Platinum–Donor Atom Spin–Spin Coupling Constants in Complexes with Dimethyl Selenide and Dimethyl Telluride

By PETER L. GOGGIN, ROBIN J. GOODFELLOW,* and STEVE R. HADDOCK
(*Department of Inorganic Chemistry, The University, Bristol* BS8 1TS)

Summary The values of ^1J (^{195}Pt–^{77}Se) and ^1J (^{195}Pt–^{125}Te) for $[PtX_3SeMe_2]^-$, $[PtX_5SeMe_2]^-$, and $[PtX_3TeMe_2]^-$ (X = Cl, Br, or I) obtained by heteronuclear INDOR spectroscopy decrease markedly in the order Cl > Br > I and are much less than the values of ^1J (^{195}Pt–^{125}Te) in $[(PtX_3)_2TeMe_2]^{2-}$ (X = Cl or Br) which were obtained by direct Fourier transform n.m.r. spectroscopy.

THERE has been wide interest in the values of metal–donor atom spin–spin coupling constants in complexes,[1] especially the comparison of such values in similar species *e.g. cis*-$[PtCl_2(PBu^n_3)_2]$ and *cis*-$[PtCl_4(PBu^n_3)_2]$[2]. Discussions have normally been based on the assumptions that, for a given ligand, the values are governed solely by the hybridisation of the metal and the *s*-orbital bond order of the metal–ligand bond, *i.e.*, changes in hybridisation of the donor atom are unimportant. Systematic studies of trends in metal-donor atom coupling constants have been largely confined to cases in which all valence shell electrons of the donor atom are involved in bonding. Typically, in the series $[PtX_3PMe_3]^-$ and $[PtX_5PMe_3]^-$(X = Cl, Br, or I) the values of ^1J (^{195}Pt–^{31}P) do not show any large (percentage) dependence on the halide.[3] We have now obtained results for ^1J (^{195}Pt–^{77}Se) and ^1J (^{195}Pt–^{125}Te) in some related complexes by INDOR measurements.

Notable features of these coupling constants–reduced coupling constants (see Table) are: (i) they are much smaller than those from ^{195}Pt to ^{31}P; (ii) the percentage decrease from Cl through Br to I is much greater than in any series previously reported; and (iii) in the series $[PtX_5SeMe_2]^-$, the sign reverses between Br and I. Observation (i) might be accounted for in terms of weaker or less covalent bonds for chalcogen donors and the consequential greater similarity of *trans*-influence between these and halides may then

TABLE

Platinum–donor atom spin–spin coupling constants

X		^1J (^{195}Pt–A)^a/Hz			^1K (^{195}Pt–A)^a/10^{20}NA^2 m^{-3}	
	Cl	Br	I	Cl	Br	I
$Bu^n_4N[PtX_3SeMe_2]$	+ 670	+ 507	+ 234	+135·9	+102·8	+ 47·5
$Bu^n_4N[PtX_5SeMe_2]$	+ 259	+ 101	− 68	+ 52·5	+ 20·5	− 13·8
$Bu^n_4N[PtX_3TeMe_2]$	−1553	−1092	− 400	+190·4	+133·9	+ 49·0
$(Bu^n_4N)_2[(PtX_3)_2TeMe_2]$ ..	5923	5088	—	726·0	623·7	—
$Pr^n_4N[PtX_3PMe_3]$	+3674	+3542	+3377	+351·5	+338·9	+323·1
$Pr^n_4N[PtX_5PMe_3]$	+2119	+2095	+2181	+202·7	+200·4	+208·7

[a] A = ^{77}Se, ^{125}Te, or ^{31}P respectively.

account for (ii). However (iii) shows that the behaviour parallels that of $^1J_{PP}$ which Finer and Harris[4] have explained by an extension of the theory of Pople and Santry.[5] Since the lone pair can be regarded as a substituent of very low electronegativity, it will favour less positive values of the metal donor coupling constant. As the electronegativity of the halides co-ordinated to platinum decreases (Cl > Br > I), the coupling constant should become more negative as observed. Because of the change of co-ordination number, the *s*-orbital contribution to the metal–donor bond should be lower in platinum(IV) complexes than platinum(II) complexes resulting in a less positive coupling constant. In a situation such as this where the values of a coupling constant are low because of competition between terms of opposite sign, ratios of coupling constants will be of doubtful significance. Thus the fact that the ratios of the coupling constants in *cis*- and *trans*-$[PtCl_2L_2]$ are similar for K (^{195}Pt–^{77}Se) (L = $SeMe_2$) and K (^{195}Pt–^{31}P) (L = PEt_3)[6] must be fortuitous.

A demonstration that the low value of these coupling constants is related to the presence of the lone pair might be provided by complexes analogous to the recently reported[7] anions $[(PtX_3)_2SMe_2]^{2-}$ where both the lone pairs of the ligand are involved in bonding. We have not been able to obtain any evidence for the formation of such species with dimethyl selenide but the reaction of $2[PtX_3TeMe_2]^-$ with $[Pt_2X_6]^{2-}$ (X = Cl or Br) yielded the required dimethyl tellurium complexes. No obvious ^{125}Te satellites could be identified in their ^{1}H n.m.r. spectra, precluding ^{1}H{^{125}Te} INDOR studies. However, the resonant frequency of ^{125}Te at 2·14 T is sufficiently close to that of ^{11}B to allow satisfactory spectra to be obtained with a JEOL PFT 100 Fourier transform n.m.r. spectrometer equipped for ^{11}B, after readjustment of the pulse amplifier and 'Analytical Tuning.' For 0·5M solutions (in an 8 mm tube) *ca.* 50,000 pulses were required to obtain well defined spectra including the ^{195}Pt satellites. The coupling constants are very much larger than in the anions $[PtX_3TeMe_2]^-$ and indeed the reduced coupling constant in $[(PtCl_3)_2TeMe_2]^{2-}$ is now about twice that in $[PtCl_3PMe_3]^-$. There is still a much larger percentage drop from the chloride to the bromide than in the trimethyl phosphine complexes and so these changes probably do reflect the greater similarity of *trans*-influence between dimethyl telluride and halide than between phosphines and halide.

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