by the entropy of mixing. The formation of the mixed complex accounts for the increase in magnetic susceptibility as well as for the optical data which indicate the presence of five-coordinate paramagnetic species, mixed or not, and of diamagnetic ones. The presence of relatively small amounts of tetrahedral species in the mixed solutions with the isopropyl derivatives is not revealed by the latter method. The pmr spectra are diagnostic of this equilibrium; in fact besides the peaks of the parent complexes two peaks for each ring position are present. The appearance of the new double peaks can be well accounted for considering the mixed complex 2. The two aromatic fragments, belonging to two different ligands, are nonequivalent, especially if we assume that they are *cis* to each other as found for complex 1. This explanation is consistent with those proposed for other salicylaldimine complexes showing a double set of peaks.[10,11] The shifts of the aromatic fragment alternate between downfield at positions 4 and 6 and upfield at 3 and 5, indicative of large positive and negative spin densities involving π orbitals and in agreement with the spectra of other five-coordinate complexes.[3,10]

These results are comparable to those obtained by Holm[11] through nmr measurements on solutions containing the same molar amounts of two bis(N-α-branched alkylsalicylaldiminato)nickel(II) complexes differing in the alkyl group. The presence of a double set of peaks for each ring position, besides the peaks of the parent complexes, was explained assuming the existence of mixed complexes.

Compounds of the Solid State.—Solid compounds can be obtained from the mixed solutions only by evaporating thoroughly. The solids are fine powders

(10) G. N. La Mar and L. Sacconi, *J. Am. Chem. Soc.*, **89**, 2282 (1967).
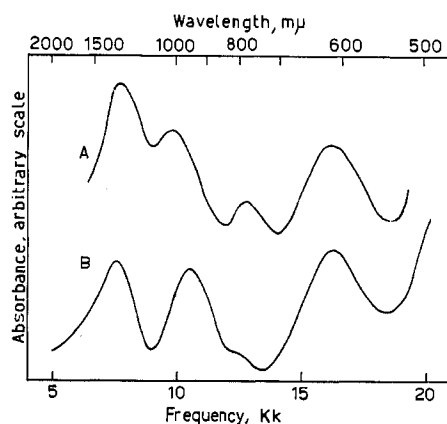(11) A. Chakravorty and R. H. Holm, *ibid.*, **86**, 3999 (1964).

Figure 3.—Reflectance spectra of: A, [5-Cl-SALen-N(C_2H_5)$_2$-Ni; B, mixed compound [(5-Cl-SALen-N(C_2H_5)$_2$)(3-Cl-SAL-N-i-C_3H_7)]Ni.

and in some cases the analyses, magnetic moments, and reflectance spectra indicate that impurities or mixtures of different complexes are present. In fact lattice forces are expected to be as important as the differences in energies of the various stereochemical species in solution. Here is reported the compound obtained from the solution containing bis(3-chloro-N-isopropylsalicylaldiminato)nickel(II) and complex 1. The compound is fully paramagnetic even if the starting isopropyl complex is diamagnetic. The reflectance spectrum (Figure 3) is quite different from that of the starting complex and resembles the spectrum of complex 1. Also the narrow range of melting point is indicative of a new compound. We tentatively assign to this compound the structure of complex 2.

Iridium–Tin Complexes with Acetylene and Ethylene

BY M. CAMIA, M. P. LACHI, L. BENZONI, C. ZANZOTTERA, AND M. TACCHI VENTURI

This paper presents a description of the complexes Ir(SnCl$_3$)(CO)(P(C$_6$H$_5$)$_3$)$_2$(C$_2$H$_2$) and Ir(SnCl$_3$)(CO)(P(C$_6$H$_5$)$_3$)$_2$(C$_2$H$_4$). These complexes have been obtained adding anhydrous SnCl$_2$ and C$_2$H$_2$, or C$_2$H$_4$, to the complex IrCl(CO)(P(C$_6$H$_5$)$_3$)$_2$. A description of the intermediate product IrCl(CO)(P(C$_6$H$_5$)$_3$)$_2$(SnCl$_2$) is also presented.

Introduction

The complexes having the metal–metal bond have been studied extensively in recent years.[1] One of the aspects studied in the course of this work was the reactivity of SnCl$_2$.[1,2] For IrCl(CO)(P(C$_6$H$_5$)$_3$)$_2$

it is possible to isolate the relative complexes with substituted acetylene[3] and with substituted ethylene[4] (the stability of complexes is properly attributed to these electronegative substituents). The complexes

(1) M. C. Baird, *Progr. Inorg. Chem.*, **9**, 1 (1968).
(2) R. C. Taylor, J. F. Young, and G. Wilkinson, *Inorg. Chem.*, **5**, 20 (1966).

(3) J. P. Collman and J. W. Kang, *J. Am. Chem. Soc.*, **89**, 844 (1967), and cited references.
(4) (a) G. W. Parshall and F. N. Jones, *ibid.*, **87**, 5356 (1965); (b) W. H. Baddley, *ibid.*, **88**, 4545 (1966).

TABLE I
ANALYTICAL DATA OF THE COMPLEXES

Complex	% calcd				% found				Mol/mol Calcd			Found		
	C	H	Cl	P	C	H	Cl	P	C_2H_2	C_2H_4	C_6H_6	C_2H_2	C_2H_4	C_6H_6
$Ir(SnCl)_3(CO)_2(P(C_6H_5)_3)_2(C_2H_2)$	47.0	3.2	10.7	6.2	48.0	3.6	10.8	5.9	1.0	...	...	0.9	...	...
$Ir(SnCl_3)(CO)(P(C_6H_5)_3)_2(C_2H_4)\cdot C_6H_6$	49.8	3.7	10.0	5.8	49.0	3.7	11.4	5.8	...	1.0	1.0	...	0.9	0.9
$IrCl(CO)(P(C_6H_5)_3)_2(SnCl_2)\cdot C_6H_6$	49.3	3.5	10.2	5.9	49.3	3.8	9.7	5.4	...	...	1.0	...	...	1.0
$IrCl(CO)(P(C_6H_5)_3)_2(SnCl_2)\cdot 3C_6H_6$	54.9	4.0	8.8	5.1	54.6	4.0	9.0	5.2	...	...	3.0	...	...	3.0

with unsubstituted acetylene and ethylene have not been isolated.[5]

We have previously seen[6] that the product of the reaction between $SnCl_2$ and $IrCl(CO)(P(C_6H_5)_3)_2$ in benzene adds CO forming the complex $Ir(SnCl_3)(CO)_2(P(C_6H_5)_3)_2$ that is more stable than the analogous $IrCl(CO)_2(P(C_6H_5)_3)_2$. We now wish to utilize the stabilizing property of the ligand $SnCl_3^-$ in order to obtain acetylene and ethylene complexes.

Experimental Section

Apparatus.—Ir spectra were recorded between 5000 and 400 cm^{-1} with a Perkin-Elmer Model 125 spectrophotometer and between 400 and 200 cm^{-1} with a Perkin-Elmer Model 225 spectrophotometer. Uv spectra (benzene solution) were determined with a Beckman Model DK2 spectrophotometer. The nmr spectra were recorded using a Perkin-Elmer Model R-10 spectrophotometer at 34° in CDCl$_3$ using tetramethylsilane as the internal reference.

Reagent.—Anhydrous stannous chloride was obtained by crystallizing from a mixture of acetic acid–acetic anhydride, washing with ether, and drying under vacuum at 100°.

Solvents.—The solvents were dried with Na–K alloy and distilled in a nitrogen system.

Synthesis. (a) $IrCl(CO)(P(C_6H_5)_3)_2(SnCl_2)\cdot nC_6H_6$ ($n = 3$). —A 0.6151-mmol (0.48-g) sample of $IrCl(CO)(P(C_6H_5)_3)_2$ and 0.7067 mmol (0.13 g) of SnCl$_2$ were allowed to react in 28 ml of benzene, in an inert atmosphere, at 35°. A green solution was obtained. This was then filtered after 10 min, in order to remove unreacted SnCl$_2$. Green needlelike crystals were obtained from the solution on cooling at 15°; after filtering and drying at 40° under vacuum 0.32 g of product was obtained.

(b) $IrCl(CO)(P(C_6H_5)_3)_2(SnCl_2)\cdot nC_6H_6$ ($n = 1$).—This was prepared in the same manner as described in part a, using one-third of the benzene; the adduct with 1 mol of solvent was obtained, with a yield of 83%.

(c) $Ir(SnCl_3)(CO)(P(C_6H_5)_3)_2(C_2H_2)$.—A 3.63-mmol (2.83-g) sample of $IrCl(CO)(P(C_6H_5)_3)_2$ and 4.54 mmol (0.86 g) of SnCl$_2$ were allowed to react in 170 ml of benzene, in an inert atmosphere, at 40°. Acetylene was bubbled into the solution, after it had been filtered and cooled at 5°. After about 1 hr a pale yellow solution was obtained. To this solution 120 ml of heptane was added and a precipitate was formed. This precipitate was filtered and then washed with heptane and dried in acetylene atmosphere at room temperature. The yield of the dried product was 2.67 g.

(d) $Ir(SnCl_3)(CO)(P(C_6H_5)_3)_2(C_2H_4)\cdot C_6H_6$.—This complex was obtained in the same manner as described in part c, using ethylene instead of acetylene. A 2.12-mmol (1.65-g) sample of $IrCl(CO)(P(C_6H_5)_3)_2$ and 2.54 mmol (0.48 g) of SnCl$_2$ in 100 ml of benzene gave 1.99 g of the product desired.

See Table I for analytical data of the complexes prepared.

Determination of Acetylene and Ethylene in the Complexes.—Weighted quantities of $IrCl(CO)(P(C_6H_5)_3)_4$ and SnCl$_2$ were introduced into a thermostatic apparatus, fitted with a gas buret and containing benzene previously saturated with acetylene (or

ethylene). After the reaction had taken place, the volume of gas absorbed from the buret was read.

Determination of Benzene.—Into a known volume of hexane, under an inert atmosphere, a weighed quantity of sample was suspended, and the entire suspension was stirred. After 2 hr the sample was filtered and the amount of benzene in the solution was determined by uv spectroscopy.

Results and Discussion

Spectroscopic Section.—In the ir spectra of the complex $Ir(SnCl_3)(CO)(P(C_6H_5)_3)_2(C_2H_2)$ have been found the absorptions listed in Table II. The band at 1988 cm^{-1} (ν_{CO}), in the solid sample spectra, has a shoulder at higher frequencies; this fact is attributed to crystallinity. In the spectra of the dissolved sample there is a single band. The medium band at 1682 cm^{-1} is significant because it shows the olefinic character of the C–C bond. This fact may be related to a complexation with σ-bond type. The nmr spectrum confirms this hypothesis; besides the peaks relating to aromatic hydrogens, it only shows a peak at τ 5.40 assignable to olefinic hydrogens.

Many authors have described complexes of transition metals with acetylene derivatives[8,7] showing the same lowering of the bond order.

In the complex we have obtained, the stabilizing action is not due to the electron-withdrawing substituents but to the π-acceptor character of the $SnCl_3^-$ ligand.

The bands at 319 and at 300 cm^{-1} are attributed, respectively, to the unsymmetrical and symmetrical stretchings of the Sn–Cl bond. The frequencies are in agreement with those expected for the $SnCl_3^-$ ligand.[8]

If the phosphines are in the *trans* position [we have found this steric arrangement by an nmr determination in the complex $Ir(SnCl_3)(CO)(PCH_3(C_6H_5)_2)_2(C_2H_4)$], the hexacoordinate structure can be attributed to the complex $Ir(SnCl_3)(CO)(P(C_6H_5)_3)_2(C_2H_2)$
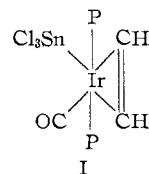

I

Table II shows the absorption of the ir spectra of the complexes $Ir(SnCl_3)(CO)(P(C_6H_5)_3)_2(C_2H_4)$ and

(5) (a) L. Vaska, *Inorg. Nucl. Chem. Letters*, **1**, 89 (1965); (b) L. Vaska and R. E. Rhodes, *J. Am. Chem. Soc.*, **87**, 4970 (1965); (c) L. Vaska, *Accounts Chem. Res.*, **1**, 335 (1968).

(6) L. Benzoni, M. Camia, C. Zanzottera, and M. De Innocentiis, *Chim. Ind.* (Milan), **50**, 347 (1968).

(7) (a) M. A. Bennett, *Chem. Rev.*, **62**, 611 (1962); (b) R. G. Guy and B. L. Shaw, *Advan. Inorg. Chem. Radiochem.*, **4**, 77 (1962); (c) W. Hübel, "Organic Syntheses via Metal Carbonyls," Vol. 1, Interscience Publishers, New York, N. Y., 1968, p 273.

(8) (a) R. V. Lindsey, Jr., G. W Parshall, and U. G. Stolberg, *Inorg. Chem.*, **5**, 109 (1966); (b) R. V. Lindsey, Jr., G. W. Parshall, and U. G. Stolberg, *J. Am. Chem. Soc.*, **87**, 658 (1965); (c) D. M. Adams and P. J. Chandler, *Chem. Ind.* (London), 269 (1965).

Complex		ν_{CO}	ν_{C-C}	ν_{M-Cl}[d]			
Ir(SnCl₃)(CO)(P(C₆H₅)₃)₂(C₂H₂)	a	1988 s[e]	1682 m	319 m	305 sh	300 m	296 sh
	b	1992 s	1678 m				
	c	1988 s	1682 m				
Ir(SnCl₃)(CO)(P(C₆H₅)₃)₂(C₂H₄)	a	1968 s	...	318 m		302 m	
	b	1987 s	...				
Ir(SnCl₃)(CO)(P(C₆H₅)₃)₂(C₂H₄)·C₆H₆	a	1984 s	...	316 m		297 m	
	b	1987 s	...				
Ir(SnCl₃)(CO)(PCH₃(C₆H₅)₂)₂(C₂H₄)	a	1975 s	...				
IrCl(CO)(P(C₆H₅)₃)₂(SnCl₂)·C₆H₆	a	2017 s	...	290 s		266 m	
IrBr(CO)(P(C₆H₅)₃)₂(SnCl₂)·C₆H₆	a	2018 s	...	288 m		269 m	

a Nujol mulled. *b* CHCl₃ solution. *c* C₆H₆ solution. *d* M = Sn, Ir. *e* Abbreviations: s, strong; m, medium; sh, shoulder.

Ir(SnCl₃)(CO)(P(C₆H₅)₃)₂(C₂H₄)·C₆H₆. The ir spectrum of the benzene-solvated complex shows a ν_{CO} at 1984 cm^{-1} with a shoulder at 1990 cm^{-1}; if the benzene is withdrawn by washing with hexane (which does not dissolve the complex), that band is shifted to 1968 cm^{-1}. It is not thought that the shift is due to an isomerization (which would take place in the solid state) but to the benzene influencing the π-acceptor character of the ligand SnCl₃$^{-}$. Both the solvated product and the washed product absorb at 1987 cm^{-1} in CHCl₃ solution.

In the ir spectrum ethylenic bond bands are not present; the nmr spectrum shows two broad signals, at τ 8.25 and at 9.1, due to aliphatic hydrogens. There are also the signals due to aromatic hydrogens. So it may be concluded that ethylene is bonded to iridium by two σ bonds.

In the ir spectrum of the complex washed with hexane, the antisymmetric and symmetric stretching frequencies of the Sn–Cl bond are at 318 and at 302 cm^{-1}, respectively. These absorptions confirm the presence of the ligand SnCl₃$^{-}$.

The analogous complex Ir(SnCl₃)(CO)(PCH₃(C₆H₅)₂)₂(C₂H₄) has been prepared in order to determine the phosphine position. The nmr spectrum, showing a triplet centered at τ 7.56 due to the CH₃ of the phosphines (apparent J_{P-H} = 3.4 cps), suggests that the two phosphorus atoms are in the *trans* position.[9] Two very broad signals are also present, centered at τ 8.00 and 8.95, which confirms the disappearance of the olefinic character of the complexed ethylene. In the ir spectrum of the solid complex, ν_{CO} is at 1975 cm^{-1}.

The hexacoordinated structure II can be now attributed to the complexes Ir(SnCl₃)(CO)(P(C₆H₅)₃)₂(C₂H₄) and Ir(SnCl₃)(CO)(PCH₃(C₆H₅)₂)₂(C₂H₄). During the course of the synthesis of the above-described complexes the intermediate product, stated as IrCl(CO)(P(C₆H₅)₃)₂(SnCl₂), can be isolated, showing the
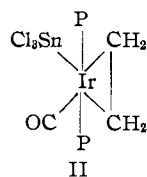
II

significant ir absorptions listed in Table II.

The X-ray determination shows that the complex is a monomer.[10] Among the possible structures, the tetracoordinated one (III) does not agree with the

III
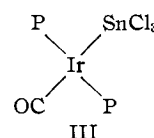
ir spectrum. The ν_{CO} at 2017 cm^{-1} is too high for a CO *trans* to the ligand SnCl₃$^{-}$.

In the spectra of the Ir,[11] Pt,[8a,b,12] and Rh[8c] complexes, the ligand SnCl₃$^{-}$ shows an Sn–Cl stretching band between 360 and 320 cm^{-1}. The complex IrCl(CO)(P(C₆H₅)₃)₂(SnCl₂) does not absorb in this region of the spectrum.

A pentacoordinated structure agrees better with the spectroscopic data. In fact the absorption at 290 cm^{-1} may be attributed to the antisymmetrical stretching Sn–Cl band of the ligand SnCl₂ and the absorption at 266 cm^{-1} may be considered as the sum of the Sn–Cl symmetrical stretching and the Ir–Cl stretching. This interpretation agrees with the ir spectrum of the complex IrBr(CO)(P(C₆H₅)₃)₂(SnCl₂) which shows the ν_{CO} in the same positions at 2018 cm^{-1}, the Sn–Cl antisymmetrical stretching at 288 cm^{-1}, and the second Sn–Cl band at 269 cm^{-1} clearly less strong than the corresponding one in the ir spectrum of IrCl(CO)(P(C₆H₅)₃)₂(SnCl₂).

The hexacoordinated structures IV and V are

IV   V
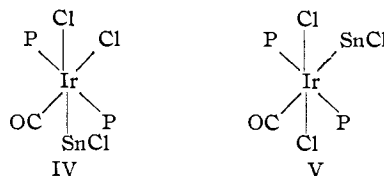
inconsistent if the complex reactivity is considered or if the absence of bands ascribable to the Ir–Cl bond in a *trans* position to CO (about at 315 cm^{-1}) or to a chlorine atom (about 326 cm^{-1}) is taken into account.

(9) J. M. Jenkins and B. L. Shaw, *Proc. Chem. Soc.*, 279 (1963).

(10) G. Fagherazzi, unpublished data: unit cell parameters a = 19.5 Å, b = 12.9 Å, c = 10.3 Å, α = 83°, β = 80°, γ = 97°; triclinic cell; space group P$\bar{1}$; two molecules per cell; observed density (pycnometer) 1.55 g/cm³; calculated density 1.59 g/cm³.

(11) Unpublished data: IrHCl(SnCl₃)(CO)(P(C₆H₅)₃)₂, ν_{Sn-Cl} 332 cm^{-1}; Ir(SnCl₃)(CO)₂(P(C₆H₅)₃)₂, ν_{Sn-Cl} 322 cm^{-1}.

(12) M. C. Baird, *J. Inorg. Nucl. Chem.*, 29, 367 (1967).

Therefore taking into account the spectroscopic data, a pentacoordinated structure may be suggested for the complexes IrX(CO)(P(C6H5)3)2(SnCl2) (X = Cl, Br). The relative steric configuration may be either a tetragonal pyramid [like IrCl(CO)(L)2(SO2)] or a trigonal bipyramid.

**Chemical Section.**—The complex IrCl(CO)(P(C6-H5)3)2(SnCl2) adds hydrogen, hydrocyanic acid, and halogen halides at room temperature, yielding stable products.[13] The study of the chemical behavior of the complex IrX(CO)(P(C6H5)3)2(SnCl2) (X = Cl, Br) toward the halogen hydrides gives some evidence for the pentacoordinated structure of the complex (now formulated taking into account the spectroscopic data only).

The complex IrHCl(SnCl3)(CO)(P(C6H5)3)2[2] is obtained by adding HCl to IrCl(CO)(P(C6H5)3)2-(SnCl2) and also from IrHCl2(CO)(P(C6H5)3)2 by an insertion reaction of SnCl2 into the Ir–Cl bond *trans* to the hydrogen
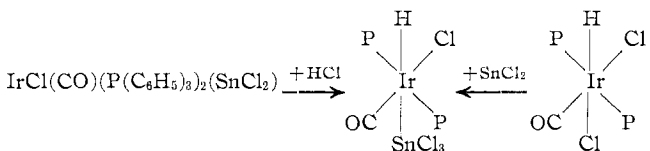
Analogous results are obtained by treating IrCl(CO)-(P(C6H5)3)2(SnCl2) with HBr, or IrHBrCl(CO)(P(C6-H5)3)2 with SnCl2

(13) Work in progress.
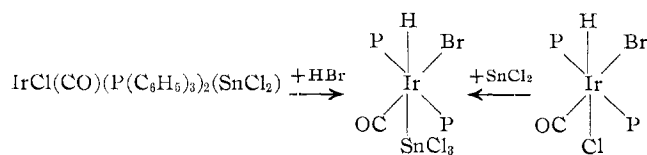
while the complex IrBr(CO)(P(C6H5)3)2(SnCl2) reacts with HCl forming IrHClBr(CO)(P(C6H5)3)2
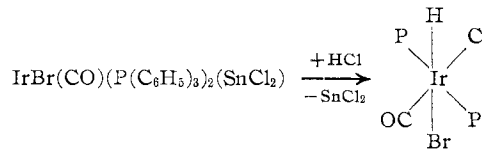
The complex IrHClBr(CO)(P(C6H5)3)2 does not add SnCl2.

From these results it can be concluded that (a) the SnCl2 insertion in the Ir–Cl bond *trans* to CO is not possible under the operating conditions adopted and (b) the ligand SnCl2Br⁻ is not obtained by the SnCl2 insertion into the Ir–Br bond *trans* to hydrogen. These considerations exclude the possibility of obtaining a tetracoordinated complex by adding SnCl2 to IrX(CO)(P(C6H5)3)2 (X = Cl, Br) and confirm the proposed pentacoordinated structure of the IrX(CO)(P-(C6H5)3)2(SnCl2).

The Reaction of Imides with Some Zerovalent Platinum and Palladium Complexes[1]

BY D. M. ROUNDHILL

The reaction of some imides with tetrakis(triphenylphosphine)platinum, tetrakis(triphenylarsine)platinum, and tetrakis-(triphenylphosphine)palladium has been studied. With the platinum complexes, imide hydride complexes of the type L2Pt(H)(imide) have been prepared using succinimide, phthalimide, saccharin, and parabanic acid. The structure of these complexes was confirmed by ir spectra and also by the presence of a high-field line in the ¹H nmr spectra. Tetrakis(triphenylphosphine)palladium reacted with succinimide but a complex of stoichiometry (P(C6H5)3)2Pd(succinimide)2 was formed rather than a hydride. Maleimide readily reacted with all three complexes to give compounds which still showed an N–H stretch in the ir spectrum and were of stoichiometry L2M(maleimide), with the imide coordinated *via* the olefinic double bond.

Transition metal hydrides have been prepared using strong reducing agents, such as sodium borohydride and hydrazine,[2] and by oxidative addition reactions.[3] These latter reactions are usually carried out with strong mineral acids, and in the case of tetrakis(triphenylphosphine)platinum it was found that two types of

hydride were formed, depending on the coordinating ability of the anion. Weakly coordinating anions (X̄) gave ionic hydride complexes of the type [PtH-(P(C6H5)3)3]X, whereas ones with strong coordinating ability (Ȳ) gave covalent complexes, PtHY(P(C6H5)3)2.[4] The preparation of hydrides from weak acids has however received little study, although recent publications have described their preparation from HCN[4,5]

(1) D. M. Roundhill, *Chem. Commun.*, 567 (1969).
(2) B. L. Shaw, "Inorganic Hydrides," Pergamon Press, Ltd., Oxford, 1967, p 82.
(3) J. P. Collman, *Accounts Chem. Res.*, 1, 136 (1968).
(4) F. Cariati, R. Ugo, and F. Bonati, *Inorg. Chem.*, 5, 1128 (1966).
(5) H. Singer and G. Wilkinson, *J. Chem. Soc., A*, 2516 (1968).