NOTE

31P NUCLEAR MAGNETIC RESONANCE SPECTRA OF SOME ARYL, SILYL AND GERMYL DERIVATIVES OF PLATINUM(II)

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Bonds from silicon or germanium to platinum can be classified as metal–metal bonds, but in their mode of formation, and in their reactions, they also have a considerable resemblance to aryl– and alkyl–platinum bonds[1,2]. In this paper, we examine the way in which phosphine–platinum bonds are affected by the presence of the ligand atoms C, Si and Ge, and some data for complexes containing Cl, Br and I have been included for comparison.

Platinum–phosphorus coupling constants, ^1J(Pt–P), in platinum(II) complexes of a given phosphine have been shown to depend on the covalency of the Pt–P bond and on the s-character of the platinum orbital used in the bond[3]. This latter dependence arises because only the s-orbitals have non-vanishing values at the nucleus. The couplings are therefore small when the phosphorus atom is *trans* to a ligand of high *trans*-influence[3] such as Me, Ph, or R_3P, because the Pt–P bond is made less covalent, and the couplings are large when *trans* to such ligands as the halides. Variation of the ligands *cis* to the phosphine causes rather smaller changes in J[3]. Thus, for the phenyl–platinum compounds in the Table, the couplings are *ca.* 2.8 kcps *trans* to R_3P, *ca.* 1.65 kcps *trans* to Ph and *ca.* 4 kcps *trans* to Cl, so there are two very different couplings in *cis*-[PtPhCl(Et$_3$P)$_2$].

The 31P-spectra of the compounds [PtXY(PhMe$_2$P)$_2$] [X=Cl, Br; Y=Si, Ge radical) have a single resonance split by interaction with platinum nuclei, so they must be in the *trans* configuration in solution. The disilyl and the digermyl complexes are assigned to the configurations given in Table 1 by comparing the magnitudes of their couplings with those of the two isomeric diphenyl complexes. This comparison is not invalidated by the change of phosphine from PhMe$_2$P to Et$_3$P, since Grim *et al.*[4] have shown that, in similar complexes, these ligands give couplings differing only by *ca.* 30 cps.

By comparing the couplings in the *cis* and *trans* phenyl and silyl complexes with the corresponding dihalide complexes, it is clear that the phenyl and silyl groups (and probably also the germyl group) tend to reduce the coupling constants in the *trans* bonds very markedly, and to increase the coupling in the *cis* bonds slightly. Since the phenyl group has been shown to be very similar to the methyl group in this

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TABLE 1

^{195}Pt–^{31}P COUPLING CONSTANTS AND ^{31}P CHEMICAL SHIFTS IN PLATINUM(II) COMPLEXES

Complex	J(cps)	δ(ppm)^a
cis-[PtPh$_2$(Et$_3$P)$_2$]^b	1704	−3.5
trans-[PtPh$_2$(Et$_3$P)$_2$]^b	2824	−8.0
cis-[PtPhCl(Et$_3$P)$_2$]^b	4138	−3.1
	1577	−9.2
trans-[PtPhCl(Et$_3$P)$_2$]^b	2800	−13.6
cis-[Pt(Ph$_2$MeSi)$_2$(PhMe$_2$P)$_2$]^{b,c}	1559	+8.3
trans-[Pt(Ph$_2$MeGe)$_2$(PhMe$_2$P)$_2$]^b	2629	+3.6
trans-[PtCl(Ph$_3$Ge)(PhMe$_2$P)$_2$]^b	2667	+8.4
trans-[PtCl(Ph$_3$Si)(PhMe$_2$P)$_2$]^b	2772	+5.0
trans-[PtCl{(p-CF$_3$C$_6$H$_4$)$_3$Si}(PhMe$_2$P)$_2$]^b	2633	+4.9
trans-[PtCl(Cl$_3$Si)(PhMe$_2$P)$_2$]^b	2873	+2.5
trans-[PtCl(Ph$_2$MeSi)(PhMe$_2$P)$_2$]^b	2842	+3.4
trans-[PtBr(Ph$_2$MeSi)(PhMe$_2$P)$_2$]^b	2822	+4.7
cis-[PtCl$_2$(Bu$_3$P)$_2$]^c	3502	−0.9
cis-[PtBr$_2$(Bu$_3$P)$_2$]^c	3477	−1.1
cis-[PtI$_2$(Bu$_3$P)$_2$]^c	3345	+1.7
trans-[PtCl$_2$(Bu$_3$P)$_2$]^c	2400	−4.3
trans-[PtBr$_2$(Bu$_3$P)$_2$]^c	2327	+1.0
trans-[PtI$_2$(Bu$_3$P)$_2$]^c	2265	+8.0

^{a} Shift from 85% phosphoric acid. ^{b} Dissolved in benzene. ^{c} Dissolved in dichloromethane.

respect[3], the origin of the effect is almost certainly an inductive interaction through the σ-electrons, rather than the π-electrons, of the complex. Thus, the ligand atoms C and Si have strong σ-inductive effects which increase slightly in the order C < Si and the principal consequence of which is to cause the bonds trans to these ligand atoms to have low covalent characters. The couplings in the trans complexes decrease slightly in the order of ligand atoms C > Si > Ge which is similar to the order Cl > Br > I found in the dihalide complexes, so within each of these two sets there may be a relation between the inductive effects and the electronegativities of the ligand atoms. However, the very different inductive effects of C and I, both of which have a Pauling electronegativity[5] of 2.5, shows that the inductive effect is not only a function of the electronegativity of the ligand atom.

The large inductive effects of Si and Ge have also been detected by the low stretching frequencies of trans Pt–Cl bonds[2], but in these compounds there is some possibility that the normal modes involve significant contributions from the vibrations of more than one metal–ligand bond, so such measurements may be unsuitable for *comparing* the inductive effects of the Group IV atoms.

EXPERIMENTAL

Most of the complexes were available in this laboratory[6]. The preparations of the phenyl[7] and the dihalide[8] complexes have been described fully, and the preparations of some of the silyl and germyl complexes have been given in a preliminary communication[2].

The NMR spectra were recorded at 24.29 Mcps using a Perkin–Elmer R10

Spectrometer and a stationary 8.5 mm sample tube. The shifts of the more soluble complexes were measured relative to an external 85% phosphoric acid sample. To obtain satisfactory spectra of the less soluble complexes, repetetive scanning of the spectra was used, in conjunction with an NS 544 Digital Memory Oscilloscope. This technique requires the use of a capillary of phosphorus(III) oxide to provide a trigger signal, so it is convenient to measure the shifts relative to this resonance. All the shift data in the Table are given relative to 85% phosphoric acid, which was found to be 112.5 ppm to high field of the trigger signal[9].

REFERENCES

1 F. GLOCKLING AND K. A. HOOTON, J. Chem. Soc., A, (1968) 826; E. H. BROOKS AND F. GLOCKLING, J. Chem. Soc., A, (1966) 1241; R. J. CROSS, Organometal. Chem. Rev., 2 (1967) 97.
2 J. CHATT, C. EABORN AND S. IBEKWE, Chem. Commun., (1966) 700.
3 A. PIDCOCK, R. E. RICHARDS AND L. M. VENANZI, J. Chem. Soc., A, (1966) 1707; F. H. ALLEN AND A. PIDCOCK, submitted for publication.
4 S. O. GRIM, R. L. KEITER AND W. MCFARLANE, Inorg. Chem., 6 (1967) 1133.
5 L. PAULING, The Nature of the Chemical Bond, Cornell University Press, New York, 3rd ed., 1960, p. 93.
6 J. CHATT, C. EABORN, S. IBEKWE AND P. N. KAPOOR, unpublished work.
7 J. CHATT AND B. L. SHAW, J. Chem. Soc., (1959) 4020.
8 GMELIN, Handbuch der anorganischen Chemie, No. 68, Platinum (D), 8th ed., Verlag Chemie, Weinheim/Bergstrasse, 1957.
9 A. C. CHAPMAN, J. HOMER, D. J. MOWTHORPE AND R. T. JONES, Chem. Commun., (1965) 121.