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The Existence of Five-Coordinate High-Spin Nickel(II) Complexes with Mixed Salicylaldimine Ligands

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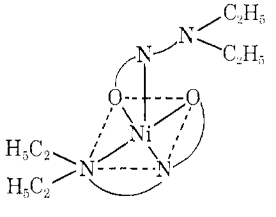
It is known that the tridentate Schiff base formed from 5-chlorosalicylaldehyde and N,N-diethylethylenediamine gives rise to a five-coordinate complex Ni[5-Cl-SALen-N$(C_2H_5)_2$]$_2$ (1) in which one Schiff base acts as bidentate and the other as a tridentate. This research shows that one 5-Cl-SALen-N$(C_2H_5)_2$ ligand in 1 can be replaced by a bidentate Schiff base formed from salicylaldehyde and alkylamine, giving rise to five-coordinate mixed complexes. Evidence for this replacement is obtained from magnetic, optical, and pmr measurements in solution. The pmr spectra show two peaks for each ring position for the two aromatic fragments in the same mixed complex. One solid mixed complex is also reported.

Introduction

The nickel(II) complex with the Schiff base formed from 5-chlorosalicylaldehyde and N,N-diethylethylenediamine, Ni[5-Cl-SALen-N$(C_2H_5)_2$]$_2$ (1), is high spin five-coordinate with a magnetic moment of 3.30 BM.[1] The structure has been shown by X-ray analysis[2] to be a distorted square pyramid of the type in which one N atom is not bound to the metal. This compound shows a ligand field spectrum with bands at *ca.* 7700, 10,000 12,800, and 16,200 cm^{-1}. The chloroform solution spectrum is quite similar to that of the solid compound though the value of the magnetic moment in solution is 3.15 BM indicative of only *ca.* 90% of paramagnetic forms. The nmr spectrum in deuteriochloroform solution showed that the two β nitrogens are equivalent.[3] It was concluded that the five-coordinate species in solution has a structure close to 1 in which the fifth coordination position is shared by the two β nitrogens in rapid equilibrium.



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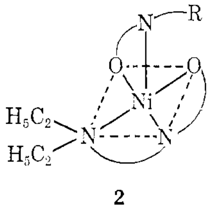
In this article the possibility of substituting a tridentate Schiff base for a bidentate one in order to obtain the complex of type 2 is reported. With this aim equimolar amounts of complex 1 and various bis(N-alkylsalicylaldiminato)nickel(II) compounds which are known to be predominantly tetracoordinate[4] were dissolved in chloroform and the solutions were studied. Compound 2 which could be formed through the exchange of a ligand molecule between the starting complexes would be favored by establishment of another nickel–nitrogen bond.



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Experimental Section

The preparation and characterization of all the starting compounds have already been reported elsewhere.[1,4] The magnetic and spectrophotometric measurements were performed with the apparatus and the techniques already described.[5] These measurements have all been performed at almost the same concentration of nickel, *i.e.*, *ca.* 5×10^{-2} *M*.

Molecular weights were determined in chloroform at 37° with a Mechrolab Model 301 A vapor pressure osmometer calibrated with benzil. The solutions were approximately 2×10^{-2} *M*. The association degree values obtained are: mixed solution[6] with bis(3-chloro-N-isopropylsalicylaldiminato)nickel(II), $\bar{n} = 0.97$; with bis(5-chloro-N-isopropylsalicylaldiminato)nickel(II), $\bar{n} = 1.02$; with bis(5-chloro-N-methylsalicylaldiminato)nickel(II), $\bar{n} = 0.98$.

Proton Resonance Measurements.—All of the spectra were recorded on a Varian A-60 spectrophotometer operating at 39° using tetramethylsilane as internal reference. The concentration of the chloroform-*d* solutions was *ca.* 0.1 *M*.

Preparation of a Solid Mixed Compound.—An equimolar amount of complex 1 and bis(3-chloro-N-propylsalicylaldiminato)-nickel(II) complex were dissolved in chloroform. The solution was then concentrated and petroleum ether was added. After cooling overnight, the compound was filtered off and dried *in vacuo;* mp 152–155°. *Anal.* Calcd for $C_{23}H_{29}Cl_2N_3O_2Ni$: C, 54.22; H, 5.54; N, 8.25; Ni, 11.53. Found: C, 54.20; H, 5.76; N, 8.19; Ni, 11.74; $\mu_{\text{eff}} = 3.20$ BM.

Results

Magnetic Measurements.—The percentage of nickel(II) with triplet ground state in the mixed solutions has been determined from the values of magnetic moment according to the formula % paramagnetic species = $100[\mu^2/(3.3)^2]$, 3.3 BM being the value of complex 1 in the solid state. The values are sum-

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(1) L. Sacconi, P. Nannelli, N. Nardi, and U. Campigli, *Inorg. Chem.*, **4**, 943 (1965).

(2) L. Sacconi, P. L. Orioli, and M. Di Vaira, *J. Am. Chem. Soc.*, **87**, 2059 (1965).

(3) J. D. Thwaites, I. Bertini, and L. Sacconi, *Inorg. Chem.*, **5**, 1036 (1966).

(4) (a) L. Sacconi, *J. Chem. Soc.*, 4608 (1963); L. Sacconi, M. Ciampolini, and N. Nardi, *J. Am. Chem. Soc.*, **86**, 819 (1964); (b) R. H. Holm and T. M. McKinney, *ibid.*, **82**, 5506 (1960); R. H. Holm, G. W. Everett, and A. Chakravorty, *Progr. Inorg. Chem.*, **7**, 135 (1966).

(5) I. Bertini and F. Mani, *Inorg. Chem.*, **6**, 2032 (1967).

(6) We call mixed solutions equimolar chloroform solutions of complex 1 and one of the bis(N-alkylsalicylaldiminato)nickel(II) compounds.

TABLE I

PERCENTAGE OF PARAMAGNETIC SPECIES IN $CHCl_3$ SOLUTIONS[a]

Bis(N-alkylsalicylaldiminato)-nickel(II)	% A	% B	% C
$[SAL\text{-}N\text{-}i\text{-}C_3H_7]_2Ni$	50	74	70
$[3\text{-}Cl\text{-}SAL\text{-}N\text{-}i\text{-}C_3H_7]_2Ni$	21	76	56
$[5\text{-}Cl\text{-}SAL\text{-}N\text{-}i\text{-}C_3H_7]_2Ni$	62	84	76
$[5\text{-}Cl\text{-}SAL\text{-}NCH_3]_2Ni$		93	
$[5\text{-}Cl\text{-}SAL\text{-}NC_2H_5]_2Ni$		77	
$[5\text{-}Cl\text{-}SAL\text{-}N\text{-}n\text{-}C_3H_7]_3Ni$	15	70	53
$[5\text{-}Cl\text{-}SAL\text{-}N\text{-}n\text{-}C_4H_9]_2Ni$	19	72	55

[a] Percentage of paramagnetic species in $CHCl_3$ solutions of: A, N-alkyl complexes; B, mixed solutions of N-alkyl complexes and complex **1**; C, average value of the percentage of paramagnetic species in the two starting solutions. The amount of paramagnetic species in complex 1 solution is 91%.

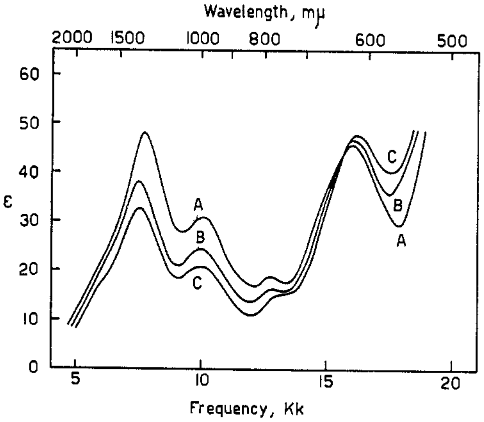

Figure 1.—Absorption spectra in $CHCl_3$ of: A, $[5\text{-}Cl\text{-}SALen\text{-}N(C_2H_5)_2]_2Ni$; B, mixed solution of $[5\text{-}Cl\text{-}SAL\text{-}N\text{-}i\text{-}C_3H_7]_2Ni$ and complex **1**; C, mixed solution of $[3\text{-}Cl\text{-}SAL\text{-}N\text{-}i\text{-}C_3H_7]_2Ni$ and complex **1**.

marized in Table I along with the average of the percentage of paramagnetic form for the solutions of the starting complexes. These results show that the percentage of paramagnetic form in the mixed solutions is always higher than that calculated if no interaction took place between the two starting complexes.

When solutions of the complexes bis(5-chloro-N-*n*-propylsalicylaldiminato)nickel(II) and bis(5-chloro-N-*n*-butylsalicylaldiminato)nickel(II) which are mostly planar in chloroform solution[4a] are mixed with a solution of complex **1**, an increase of 17% in paramagnetic species is observed. The mixed solutions with bis(5-chloro-N-methylsalicylaldiminato)nickel(II) and bis(5-chloro-N-ethylsalicylaldominato)nickel(II) are highly paramagnetic, 93 and 77%, respectively. However no comparison can be made with the starting solutions which do not allow reliable values to be obtained. Only from optical spectra was it known that some paramagnetic species are present in the solutions of these complexes. On the other hand, their high solubility in solutions of complex **1** is indicative of an interaction between the two types of complexes.

For the isopropyl complexes the increase in paramagnetism is smaller than in the previous examples. This is due to the high percentage of paramagnetic tetrahedral species present in the starting solutions.[4]

Optical Spectra and Molecular Weight Measurements.—The absorption spectra of the mixed solutions, apart from the relative intensity of the peaks, are very similar to each other and to that of complex **1** (Figure 1). The spectra show peaks characteristic of the five-coordinate complex **1** at *ca.* 8000, 10,000, 13,000, and 16,000 cm^{-1} (Table II). The diamagnetic form, presumably planar, absorbs at *ca.* 16,000 cm^{-1}. In Table II the molar absorbance values of the four peaks for both the complex **1** solution and mixed solutions are reported. The ratios between the molar absorbance of the first two peaks for the mixed solutions and those of complex **1** are constant within 10% and are close to the percentages of paramagnetic species determined *via* magnetic measurements. This indicates that five-coordinate species are the predominant paramagnetic species and that their molar absorbancies are close to each other. Furthermore it is interesting to note that all the spectra intersect near one point at *ca.* 15,000 cm^{-1} as shown in Figure 1. This point, which looks like an isosbestic point for an equilibrium between two species, indicates that these solutions exhibit tetra–pentacoordinate equilibria to different extents, the tetra- and pentacoordinate chromophores being essentially the same for all the mixed solutions.

TABLE II

THE MAXIMA AND EXTINCTION COEFFICIENTS FOR THE ELECTRONIC SPECTRA OF THE MIXED SOLUTIONS

Complex **1**	7700 (46.5), 10,000 (28.5), 12,750 (17.5), 16,150 (44.5)
$[SAL\text{-}N\text{-}i\text{-}C_3H_7]_2Ni$ + **1**	7570 (34), 10,000 (20.5), 12,900 (14), 16,250 (47.5)
$[5\text{-}Cl\text{-}SAL\text{-}N\text{-}i\text{-}C_3H_7]_2Ni$ + 1	7550 (38.5), 10,000 (24.5), 12,900 (16), 16,250 (47)
$[3\text{-}Cl\text{-}SAL\text{-}N\text{-}i\text{-}C_3H_7]_2Ni$ + **1**	7600 (35.5), 10,000 (23.5), 12,810 (16), 16,120 (49.5)
$[5\text{-}Cl\text{-}SAL\text{-}NCH_3]_2Ni$ + 1	7870 (43.5), 10,200 (30.5), 12,900 (17.5), 16,390 (43)
$[5\text{-}Cl\text{-}SAL\text{-}NC_2H_5]_2Ni$ + **1**	7720 (36.8), 10,000 (24.5), 12,810 (14.5), 16,250 (59)
$[5\text{-}Cl\text{-}SAL\text{-}N\text{-}n\text{-}C_3H_7]_2Ni$ + 1	7690 (35.5), 10,000 (23), 12,650 (14), 16,000 (55)
$[5\text{-}Cl\text{-}SAL\text{-}N\text{-}n\text{-}C_4H_9]_2Ni$ + **1**	7630 (33.5), 10,000 (22), 12,650 (13.5), 16,000 (53)

Spectrophotometric measurements performed on the mixed solutions with bis(5-chloro-N-methylsalicylaldiminato)nickel(II) in nitrobenzene from 20 to 140° show that with the increase of the temperature the intensities of the peaks between 7000 and 10,000 cm^{-1} diminish. This is where the five-coordinate species absorb. The peak at 16,000 cm^{-1}, where the diamagnetic form intensely absorbs, increases in intensity.

Molecular weight measurements at 37° on the mixed solutions with bis(X-chloro-N-R-salicylaldiminato)-nickel(II) (X = 3, 5; R = methyl, ethyl, isopropyl) indicate that the complexes are essentially monomeric; *i.e.*, the values of molecular weight found are, within experimental error, the average values of the two starting complexes calculated as monomeric. This

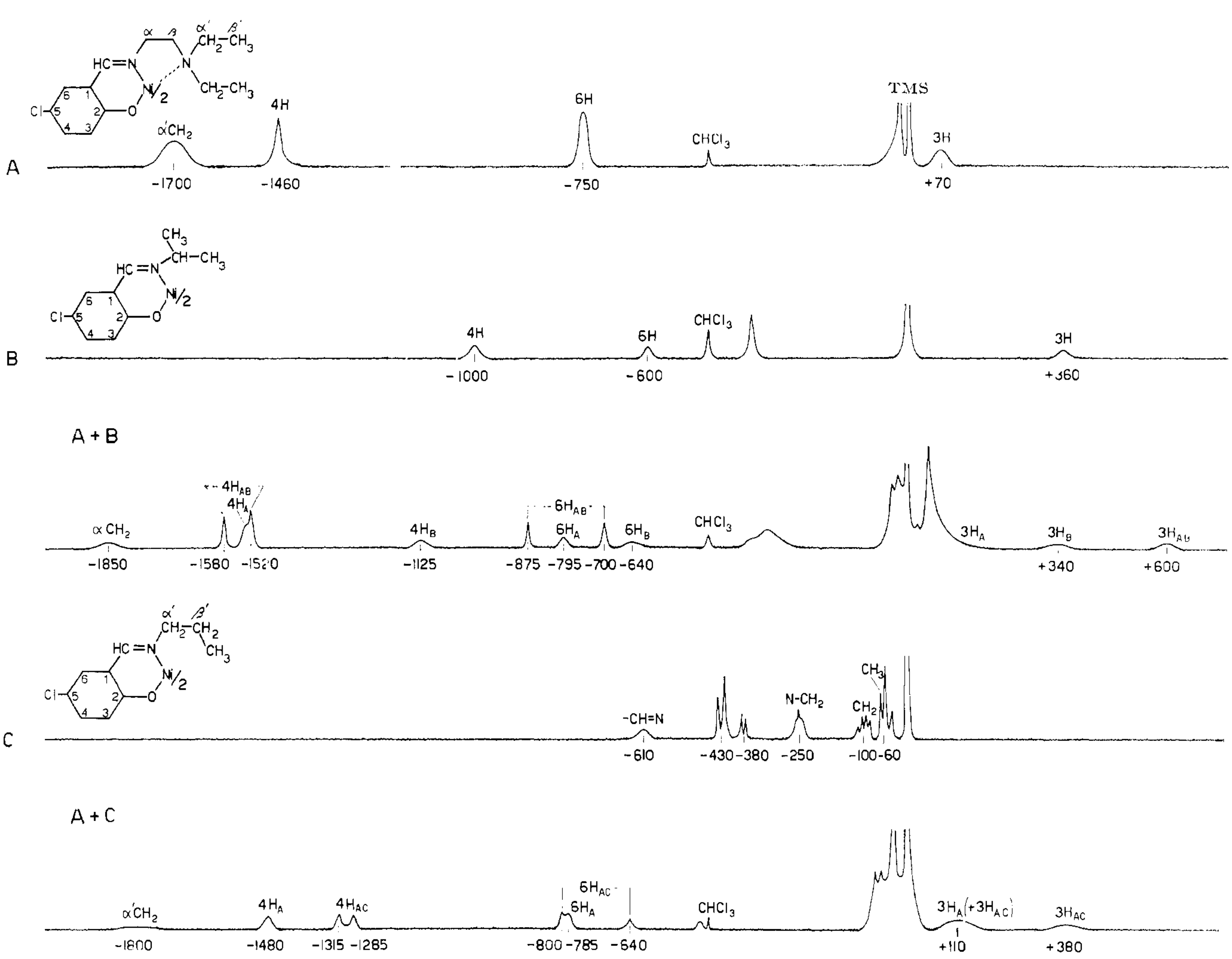

Figure 2.—Proton magnetic resonance spectra from TMS as internal reference at 60 Mc of: A, [5-Cl-SALen-N(C_2H_5)$_2$]$_2$Ni; B, [5-Cl-SAL-N-*i*-C_3H_7]$_2$ Ni; A + B, mixed solution of [5-Cl-SAL-N-*i*-C_3H_7]$_2$Ni and complex 1; C, [5-Cl-SAL-N-*n*-C_3H_7]$_2$Ni; A + C, mixed solution of [5-Cl-SAL-N-*n*-C_3H_7]$_2$Ni and complex 1.

rules out the possibility that the increase in paramagnetism is due to intermolecular association.

Proton Magnetic Resonance Spectra.—The pmr spectroscopy on paramagnetic compounds has been found to be the most sensitive method to reveal the presence of new species in solution.[7] We have recorded spectra of mixed solutions with bis(5-chloro-N-R-salicylaldiminato)nickel(II) (R = *n*-propyl, isopropyl) (Figure 2). The spectra are reported over the region where all the ring protons lie, together with the spectra of the parent complexes. The spectrum of the *n*-propyl complex is within 0–10 ppm from TMS as expected for an almost completely diamagnetic complex. The spectrum of complex **1** was already reported[3] and that of bis(5-chloro-N-isopropylsalicylaldiminato)-nickel(II) is similar to those reported by Holm for analogous complexes.[8] The assignment of all the peaks is then obtained by analogy. The spectra of mixed solutions show, besides the peaks of the starting complexes, two other peaks for each ring position, perhaps with the exception of 3 H whose peak is very broad.[9]

Discussion

All of these results are consistent with the assumption that in the mixed solution the following equilibrium takes place

$$\mathrm{Ni(5\text{-}Cl\text{-}SALen\text{-}N(C_2H_5)_2)_2 + Ni(X\text{-}SAL\text{-}N\text{-}alkyl)_2 \rightleftarrows 2Ni[(5\text{-}Cl\text{-}SALen\text{-}N(C_2H_5)_2)(X\text{-}SAL\text{-}N\text{-}alkyl)]}$$

The reaction toward the right is energetically favored by the formation of a new metal to ligand bond and

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[7] D. R. Eaton and W. D. Phillips, *Advan. Magn. Resonance*, **1**, 103 (1965).

[8] R. H. Holm, A. Chakravorty, and G. O. Dudek, *J. Am. Chem. Soc.*, **86**, 379 (1964).

[9] The proton shifts of the parent complexes in mixed solutions are slightly different from the proton shifts of the same complexes measured separately. This is evident especially for the A + B spectrum (Figure 2) in which such a difference amounts to *ca.* 10%. Differences in concentration may alter equilibria between planar and tetrahedral forms even if all the species concerned in the equilibria are monomeric (for example bis-(diphenylphosphine)nickel(II) halides): L. H. Pignolet and W. D. W. Horrocks, *J. Am. Chem. Soc.*, **91**, 3976 (1969). Moreover the equilibria reported here are known to be very sensitive to the polarity of the solvent.[1,4] In the case of the mixed solutions A + B the remaining parent complexes are *ca.* 15% of the total nickel complexes (according to the integrals of the peaks) and they are surrounded by other five-coordinate nickel complexes in high concentration which are expected to have a dipolar moment of 8–10 D.[1] Then the increased polarity of the environment resulting from the formation of new polar molecules may alter the equilibria of the remaining parent complexes.

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 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**.

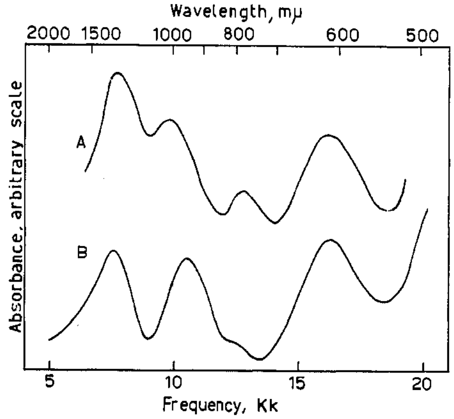

Figure 3.—Reflectance spectra of: A, [5-Cl-SALen-N(C_2H_5)$_2$-Ni; B, mixed compound [(5-Cl-SALen-N(C_2H_5)$_2$)(3-Cl-SAL-N-*i*-C_3H_7)]Ni.

Acknowledgment.—The authors wish to thank Professor L. Sacconi and Professor W. D. W. Horrocks, Jr., for helpful discussions.

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[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).

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Iridium–Tin Complexes with Acetylene and Ethylene

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This paper presents a description of the complexes Ir($SnCl_3$)(CO)(P(C_6H_5)$_3$)$_2$(C_2H_2) and Ir($SnCl_3$)(CO)(P(C_6H_5)$_3$)$_2$(C_2H_4). These complexes have been obtained adding anhydrous $SnCl_2$ and C_2H_2, or C_2H_4, to the complex IrCl(CO)(P(C_6H_5)$_3$)$_2$. A description of the intermediate product IrCl(CO)(P(C_6H_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_6H_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

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[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).