(P—M—CNR) (M = Pt or Os) have been obtained in some cases and a correlation of chemical shifts of 4-R^{1}C$_6$H$_4$NC ligands with the $\sigma_p{}^+$ substituent constant for R^1 is presented and discussed.

The ^{13}C NMR spectra of isonitrile complexes have had limited study, one of the main hindrances being the difficulty of detection of the resonance of the terminal carbon atom of the isonitrile ligands [1,2]. As a continuation of our investigation of the properties of isonitriles and derived species we have determined the ^{13}C NMR spectra of a number of isonitrile complexes of platinum(II), palladium(II), osmium(II) and ruthenium(II). We have been able to assign the isonitrile—carbon chemical shift in a number of cases, the signal being particularly clear for osmium complexes.

Results and discussion

(a) Platinum and palladium complexes

The spectral parameters and assignments are shown in Table 1. The parameters of the tertiary phosphine ligands are similar to those obtained for related systems [1,2]. The terminal isonitrile carbon signal is known to be difficult to detect because of the long relaxation times involved and the possibility of quadrupole relaxation by the nitrogen atom [1—4]. We have overcome these problems by use of a relaxing agent, long accumulation times and a repetition time of 1 sec (see Experimental). Nevertheless the signal is rather weak and poorly

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TABLE 1

^{13}C NMR DATA FOR PLATINUM COMPLEXES[a]

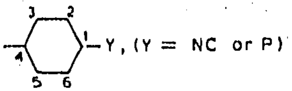
Complex[b]	δ(C)	^1J(Pt—C)	δ(C^1)	CNR	PCH$_2$[c]	PCH$_2$CH$_3$
trans-$[PtCl(CO)(PEt_3)_2]^+$	161.74 tt ^2J(PC) 8.8	1777.4			16.86 tt $\lvert ^1J + {}^3J \rvert$ 35.6 ^2J(Pt—C) 25.4	9.40 t ^3J(Pt—C) 17.6
trans-$[PtCl(CNMe)(PEt_3)_3]^+$	111.1(br)	1720		31.4 t ^3J(Pt—C) 19.2	14.9 tt $\lvert ^1J + {}^3J \rvert$ 35.4 ^2J(Pt—C) 27.5	7.96 t ^3J(Pt—C) 19.5
trans-$[PtBr(CNMe)(PEt_3)_2]^+$	111.3(br)	1721		31.2 t ^3J(Pt—C) 19.1	15.5 tt $\lvert ^1J + {}^3J \rvert$ 35.1 ^2J(Pt—C) 29.0	7.95 t ^3J(Pt—C) 19.8
trans-$[PtCl(CNBu\text{-}t)(PEt_3)_2]^+$	109.6 (br)	n.o.		61.2 t(CN$\underline{C}$Me$_3$) ^3J(Pt—C) 15.1 CNC$\underline{Me}_3$ 29.5 s	14.9 tt $\lvert ^1J + {}^3J \rvert$ 34.2 ^2J(Pt—C) 28.7	8.06 t ^3J(Pt—C) 18.9
trans-$[PtCl(CNC_6H_{11})(PEt_3)_2]^+$	108.6 (br)	n.o.		56.67 t(C1) ^3J(Pt—C) 15.1 32.03 s(C$_{2,6}$) 24.45 s(C$_4$) 23.60 s($_{3,5}$)	14.93 tt $\lvert ^1J + {}^3J \rvert$ 35.5 ^2J(Pt—C) 27.5	8.07 t ^3J(Pt—C) 18.4
trans-$[PtCl(4\text{-}NO_2C_6H_4NC)(PEt_3)_2]^+$	124.8(br)	n.o	131.0 t ^3J(Pt—C) 27	128.4 s(C$_{2,6}$) 125.6 s(C$_{3,5}$) 148.2 s(C$_4$)	15.1 tt $\lvert ^1J + {}^3J \rvert$ 35.4 ^2J(Pt—C) 29.5	8.05 t ^3J(Pt—C) 18.1
trans-$[PtCl(4\text{-}ClC_6H_4NC)(PEt_3)_2]^+$	121(br) ^2J(P—C) ~15	n.o.	124.4 t ^3J(Pt—C) 27	128.1 t(C$_{2,6}$) ^4J(Pt—C) ~6 130.6 s(C$_{3,5}$) 137.3 s(C$_4$)	15.1 tt $\lvert ^1J + {}^3J \rvert$ 35.4 ^2J(Pt—C) 30	8.0 t ^3J(Pt—C) 18.6
trans-$[PtCl(CNC_6H_5)(PEt_3)_2]^+$	120(br) ^2J(P—C) ~15	n.o.	125.9 t ^3J(Pt—C) 25	126.5 t(C$_{2,6}$) ^4J(PtC) ~10 130.4 s(C$_{3,5}$) 131.4 s(C$_4$)	15.17 tt $\lvert ^1J + {}^3J \rvert$ 35.1 ^2J(Pt—C) 28.6	8.07 t ^3J(Pt—C) 16.8
trans-$[PtCl(4\text{-}MeC_6H_4NC)(PEt_3)_2]^+$	119.2(br) ^2J(P—C) ~15	1730	123.1 t ^3J(Pt—C) 27.1	126.2 t(C$_{2,6}$) ^4J(PtC) ~9 130.9 s(C$_{3,5}$) 142.2 s(C$_4$) 21.55 s(C$_6$H$_4\underline{CH}_3$)	15.1 tt $\lvert ^1J + {}^3J$ 34.2 ^2J(Pt—C) 29.1	8.0 t ^3J(Pt—C) 18.1

trans-$[PtCl(4\text{-}MeOC_6H_4NC)(PEt_3)_2]^+$	115.3 (br)	n.o.	118.2 t $^3J(Pt—C)$ ~19	128.2 s($C_{2,6}$) 115.7 s($C_{3,5}$) 161.6 s(C_4) 55.94 s(OCH_3)	15.17 tt $\|^1J + {}^3J\|$ 33.6	8.13 t(br)
trans-$[PtCl(2,6\text{-}Cl_2C_6H_3NC)(PEt_3)_2]^+$	124 (br) $^2J(P—C)$ ~15	n.o.	n.o.	131.8 t($C_{2,6}$) $^4J(Pt—C)$ 10.4 129.5 s($C_{3,5}$) 133.7 s(C_4)	15.1 tt $\|^1J + {}^3J\|$ 35.5 $^2J(Pt—C)$ 28.3	8.0 t $^3J(Pt—C)$ 18.9
cis-$[PtCl_2(CNMe)(PEt_3)]$	111.6 (br)	1726	—	31.0 t($CN\underline{C}H_3$) $^3J(Pt—C)$ 22.5	16.4 dt $^1J(P—C)$ 40.3 $^2J(Pt—C)$ 40.3	8.1 dt $^2J(P—C)$ 3.75 $^3J(Pt—C)$ 37.8
cis-$[PtCl_2(CNBu\text{-}t)(PEt_3)]$	n.o.			59.4 s($CN\underline{C}Me_3$) 30.0 s($CNC\underline{Me}_3$)	16.5 dt $^1J(P—C)$ 40.3 $^2J(Pt—C)$ ~40	8.1 dt $^2J(P—C)$ ~3 $^3J(Pt—C)$ 30.2
cis-$[PtCl_2(CNC_6H_{11})(PEt_3)]$	111.4 (br)	1742		55.5 t(C_1) $^3J(PtC)$ ~18 32.0 s($C_{2,6}$) 22.8 s($C_{3,5}$) 24.6 s(C_4)	16.47 dt $^1J(P—C)$ 40.3 $^2J(Pt—C)$ 40.0	8.01 dt $^2J(P—C)$ 3 $^3J(Pt—C)$ 26.5
cis-$[PtCl_2(4\text{-}ClC_6H_4NC)(PEt_3)]$	122.1 (br) $^2J(P—C)$ ~ 15	1740	124.9 t $^3J(Pt—C)$ 25	127.7 t($C_{2,6}$) $^4J(PtC)$ ~8 130.3 s($C_{3,5}$) 136.9 s(C_4)	16.7 dt $^1J(P—C)$ 39.1 $^2J(Pt—C)$ 40.5	8.1 dt $^2J(P—C)$ 3.3 $^3J(Pt—C)$ 24
cis-$[PtCl_2(CNC_6H_5)(PEt_3)]$	120.2 (br)	1740		126.3 s($C_{2,6}$ + C_1) 130.0 s($C_{3,5}$) 130.8 s(C_4)	16.7 dt $^1J(P—C)$ 40.3 $^2J(Pt—C)$ 39.8	8.2 dt $^2J(P—C)$ 3.4 $^3J(Pt—C)$ 26
cis-$[PtCl_2(4\text{-}MeC_6H_4NC)(PEt_3)]$	120.3 (br)	1720	123.9 t $^3J(Pt—C)$ 24	126.0 t($C_{2,6}$) $^4J(PtC)$ ~12 130.5 s($C_{3,5}$) 141.4 s(C_4) 21.5 s($\underline{C}H_3C_6H_4$)	16.6 dt $^1J(P—C)$ 40.3 $^2J(Pt—C)$ 40.2	8.01 dt $^2J(P—C)$ ~3 $^3J(Pt—C)$ 25.2
cis-$[PtCl_2(4\text{-}MeOC_6H_4NC)(PEt_3)]$	114.0 (br)	n.o.	118.7 t $^3J(Pt—C)$ ~24	115.2 s($C_{3,5}$) 127.8 s($C_{2,6}$) 160.8 s(C_4) 55.9 (OCH_3)	16.7 dt $^1J(P—C)$ 40.3 $^2J(Pt—C)$ 40.3	8.15 dt $^2J(P—C)$ ~3 $^3J(Pt—C)$ ~30
cis-$[PtCl_2(CNC_6H_{11})_2$	105.8 (br)	n.o.		55.82 s(C1) 31.80 s($C_{3,6}$) 22.57 s($C_{3,5}$) 24.70 s(C4)		

TABLE 1 (Continued)

Complex[b]	δ(C)	^1J(Pt—C)	δ(C^1)	CN$\underline{R}$	P$\underline{C}H_2$[c]	$PCH_2\underline{C}H_3$
cis-[$PdCl_2(4\text{-}MeOC_6H_4NC)(PEt_3)$]	114.3[d] ^2J(P—C) ~15		117.3	115.2 s($C_{3,5}$) 128.2 s($C_{2,6}$) 161.5 s(C_4) 55.9 s(OCH_3)	18.1 d ^1J(P—C) 33.6	8.4 d ^2J(P—C) 3.0

[a] In $CDCl_3$ solution, relative to $SiMe_4$; δ values ppm, coupling constants in Hz (±0.1). [b] Cationic complexes as ClO_4 salts. [c] $|^1J + {}^3J|$ = parameter for phosphorus—phosphorus coupled spectrum, see refs. 1 and 2. [d] Tentative assignment — weak signal, s = singlet, t = triplet, tt = triplet of triplets, d = doublet, dt = doublet of triplets, n.o. = not observed, (br) = broad, m = masked by other absorbtions. Ring carbon atoms numbered as



resolved in most cases. It has been most clearly observed in complexes of aliphatic isonitriles, either *trans*-[PtX(CNR)(PEt$_3$)$_2$]$^+$ (X = Cl or Br; R = Me, t-Bu or C_6H_{11}) or *cis*-[PtCl$_2$(CNR)(PEt$_3$)] and the observed value of ^1J(Pt—C) (Table 1) in the region of 1720—1742 Hz, is close to the value of ^1J(Pt—CO) observed for analogous carbonyl compounds [1,2,5]. There appears to be little dependence of ^1J(Pt—C) upon the *trans*-halide ligand in these isonitrile complexes, as was also observed for the carbonyl analogues [5]. Although we have been able to observe ^2J(P—C) for the carbonyl complex *trans*-[PtCl(CO)-(PEt$_3$)$_2$]$^+$ (Table 1) there was insufficient resolution in the spectra of the isonitrile analogues to allow measurement of their corresponding parameter. Chemical shift data and ^3J(Pt—C) values for the aliphatic substituents of the isonitriles are also shown in Table 1.

Similar data have also been obtained for analogous complexes with the ligands-CNC$_6$H$_4$R^1 (R^1 = H, Me, OMe, Cl or NO$_2$) and CN(2,6-C$_6$H$_3$Cl$_2$). The values of ^1J(Pt—C), where observed, are in the same range as those of complexes of aliphatic isonitriles (Table 1). The chemical shifts of the carbon atoms of the phenyl rings (Table 1) have been assigned on the basis of ^{195}Pt coupling (where observed), the relative magnitude of chemical shifts (e.g. C$_4$ of 4-MeOC$_6$H$_4$NC is at low field, ca. 161 ppm below SiMe$_4$) and to some extent relative integration. Occasionally, overlap or coincidence of resonance absorptions occurs (Table 1). Again the terminal isonitrile carbon signal is poorly resolved, but in some cases an approximate value of ^2J(P—C) (15 Hz) has been obtained. The shifts of the ligating isonitrile carbon atoms (δ(C), ppm) are found in the range 105—125 ppm downfield from SiMe$_4$. This range is higher than that observed for the free ligands (about 154—165 ppm downfield from SiMe$_4$ [3]). This effect also occurs in isonitrile complexes of other transition metals, but not for complexes of the σ-acceptor, BMe$_3$ [3]. Values of δ(C) for some t-BuNC complexes are shown in Table 2 to demonstrate this phenomenon. It is difficult to draw any convincing conclusion about this difference since these complexes are neither isostructural nor isoelectronic, but it appears that among the factors which affect the chemical shift, the shielding effect of the non-bonding *d*-electrons of the transition metals must be important.

We also note that when a decrease of oxidation state and coordination number of rhodium occurs on passing from [RhI(Me)(CNBu-t)$_4$]$^+$ to [Rh(CNBu-t)$_4$]$^+$, the value of ν(CN) decreases and δ(C) moves to lower field [6]. This probably reflects the increase of π-character in the Rh—C bond, a similar trend is also ob-

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TABLE 2

^{13}C DATA FOR SOME CNBu-t COMPLEXES

	δ(C)	$\Delta\delta$ ^{a}	ν(CN)	$\Delta\nu$(CN) ^{b}	Reference
CNBu-t	154.4	—	2134	—	3
BMe$_3$ · CNBu-t	157.8	+3.4	2247	+113	3
[Mo(CN)$_4$(CNBu-t)$_4$]	136.0	—18.4	2212	+78	13
[Rh(CNBu-t)$_4$]$^+$	130.7	—23.7	2168	+34	6
[RhI(Me)(CNBu-t)$_4$]$^+$	123.0	—31.4	2220	+86	6
trans-[PtCl(CNBu-t)(PEt$_3$)$_2$]$^+$	109.6	—44.8	2235	+101	this work

^{a} $\Delta\delta = \delta(C)_{complex} - \delta(C)_{ligand}$. ^{b} $\Delta\nu = \nu(NC)_{complex} - \nu(NC)_{ligand}$.

TABLE 3

^{13}C DATA FOR OSMIUM AND RUTHENIUM COMPLEXES [a]

Complex [b]	δ(C)	$CN\underline{C}H_3$	CN_{aryl}	$P—\underline{C}H_2$	$P—CH_2—\underline{C}H_3$	$P—C_6H_5$
$[OsCl_2(MeNC)_2(PEt_3)_2]$ (C)	144.6 (br)t $^2J(P—C)$ 12	29.6 s		15.53 t $\|^3J + {}^1J\|$ 24.1	7.38 s	
$[OsCl_2(MeNC)_2(PEt_2Ph)_2]$ (C)	142.4 t $^2J(P—C)$ 12.1	28.6 s		14.0 t $\|^3J + {}^1J\|$ 30.5	7.33 s	136.8 t(1) $\|^3J + {}^1J\|$ 41.5 130.47 t($C_{2,6}$) $\|^4J + {}^2J\|$ 7.5 127.9 t($C_{3,5}$) $\|^5J + {}^3J\|$ 5.4 128.15 s(C_4)
$[OsCl_2(MeNC)_2(PEt_3)_2]$ (D)	124.7 (br)	29.8 s		16.11 t $\|^3J + {}^1J\|$ 30.0	7.96 s	
$[OsCl_2(MeNC)(PMe_2Ph)_3]$ (A)	142 (br)m	28.5 s		12.7 t(*trans*) $\|^1J + {}^3J\|$ 32.6 13.6 d(*cis*) $^1J(P—C)$ 30.0		130.7—127.9 m
$[OsCl(MeNC)_2(PEt_3)_3]^+$ (F)	128 (br)	30.5 30.2 s		17.6 t(*trans*) $\|^1J + {}^3J\|$ 31.0 18.3 d(*cis*) $^1J(P—C)$ 29	8.0 (br) t(*trans*) 8.9 d(*cis*) $^2J(P—C)$ 4.8	

[$OsCl_2(CNC_6H_5)_2(PEt_3)_2$] (C)	152.8 t ^2J(P—C) ~13	126.2 s($C_{2,6}$) 129.5 s($C_{3,5}$) 127.9 s ^{c}	15.73 t $\|^1J + {}^3J\|$ 27.1	7.57 s	
[$OsCl_2(CNC_6H_5)_2(PEt_3)_2$] (D)	147 br	131.1 s(C_4) 129.5 s($C_{3,5}$) 126.8 s(C_1) 125.6 s($C_{2,6}$)	15.39 t $\|^1J + {}^3J\|$ 30.0	7.67 s	
[$OsCl_2(4\text{-}NO_2C_6H_4NC)_2(PEt_3)_2$] (C)	n.o.	146.3 s(C_4) 127.1 s($C_{2,6}$) 125.4 s($C_{3,5}$) 134.1 s(C_1)	15.73 t $\|^1J + {}^3J\|$ 30.5	7.52 s	
[$OsCl_2(4\text{-}MeOC_6H_4NC)_2(PBu\text{-}n_2Ph)_2$] (C)	150.6 t ^2J(P—C) 12.6	158.6 s(C_4) 122.0 s(C_1) 113.8 s($C_{3,5}$) 127.5 s($C_{2,6}$) 55.4 s(OCH_3)	21.45 t $\|^2J + {}^4J\|$ 12.3	24.27 t $\|^2J + {}^4J\|$ 12.3 25.29 s [$P(CH_2)_2CH_2$] 13.88 s [$P(CH_2)_3CH_3$]	137.2 (C_1) $\|^3J + {}^1J\|$ 43.6 130.5 ($C_{2,6}$) $\|^4J + {}^2J\|$ 8.4 127.9 ($C_{3,5}$) $\|^5J + {}^3J\|$ 7 128.1 (C_4)
[$RuCl_2(CNC_6H_5)_2(PMe_2Ph)_2$] (H) ^{d}	149.9 (br)	126.2 128.2 P—C_6H_5 + 128.5 CNC_6H_5 128.9 129.8	14.2 d(PCH_3) ^1J(P—C) 15.9		

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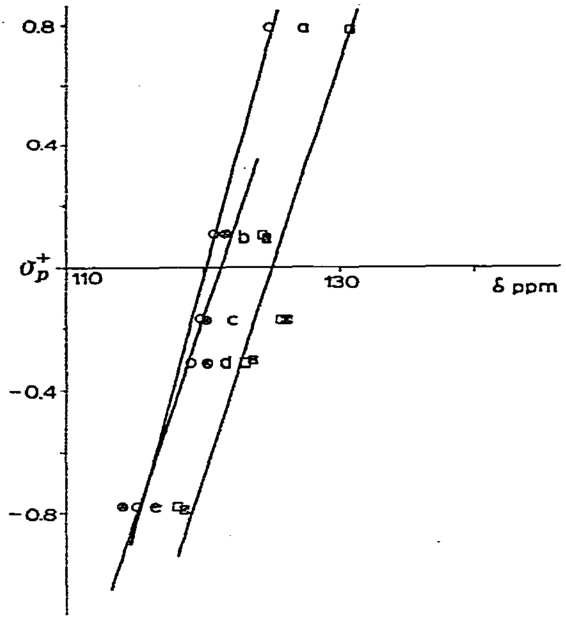
[a] In $CDCl_3$ solution relative to $SiMe_4$, δ in ppm, J values in Hz (± 0.1). [b] Configuration (see ref. 11) in parentheses. [c] Either C_1 or C_4, one being masked. [d] *cis*-Phosphines (see ref. 12). (br) = broad; (br)t = broad triplet; t = triplet, d = doublet, n.o. = not observed, m = multiplet, s = singlet. Ring carbons labeled as in Table 1.

served in carbonyl complexes [5,7]. There appears to be no correlation of δ(C) with ν(CN) values since in the $BMe_3\cdot CNBu\text{-}t$ adduct, ν(NC) increases as a result of σ-electron-withdrawal and a downfield shift of δ(C) occurs, whereas the transition metal complexes also show an increase of ν(NC), but an upfield shift of δ(C) (Table 2).

A correlation is obtained, however, if the δ(C) values or the chemical shift [$\delta(C^1)$] of the aromatic carbon atom attached to the nitrogen atom in $4\text{-}R^1C_6H_4NC$ (R^1 = H, Me, OMe or NO_2) are plotted vs. the Hammett $\sigma_p{}^+$-values [8] of the R^1 substituents (Fig. 1). Thus the electronic effects of the R^1 substituents are transmitted along the delocalised system of these ligand and affect the isonitrile carbon. This interaction would be expected to influence the reactivity of the isonitrile carbon atom. The order of reactivity of isonitriles ($4\text{-}R^1C_6H_4NC$) ligating palladium towards amines as attacking nucleophiles (NO_2 > Cl > H > Me > MeO in order of R^1) deduced from kinetic studies [9], is similar to the order of both δ(C) and $\delta(C^1)$ shown in Fig. 1. It can thus be reasonably predicted that a similar order of reactivity will occur for platinum complexes and that the more deshielded is the isonitrile carbon atom in these particular platinum compounds, the more susceptible is that atom to nucleophilic attack. This correlation also extends to the aliphatic isonitriles in the sense that the chemical shift of their carbon atoms is to high field of their aromatic analogues, in keeping with their lower reactivity in this series of complexes towards nucleophiles [10]. Probably the ^{13}C NMR parameters of the analogous palladium complexes [11], one example of which is shown in Table 1, will show a similar effect.



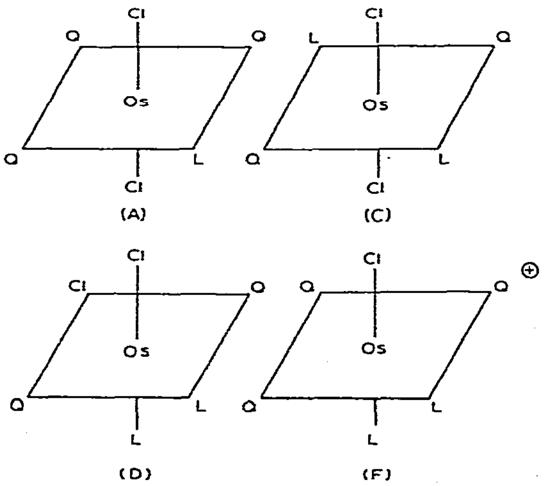


Fig. 1. σ_p^+ vs. δ(C) and $\delta(C^1)$ for platinum complexes. δ(C) = ○ (*trans* complex) and ⊖ (*cis* complex); $\delta(C^1)$ = □ (*trans* complex) and ▣ (*cis* complex); a, R^1 = 4-NO_2; b, R^1 = 4-Cl; c, R^1 = 4-H; d, R^1 = 4-Me; e, R^1 = 4-OMe.

Fig. 2. Configuration of osmium complexes. Q = $PR^2{}_3$; L = RNC.

(b) Osmium and ruthenium complexes

The spectral parameters and assignments for these compounds are shown in Table 3. Again the parameters of the phosphine ligands, particularly those having only aliphatic groups, are similar to those obtained in related systems and like ^1H NMR parameters, appear to be useful in deducing the stereochemistry of the phosphine groups [1,2].

The isonitrile carbon resonance is clearly observed for most complexes of this series and, where directly analogous compounds can be compared (see Fig. 2 for configurations [12]) e.g. $[OsCl_2(CNR)_2(PEt_3)_2]$ (C isomer)(R = Me or C_6H_5) [12] the δ(C) value for aliphatic isonitriles is to high field of the value for aromatic isonitriles. The value of δ(C) for isonitrile *trans* to chloride (D isomers) is to high field of the value for isonitrile *trans* to isonitrile (C isomers) and thus one might cautiously anticipate a *trans*-influence series for these six-coordinate compounds resembling that observed for the square planar platinum(II) series of carbonyls [1,2,5], although a far wider range of measurements are clearly needed.

Ruthenium compounds, as judged from the spectrum of $[RuCl_2(PhNC)_2(PMe_2Ph)_2]$ (H isomer see ref. 12) (Table 3), shows similar behaviour to their osmium analogues.

Experimental

Isonitriles [12] and their platinum [10], palladium [11], osmium [12] and ruthenium [12] complexes were prepared and purified by published methods. NMR spectra were obtained on a Jeol PS 100 spectrometer, at 25°C, operating in the Fourier Transform mode at 25.155 MHz using solvent deuterium lock. A few mg of $[Fe(pd)_3]$ (pd = pentane-2,4-dionate) were added to the sample solutions as routine and chemical shifts (ppm) are measured relative to $SiMe_4$. Repetition time was 1 sec. over at least 8000 data points.

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