Unsaturated σ-Hydrocarbyl Transition-metal Complexes. Part 4.[1] Crystal and Molecular Structure of *trans*-Chlorobis(diethylphenylphosphine)-(phenylethynyl)platinum(II) and Comments on the Relative *trans* Influence of Various Carbon Ligands †

By **Christine J. Cardin, David J. Cardin, Michael F. Lappert,*** and **Kenneth W. Muir,*** School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ

The molecular structure of *trans*-[PtCl(C≡CPh)(PEt$_2$Ph)$_2$] has been determined by *X*-ray diffraction methods. The crystals are monoclinic, space group $P2_1$, with $a = 12.359(3)$, $b = 13.015(3)$, $c = 9.031(2)$ Å, $\beta = 101.65(2)°$, and $Z = 2$. The structure has been solved by the heavy-atom method and refined by full-matrix least squares to *R* 0.046 for 1 877 diffractometric intensity data. The crystals contain discrete molecules in which the platinum co-ordination is square planar. The phenylethynyl group is non-linear, with a Pt–C≡C angle of 163(2)°. Selected bond lengths are Pt–Cl 2.407(5) and Pt–C 1.98(2) Å. The structural *trans* influences of C≡CPh, CH=CH$_2$, and CH$_2$SiMe$_3$ ligands in platinum(II) complexes are compared; there is only a small dependence on hybridization at the ligating carbon atom.

THE present structure determination completes our study of the relation between the *trans* influence and the hybridization state of carbon atoms in σ-hydrocarbyl complexes of Pt^{II}.[1-3] We have previously described the structures of the complexes *trans*-[PtCl(R)(PR'$_2$Ph)$_2$] (R' = Me or Et) where R = CH$_2$SiMe$_3$ [4] or CH=CH$_2$.[1,3] In the title complex R is the σ-alkynyl ligand C≡CPh. The preparation and spectroscopic properties of this and related species were reported in Part 2.[2]

EXPERIMENTAL

Crystal Data.—$C_{28}H_{35}ClP_2Pt$, $M = 664.1$, Monoclinic, $a = 12.359(3)$, $b = 13.015(3)$, $c = 9.031(2)$ Å, $\beta = 101.65(2)°$, $U = 1\,422.7$ Å^3, $D_m = 1.55$, $Z = 2$, $D_c = 1.550$ g cm^{-3}, $F(000) = 656$, space group $P2_1$, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 64.4 cm^{-1}.

Measurements.—Weissenberg and precession photographs yielded preliminary cell dimensions and indicated that the space group was either $P2_1$ or $P2_1/m$. A successful structural model has been derived in $P2_1$. Final values of the unit-cell parameters and the intensities of all the independent reflections with θ(Mo-K_α) $\leqslant 25°$ were measured on a Hilger and Watts Y290 instrument equipped with a zirconium β filter. For reflections having θ(Mo-K_α) $\leqslant 10°$ the intensities of the $\pm(hkl)$ Friedel pairs were also measured. A symmetrical θ—2θ scan was used for all the intensity measurements; 1.3-s counts were taken at intervals of 0.01° over a range of 0.55° in θ. The intensities of three strong reflections, periodically remeasured during the experiment, varied by $< \pm 3\%$ of their mean values.

Structure amplitudes and their standard deviations were derived in the usual way (q 0.05).[1] No correction was made for absorption since the transmission factors on F^2 were in the small range 0.59—0.63. 1 877 Reflections with $I \geqslant 3\sigma(I)$ (72% of those measured) were used in the subsequent analysis. The rapid decrease in intensity with scattering angle and the resulting low number of reflections with intensities above background are caused partly by higher than average thermal motion and partly by the small size of the crystals available; the dimensions of the specimen used for intensity measurement were 0.2 × 0.1 × 0.1 mm.

Structure Analysis.—The platinum atom was located from the Patterson function, and the other atoms, apart from hydrogen, from subsequent difference syntheses. The structure was refined by full-matrix least-squares minimization of $\Sigma[(|F_o| - |F_c|)/\sigma(F_o)]^2$. Atomic-scattering factors were taken from ref. 5 except for those of platinum [6] and

TABLE 1

Atomic parameters (fractional co-ordinates, × 10^3 for carbon atoms, × 10^4 for others)

Atom	*x*	*y*	*z*
Pt	2 314(1)	2 500	2 447(1)
P(1)	579(4)	2 055(4)	1 212(6)
P(2)	4 062(4)	3 022(4)	3 694(6)
Cl	1 830(6)	4 294(4)	2 330(8)
C(1)	270(2)	102(1)	254(3)
C(2)	264(2)	12(2)	252(2)
C(3)	266(2)	−98(2)	262(3)
C(4)	320(2)	−155(2)	179(3)
C(5)	324(2)	−261(5)	176(3)
C(6)	258(3)	−300(2)	275(4)
C(7)	200(2)	−252(6)	357(4)
C(8)	206(2)	−146(2)	344(3)
C(9)	−45(2)	307(2)	62(3)
C(10)	−96(2)	350(3)	192(3)
C(11)	64(2)	139(2)	−54(3)
C(12)	121(2)	211(2)	−164(3)
C(13)	−14(2)	116(2)	227(2)
C(14)	22(2)	110(2)	384(3)
C(15)	−35(2)	45(2)	463(3)
C(16)	−119(2)	−16(2)	392(3)
C(17)	−150(2)	−4(2)	248(3)
C(18)	−102(2)	59(2)	154(3)
C(19)	402(2)	365(2)	549(3)
C(20)	359(2)	295(2)	661(3)
C(21)	510(2)	204(2)	420(3)
C(22)	551(2)	159(2)	286(3)
C(23)	476(2)	395(2)	266(2)
C(24)	572(2)	442(2)	343(3)
C(25)	628(2)	511(2)	267(3)
C(26)	589(2)	530(3)	120(4)
C(27)	487(3)	489(3)	45(3)
C(28)	432(2)	420(2)	121(2)

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* *Present address:* Department of Chemistry, University of Glasgow G12 8QQ.

† No reprints available.

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hydrogen.[7] Allowance was made for the anomalous scattering of the platinum, phosphorus, and chlorine atoms.[8] Anisotropic temperature factors were used only for these atoms. No significant differences in intensity were found among the 112 Friedel pairs of reflections. The choice of hand (x,y,z or $\bar{x},\bar{y},\bar{z}$) was therefore made by comparing refined mirror-image models.

Fixed contributions for the scattering of the hydrogen atoms were added to the structure factors. The refinement converged finally at R 0.046 and R' 0.048. Atomic parameters including temperature factors, bond lengths, bond angles, torsion angles, and observed and calculated structure amplitudes are listed in Supplementary Publication No. SUP 22147 (19 pp.).* Final atomic co-ordinates and selected bond lengths and angles are presented in Tables 1 and 2. A view of the molecule is shown in the Figure. The computer programs used have been described previously.[1]

TABLE 2

Selected bond lengths (Å) and angles (°)

(*a*) Bond lengths

Pt–Cl	2.407(5)	P(1)–C(9)	1.84(2)
Pt–P(1)	2.283(5)	P(1)–C(11)	1.82(2)
Pt–P(2)	2.327(5)	P(1)–C(13)	1.84(2)
Pt–C(1)	1.98(2)	P(2)–C(19)	1.82(2)
C(1)–C(2)	1.18(3)	P(2)–C(21)	1.80(2)
C(2)–C(3)	1.44(3)	P(2)–C(23)	1.84(2)

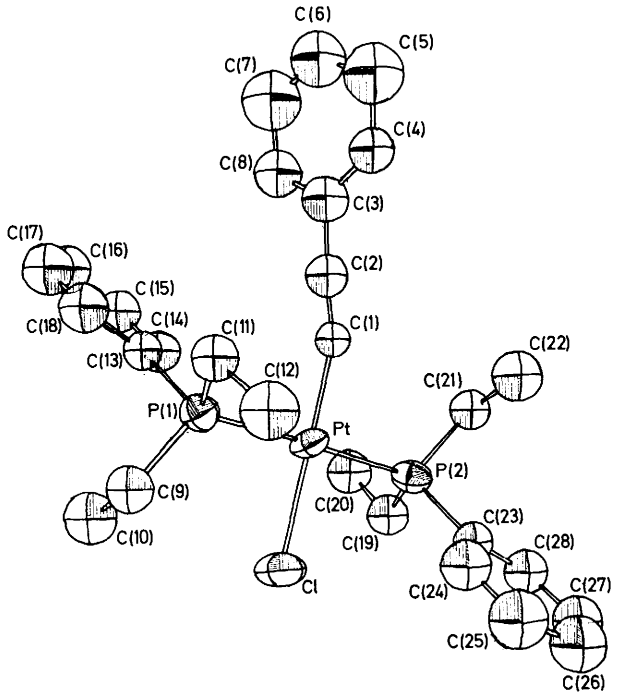
(*b*) Bond angles

Cl–Pt–P(1)	91.4(2)	P(1)–Pt–P(2)	177.7(2)
Cl–Pt–P(2)	86.3(2)	Cl–Pt–C(1)	179.6(7)
C(1)–Pt–P(1)	88.2(6)	Pt–C(1)–C(2)	163(2)
C(1)–Pt–P(2)	94.1(6)	C(1)–C(2)–C(3)	174(2)
Pt–P(1)–C(9)	119(1)	Pt–P(2)–C(19)	112(1)
Pt–P(1)–C(11)	110(1)	Pt–P(2)–C(21)	117(1)
Pt–P(1)–C(13)	114(1)	Pt–P(2)–C(23)	115(1)
C(9)–P(1)–C(11)	104(1)	C(19)–P(2)–C(21)	104(1)
C(9)–P(1)–C(13)	103(1)	C(19)–P(2)–C(23)	105(1)
C(11)–P(1)–C(13)	105(1)	C(21)–P(2)–C(23)	102(1)

(*c*) Means *

P–C	1.827(9)	C–P–C	103.9(4)
C–C	1.56[2]	P–C(sp^3)–C(sp^3)	113.0(9)
C=C	1.37(1)	X–C(sp^2)–C(sp^2)	119.9[7]

* Defined as $\Sigma w_i y_i/\Sigma w_i$, where y_i is an individual bond length or angle and w_i is the squared reciprocal of its standard deviation. The standard deviation of the mean is the greater of (*i*) $(\Sigma w_i)^{-\frac{1}{2}}$ (parentheses) and (*ii*) $[\Sigma w_i(y_i - \bar{y})^2/\{(n - 1)\Sigma w_i\}]^{\frac{1}{2}}$ (square brackets). The sums are over n individual measurements. X = P or C.



A view of the *trans*-[PtCl(C≡CPh)(PEt$_2$Ph)$_2$] molecule showing the atom-numbering scheme. Thermal ellipsoids enclose 50% probability

RESULTS AND DISCUSSION

The crystals contain discrete molecules with the expected *trans*-square-planar co-ordination at platinum. The shortest intermolecular contact between non-hydrogen atoms is that of 3.56 Å between C(6) and C(21$^{\mathrm{I}}$), where the superscript I indicates the transformation $1 - x, -\frac{1}{2} + y, 1 - z$ of the co-ordinates in Table 1. For reasons already discussed, the molecular geometry has been established with only moderate accuracy. The C–C bond lengths of the phenyl rings, for example, range between 1.29(4) and 1.42(5) Å. Since $\chi^2 = 16$ for 18 such distances, it appears that the standard deviations derived from the normal least-squares matrix represent realistic estimates of the true experimental errors.

The co-ordination of the platinum atom is distorted slightly from an accurately square-planar arrangement, apparently in order to relieve steric interactions between the ligands. The angles P(1)–Pt–Cl and P(2)–Pt–C(1) open slightly (to 91 and 94°), thus helping to relieve short contacts between C(9) and Cl and between C(1) and C(21) (respectively 3.33 and 3.32 Å). These contacts arise because the methylene carbon atoms C(9) and C(21) lie close to the metal co-ordination plane [the torsion angles C(1)–Pt–P(1)–C(9) and C(1)–Pt–P(2)–C(21) are respectively 180 and 2°]. We have previously noted the tendency of trialkyl- and dialkylaryl-phosphine ligands in platinum(II) complexes to adopt conformations such that an α-carbon atom is close to the metal co-ordination plane.[1] Usually the resulting overcrowding does not lead to serious out-of-plane distortions of the metal and ligand donor atoms {see, for example, the structure of *cis*-[PtCl$_2${C(NPhCH$_2$)$_2$}(PEt$_3$)]}.[9] In the present case none of the atoms Pt, Cl, P(1), P(2), and C(1) deviates from the plane of equation $-5.859x - 1.017y + 8.621z = 0.498$ by more than 0.001 Å.

The Cl $\cdots$ C(9) and C(1) $\cdots$ C(21) interactions are further relieved by minor distortions of the phosphorus valency angles; it is striking that Pt–P(1)–C(9) and Pt–P(2)–C(21) are the largest interbond angles at P(1)

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* For details see Notices to Authors No 7, *J.C.S. Dalton*, 1977, Index issue.

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and P(2) respectively. Other distances and angles within the phosphine ligands are normal. Close to staggered conformations are found about each of the P–C(methylene) bonds. Unlike *trans*-[PtCl(CH=CH$_2$)-(PEt$_2$Ph)$_2$],[1] where the platinum atom lies on a crystallographic diad axis, the phosphine ligands in *trans*-[PtCl(C≡CPh)(PEt$_2$Ph)$_2$] are related only approximately by a non-crystallographic symmetry centre located near the platinum atom. The Pt–P bond lengths differ by 0.044(7) Å, but their mean (2.305 Å) agrees well with the weighted average [2.302(1) Å] for Pt^{II}–P bond lengths in 22 complexes containing mutually *trans* tertiary phosphines of the type PR$_n$Ph$_{3-n}$ (R = alkyl, n = 0—3).[10]

Bond lengths and angles in the phenylethynyl ligand are compared with those in other alkynylplatinum(II) complexes [11-16] in Table 3. Most of these data are of low or unstated accuracy and firm conclusions are difficult to make. It is, however, apparent that the unusually small Pt–C≡C angle of 163(2)° in *trans*-[PtCl-(C≡CPh)(PEt$_2$Ph)$_2$] is not a general feature of alkynylplatinum(II) species. Similarly, the Pt–C≡N angle of 165° in *cis*-[PtCl$_2$(CNPh)(PEt$_3$)] [17] is not a general feature of platinum(II) isocyanides.[18] We consider that crystal-packing forces may explain the deformation of Pt–C≡C (and Pt–C≡N) angles by up to 20° from linearity. Whether one adopts a valence-shell electron-pair repulsion (VSEPR) approach, or considers the effect on intramolecular non-bonded contacts, bending at linearly hybridized carbon is expected to be a low-energy process. Confirmation of this view comes from values for bond-bending force constants, which are especially small for bond angles at *sp*-hybridized carbon.[19]

TABLE 3

Bond lengths and angles in alkynylplatinum(II) complexes

	Bond/Å		Angle/°		
Complex	Pt–C	C≡C	Pt–C≡C	C≡C–	Ref.
trans-[PtCl(C≡CPh)(PEt$_2$Ph)$_2$]	1.98(2)	1.18(3)	163(2)	174(2)	*
trans-[Pt(C≡CPh)(NH$_2$C$_6$H$_4$F)(PPh$_3$)$_2$]$^+$	1.95(3)	1.21(5)	178	172	11
trans-[Pt{C≡C–C(Me)=CH$_2$}$_2$(PPh$_3$)$_2$]	2.024(6)	1.18(1)	177.4(5)	176.5(7)	12
trans-[Pt(C≡CMe)(C$_{15}$H$_7$N$_4$)(PMe$_3$)$_2$]	2.009(15)	1.15(3)	178.5(15)	175.9(20)	13
trans-[Pt(C≡CH)$_2$(PMe$_2$Ph)$_2$]	2.010	1.188	177.8		14
cis-[Pt(C≡CCN)(CN)(PPh$_3$)$_2$]	1.96(3)	1.24(5)	172(3)	174(4)	15
[{Pt(NCS)(PEt$_3$)$_2$}$_2${*p*-C$_6$H$_4$(C≡C)$_2$}]	1.921(12)	1.22(2)	173(3)	178(2)	16

* This work.

As shown in Part 3 the mean value for a Pt–C(sp^3) bond length subject to low *trans* influence is 2.08 Å.[1] Since the covalent radii of sp^3- and *sp*-hybridized carbon atoms differ by *ca.* 0.08 Å,[20] the predicted length of a Pt–C(*sp*) single bond is 2.00 Å. Only one of the Pt–C bond lengths in Table 3 differs appreciably from this value, and we conclude that back donation from platinum to the π* orbitals of alkynyl ligands is usually insignificant. A similar conclusion was reached concerning alkenyl ligands in Part 3.[1] The unusually short Pt–C distances in *trans*-[{Pt(NCS)(PEt$_3$)$_2$}$_2${*p*-C$_6$H$_4$(C≡C)$_2$}] indicate that this complex may be an exception.[16]

The C≡C bond lengths in Table 3 do not differ significantly from the value (1.212 Å) found in acetylene by electron diffraction in the gas phase.[20]

The trans *Influence of σ-Hydrocarbyl Ligands in Platinum*(II) *Complexes*.—The *trans* influence of a ligand is usually defined as the ability of that ligand to weaken the M–X bond *trans* to itself in the ground state of the complex. A review has been published.[21]

The bond weakening has been examined in platinum(II) complexes by a number of techniques: (*i*) *X*-ray crystallography, *via* l(M–X);[22] (*ii*) n.m.r., using the dependence of coupling constants on *s* character in appropriate orbitals;[23,24] (*iii*) Mössbauer spectroscopy;[25-27] (*iv*) i.r. data, using ν(M–X);[21] and (*v*) others.[28-30] While all these methods relate essentially to the electronic ground state, (*ii*) and (*iii*) being nuclear properties are normally interpreted in terms of the *s*-electron density, and are thus dependent on the theory relating this to the observed spectroscopic parameters.

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Of the remaining methods, (*i*) is the simplest to interpret in terms of bond strengths, assuming only a relation between this and the observed bond length for a given M–X bond. We have used (*i*), and to a lesser extent (*iv*), to assess the relative *trans* influence of the ligands CH_2SiMe_3, $CH{=}CH_2$, and $C{\equiv}CPh$, which enables us to report for the first time on the consequences of changing hybridization at the ligating carbon atom. The n.m.r. method (*ii*) would have required that the complexes *cis*-$[PtX(R)(PEt_2Ph)_2]$ (X = halide or R; R = CH_2SiMe_3,[31] $CH{=}CH_2$, or $C{\equiv}CPh$) be available; a large value for $J(^{31}P-^{195}Pt)$ has been taken as an indication of a low *trans* influence for R. Using this procedure for *cis*-$[PtR_2(PMe_2Ph)_2]$, the order $SiMe_2Ph > CH_2CMe_3 > Me > CH_2Ph > CH_2GeMe_3 > CH_2SiMe_3$ (Table 4) was derived by Dr. M. M. Truelock, there being little discrimination among the *sp*^{3}-hybridized carbon ligands, except for the neopentyl case.[31-34] Similarly, thermochemical data on $[MR_4]$ (M = Ti, Zr, or Hf) showed M–C bond strengths to be almost identical for R = CH_2Ph or CH_2SiMe_3, but these ligands formed significantly stronger bonds than R = CH_2CMe_3.[35a] The anomalous position of the neopentyl ligand in complexes of both Groups 4A and 8 may be associated with a steric effect; however, recent thermochemical results on linear $[ZnR_2]$ show that, even here, where such effects are less likely, the alkyl with R = CH_2SiMe_3 has a significantly stronger metal–carbon bond than that with R = CH_2CMe_3.[35b]

TABLE 4

Selected ^{31}P n.m.r. spectroscopic *trans*-influence data for complexes *cis*-$[PtR_2(PMe_2Ph)_2]$

R	Chemical shift (δ/p.p.m.) [a]	$J(^{31}P-^{195}Pt)$/ kHz	Ref.
$SiMe_2Ph$	+8.3	1.559	32
CH_2CMe_3	+20.3	1.657	31
Me	+12.0	1.846	31,33
CH_2Ph	+15.9	1.933	31,33
CH_2GeMe_3	+16.9	1.972	31
CH_2SiMe_3	+15.5	1.999	31,33
Cl [b]	+15.2	3.549	34

[a] Relative to 85% H_3PO_4, in C_6H_6 solvent. [b] In CH_2Cl_2 solvent.

TABLE 5

Selected structural *trans*-influence data for platinum(II) complexes: some Pt–Cl bond lengths (Å)

Complex	*trans* Ligand	Pt–Cl	Ref.
cis-$[PtCl_2(CNPh)_2]$	CNPh	2.308(5)	18
$K_2[PtCl_4]$	Cl	2.308(2)	36
cis-$[PtCl_2(CNEt)(PEt_2Ph)]$	CNEt	2.314(10)	18
cis-$[PtCl_2\{C(OEt)(NHPh)\}(PEt_3)]$	C(OEt)(NHPh)	2.361(5)	17
cis-$[PtCl_2\{C(NPhCH_2)_2\}(PEt_3)]$	$C(NPhCH_2)_2$	2.362(3)	9
cis-$[PtCl_2(CNEt)(PEt_2Ph)]$	PEt_2Ph	2.390(8)	18
trans-$[PtCl(CH{=}CH_2)(PEt_2Ph)_2]$	$CH{=}CH_2$	2.398(3)	1
trans-$[PtCl(C{\equiv}CPh)(PEt_2Ph)_2]$	$C{\equiv}CPh$	2.406(5)	*
trans-$[PtCl(CH_2SiMe_3)(PMe_2Ph)_2]$	CH_2SiMe_3	2.415(5)	4
trans-$[PtCl(H)(PEt_2Ph)_2]$	H	2.422(9)	37
trans-$[PtCl(SiMe_2Ph)(PMe_2Ph)_2]$	$SiMePh_2$	2.45	22

* This work.

Selected Pt–Cl bond lengths relevant to a discussion of *trans* influence in platinum(II) complexes are shown in Table 5.[36,37] It is apparent that σ-hydrocarbyl ligands exert strong *trans* influences, being exceeded in this respect only by hydride and $[SiR_3]^-$. Gradations within the ligand series CH_2SiMe_3, $CH{=}CH_2$, and $C{\equiv}CPh$ are small, but on the basis of a difference of 0.017(6) Å in *trans*-Pt–Cl bond lengths it may tentatively be concluded that CH_2SiMe_3 has a slightly higher *trans* influence than $CH{=}CH_2$.

Infrared data, although more difficult to interpret with certainty, are available for a larger range of complexes.[38] Table 6 shows representative values. These again indicate that donor-atom hybridization has little effect on the *trans* influence exerted by a σ-carbon ligand, while confirming the placement with regard to the wider range of ligands. As ν(Pt–Cl) can clearly also be

TABLE 6

Selected i.r. *trans*-influence data for platinum(II) complexes: values of ν(Pt–Cl) (cm^{-1})

Complex	*trans* Ligand	ν(Pt–Cl) *	Ref.
trans-$[PtCl_2(PEt_3)_2]$	Cl	340	38
trans-$[PtCl(Me)(PEt_3)_2]$	Me	274	38
trans-$[PtCl(Ph)(PEt_3)_2]$	Ph	270	38
trans-$[PtCl(CH{=}CH_2)(PMe_2Ph)_2]$	$CH{=}CH_2$	284	2
trans-$[PtCl(CH{=}CH_2)(PEt_2Ph)_2]$	$CH{=}CH_2$	270	2
trans-$[PtCl(H)(PEt_3)_2]$	H	269	38
trans-$[PtCl(C{\equiv}CPh)(PMePh_2)_2]$	$C{\equiv}CPh$	285	2
trans-$[PtCl(C{\equiv}CPh)(PEt_2Ph)_2]$	$C{\equiv}CPh$	285	2
trans-$[PtCl(CF{=}CF_2)(PEt_2Ph)_2]$	$CF{=}CF_2$	273	2
trans-$[PtCl(CH_2SiMe_3)(PMe_2Ph)_2]$	CH_2SiMe_3	272	31
trans-$[PtCl(CH_2CMe_3)(PMe_2Ph)_2]$	CH_2CMe_3	265	31
trans-$[PtCl(SiPh_3)(PMe_2Ph)_2]$	$SiPh_3$	239	35

* All the spectra were recorded as Nujol mulls.

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phosphine-dependent, detailed inferences cannot usefully be made.

Our discussion both here and in Part **3** [1] indicates that σ-alkenyl and σ-alkynyl ligands do not display appreciable π acidity in their platinum(II) complexes. It is therefore appropriate to seek an explanation for the high *trans* influence of σ-hydrocarbyl ligands, and for the insensitivity of *trans* influence to the hybridization state of the ligating carbon atom, in terms of the σ-*trans*-influence theory of Mason *et al.*[22] This relates *trans* influence to the parameter $S^2/\Delta E$, where S is the metal–ligand overlap integral and ΔE is the energy separation of the orbitals being mixed. Using the overlap integrals of Mason *et al.*[22] and VOIP values from ref. **39**, the following $S^2/\Delta E$ parameters (in $\text{eV}^{-1} \times 10^2$) are obtained: Cl 0.8, C(*sp*) 1.7, C(sp^2) 1.7, C(sp^3) 1.6, and H 1.8. The theory thus correctly predicts the high *trans* influence of σ-hydrocarbyl ligands. It also suggests that the hybridization state of the donor carbon atom will not be reflected in marked variations in *trans* influence, in conformity with our results. The overlap integrals increase regularly with increasing *s* character in the carbon donor orbital, but a parallel increase in ionization potential leads to nearly constant values of $S^2/\Delta E$. We conclude that the theory of Mason *et al.* provides an adequate framework for the qualitative rationalization of our results, although the minor differences which it predicts in the *trans* influences of *sp*-, sp^2-, and sp^3-hybridized carbon are in the opposite sense to those we have observed.

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