yellow to orange with precipitation of a colorless solid. After being stirred for 4 h, the mixture was filtered. The solvent was removed from the orange filtrate under reduced pressure. The resulting orange solid was then washed with 2 × 10 ml of diethyl ether, 3 × 10 ml of water, 1 ml of absolute ethanol, and finally 2 × 10 ml of diethyl ether. The resulting bright orange solid (75 mg, 76%) was recrystallized from acetonitrile under a nitrogen atmosphere affording orange crystallites. Spectral data: IR (KBr pellet) ν_{SH} 2580 cm^{-1}, ν_{CN} 1600, 1530 cm^{-1}, ν_{NO} 1115 cm^{-1}, ν_{BO} 810 cm^{-1}, ν_{BF} 995 cm^{-1}; NMR (CD_3CN) δ -1.55 (br s, 2 H), δ 1.10 (t, J = 8 Hz, 6 H), δ 2.40 (s, 6 H), δ 2.45 (m, 2 H), δ 2.80 (q, J = 8 Hz, 4 H), δ 4.1 (br t, 4 H). Anal. Calcd for $C_{13}H_{24}BF_2N_4O_2RhS_2$: C, 32.24; H, 5.00; N, 11.57; S, 13.24. Found: C, 32.29; H, 5.04; N, 11.47; S, 13.01.

(Hydrosulfido)(hydrido)[difluoro-3,3′-(trimethylenedinitrilo)bis(2-pentanone oximato)borate]rhodium(III) (8). Hydrogen sulfide was bubbled through a solution of Rh[C_2(DO)(DOBF$_2$)], **1** (100 mg, 0.239 mmol), in 10 ml of THF. The orange precipitate which formed immediately was collected by filtration and washed with diethyl ether (70 mg, 65%). Spectral data: IR (KBr pellet) ν_{Rh-H} 1910 cm^{-1}, ν_{CN} 1590, 1520 cm^{-1}, νNO 1115 cm^{-1}, ν_{BO} 1165, 810 cm^{-1}, ν_{BF} 990 cm^{-1}. Anal. Calcd for $C_{13}H_{24}BF_2N_4O_2RhS$: C, 34.54; H, 5.36; N, 12.40; S, 7.09. Found: C, 34.41; H, 5.36; N, 12.19; S, 7.26.

Acknowledgment. We gratefully acknowledge the support of the National Science Foundation through Grant CHE75-17018.

Registry No. **1**, 53335-25-4; **2a**, 61129-06-4; **2b**, 61129-07-5; **2c**, 61129-08-6; **2d**, 61193-32-6; **3a**, 61129-09-7; **3b**, 60224-27-3; **4**, 61129-11-1; **5**, 61129-10-0; **6**, 61129-12-2; **7**, 61193-33-7; **8**, 61129-13-3; acetyl disulfide, 505-73-7; sodium triphenylgermanium selenide, 61104-43-6; $Ge(C_6H_5)_3SeSeGe(C_6H_5)_3$, 61104-44-7; CH_3SSCH_3, 624-92-0; $C_6H_5SSC_6H_5$, 882-33-7; p-$C_6H_5NH_2SS$-p-$C_6H_5NH_2$, 722-27-0; $CH_3SeSeCH_3$, 7101-31-7; $C_6H_5SeSeC_6H_5$, 1666-13-3; $Ge(C_6H_5)_3SSGe(C_6H_5)_3$, 61104-37-8; acetyl sulfenyl chloride, 18369-83-0; thioacetic acid, 507-09-5; Na_2Se, 1313-85-5; triphenylgermanium bromide, 3005-32-1.

References and Notes

(1) (a) J. P. Collman and W. R. Roper, *J. Am. Chem. Soc.*, **88**, 3504 (1966); (b) J. P. Collman and W. R. Roper, *Adv. Organomet. Chem.*, **7**, 54 (1968).

(2) J. P. Collman, *Acc. Chem. Res.*, **1**, 136 (1968).

(3) (a) I. F. Shchegolev, *Phys. Status Solidi A*, **12**, 9 (1972); (b) H. R. Zeller, *Festkoerperprobleme*, **13**, 31 (1973); (c) A. F. Garito and A. J. Heeger, *Acc. Chem. Res.*, **7**, 232 (1974); (d) E. B. Yagubskii and M. L. Khidekel, *Russ. Chem. Rev. (Engl. Transl.)*, **41**, 1011 (1972); (e) J. S. Miller and A. J. Epstein, *Prog. Inorg. Chem.*, **20**, 1 (1975); (f) W. A. Little, *Phys. Rev. A*, **134**, 1416 (1964).

(4) (a) J. P. Collman, C. G. Pitt, C. K. Monteith, L. F. Ballard, J. C. Morrow, W. R. Roper, and D. Ulku, *J. Am. Chem. Soc.*, **88**, 4286 (1966); (b) J. P. Collman, L. Slifkin, L. F. Ballard, L. K. Monteith, and C. G. Pitt, "Proceedings of the 1967 International Symposium on Decomposition of Organometallic Compounds to Refractory Ceramics, Metals and Metal Alloys", K. S. Mazdiyashi, Ed., University of Dayton Press, Dayton, Ohio, 1968, pp 269–283; (c) J. P. Collman, L. K. Monteith, L. F. Ballard, C. G. Pitt, B. K. Klein, and L. M. Slifkin, *Solid State Commun.*, **6**, 301 (1968).

(5) (a) J. P. Collman, *J. Polym. Sci., Polym. Symp.*, **29**, 136 (1970); (b) J. P. Collman, "Proceedings of the International Symposium of the Physical and Chemical Problems of Possible Organic Superconductors", W. A. Little, Ed., Wiley-Interscience, New York, N.Y., 1970, pp 211–217.

(6) (a) J. P. Collman, J. K. Hoyano, and D. W. Murphy, *J. Am. Chem. Soc.*, **95**, 3424 (1973); (b) J. P. Collman and J. K. Hoyano, unpublished results.

(7) W. Dreuth, J. G. Noltes, E. J. Bulten, and H. M. J. C. Creemers, *J. Organomet. Chem.*, **17**, 173 (1969), and references therein.

(8) (a) J. P. Collman and M. R. MacLaury, *J. Am. Chem. Soc.*, **96**, 3019 (1974); (b) J. P. Collman, D. W. Murphy, and G. Dolcetti, *ibid.*, **95**, 2687 (1973).

(9) R. Zanella, R. Ros, and M. Graziani, *Inorg. Chem.*, **12**, 2736 (1973).

(10) H. Koepf and B. Block, *Z. Naturforsch., B*, **23**, 1536 (1968).

(11) For other examples of this reaction, see T. B. Rauchfuss and D. M. Roundhill, *J. Am. Chem. Soc.*, **97**, 3386 (1975).

(12) J. P. Collman, R. K. Rothrock, J. D. Sen, T. D. Tullius, and K. O. Hodgson, *Inorg. Chem.*, **15**, 2947 (1976).

(13) (a) H. Kopf and M. Schmidt, *Angew. Chem., Int. Ed. Engl.*, **4**, 953 (1965); (b) H. Vahrenkamp, *ibid.*, **14**, 322 (1975); (c) W. Beck, W. Danzer, and G. Thiel, *ibid.*, **12**, 582 (1973); (d) D. Morelli, A. Segre, R. Ugo, G. LaMonica, S. Cenini, F. Conti, and F. Bonati, *Chem. Commun.*, 524 (1967); (e) W. Beck, W. Danzer, and R. Hofer, *Angew. Chem., Int. Ed. Engl.*, **12**, 77 (1973); (f) M. Ardon and H. Taube, *J. Am. Chem. Soc.*, **89**, 3661 (1967).

(14) H. Böhme, H. W. Goubeaud, and H. D. Stachel, *Chem. Ber.*, **92**, 362 (1959).

(15) G. E. Coates, *J. Chem. Soc.*, 2839 (1953).

(16) (a) M. C. Henry and W. E. Davidson, *Can. J. Chem.*, **41**, 1276 (1963); (b) M. C. Henry and W. E. Davidson, *J. Org. Chem.*, **27**, 2252 (1962).

(17) N. S. Vyazankin, M. N. Bochkarev, and L. P. Sanina, *J. Gen. Chem. USSR (Engl. Transl.)*, **36**, 1169 (1966).

Contribution from the Laboratoire de Chimie Minérale
Physique, Institut de Chimie, Strasbourg, France

Pentacoordinate Nickel(II) Complexes of Monodentate Ligands. Complexes of Trimethylstibine

M. F. LUDMANN, M. DARTIGUENAVE,* and Y. DARTIGUENAVE

Received February 3, 1976 AIC60082+

Five new complexes of nickel(II) and trimethylstibine, $NiX_2(SbMe_3)_3$ (X = Cl, Br, I, CN, SbMe$_3$), have been synthetized and characterized. To our knowledge, these are the first examples of stable Ni(II) complexes containing Ni–Sb bonds in which neither steric nor chelating properties of the ligand can be responsible for the observed stability. Except $[Ni(SbMe_3)_5](BF_4)_2$ which is a 2:1 electrolyte, they are molecular, diamagnetic complexes. On the basis of their variable-temperature electronic spectra in the solid state and in solution in organic solvents, they have been assigned a trans trigonal-bipyramidal structure (D_{3h} symmetry). The two ligand field bands attributed to the allowed $^1A'_1 \rightarrow {}^1E'$ and the symmetry-forbidden $^1A'_1 \rightarrow {}^1E''$ transition are present for all complexes. At low temperature, improved resolution of the spectra is marked by an increase in symmetry and in the extinction coefficient of the lower energy ligand field band. The stability of the complexes follows the order I > Br > SbMe$_3$ >> CN > Cl. Only the first three derivatives have been isolated in the solid state. $[Ni(SbMe_3)_5](BF_4)_2$ represents one of the few Ni(II) pentacoordinate complexes with five identical ligands. They are all dissociated in solution at room temperature, even in the presence of excess SbMe$_3$, but they are stable at low temperature. However no tetracoordinate species have been obtained. The particular influence of SbMe$_3$ in stabilizing pentacoordinate Ni(II) complexes is discussed by comparison with trimethylphosphine from the point of view of steric and electronic factors (polarizability and σ- and π-bonding abilities) of the ligands.

Introduction

It is well-known that monodentate tertiary phosphines, phosphites, and phosphonites readily form pentacoordinate low-spin complexes of the type NiX_2L_3 (X = halide or pseudohalide) with nickel(II).[1] However, the kinetic and thermodynamic stabilities of these complexes, as well as their stereochemistries which depend on both electronic and steric effects, are not yet fully understood.

In recent years, particular attention has been focused on the geometrical structure and characterization of these complexes, in order to determine their preferred geometry: the trigonal

---

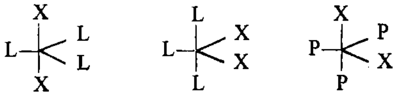
* To whom correspondence should be addressed at the Laboratoire de chime de Coordination du CNRS, BP 41-42, 31030, Toulouse, France.

Table I. Physical Properties of the Complexes

Compd	Color	Mol wt (calcd) in nitrobenzene	Mp,[a] °C	μ_{eff},[b] μ_B	Λ_M(solvent), Ω^{-1} mol^{-1} cm^2
$NiI_2(SbMe_3)_3$	Dark green	785 (813)	112 ± 2	0.38	0.6 (nitromethane)
$NiBr_2(SbMe_3)_3$	Dark green	680 (719)	125 ± 2	1.61	1.22 (nitrobenzene)
$NiCl_2(SbMe_3)_3$[c]	Dark blue				~0 (dichloromethane)
$[Ni(SbMe_3)_5](BF_4)_2$	Violet	1010 (1066)	148 ± 2 dec	0.36	180 (nitrobenzene)
$Ni(CN)_2(SbMe_3)_3$[c]	Orange				~0 (dichloromethane)

[a] Uncorrected; determined in sealed tube. [b] At 295 K. [c] Only in solution; not isolated in the solid state.

bipyramid (TBP) or the square pyramid (SP). However, we have shown recently[2] in the study of the trimethylphosphine complexes $NiX_2(PMe_3)_3$ that not only the geometry but also the stereochemistry should be considered. In the TBP geometry, which is preferred, both the trans (A) and cis (B) stereoisomers may be present, according to the nature and bonding properties of X. The cis stereoisomer C which is theoretically possible has not been characterized experimentally.



A B C

X = CN, NCS X = Cl, Br, I

This led us to consider the influence of the nature of X and L on the existence, stability, and stereochemistry of the pentacoordinate NiX_2L_3 complexes. We have therefore undertaken a detailed investigation of the interaction of nickel halides and pseudohalides with trimethylarsine and trimethylstibine.[3,4] In contrast to the numerous phosphorus complexes, very few Ni(II) complexes appear to have been reported with monodentate tertiary arsine and stibine ligands.[4-6] In fact, it is claimed that these ligands do not form stable complexes with first-row elements in their "normal" oxidation state. As the study of the trimethylarsine complexes is still in progress, we wish to report here our results on the trimethylstibine–nickel(II) compounds.

The preparation and characterization of the new pentacoordinate complexes $NiX_2(SbMe_3)_3$ (X = Cl, Br, I, CN, $SbMe_3$) are described first. The ambient- and low-temperature electronic spectra of these compounds were investigated in detail, in order to assign the ligand field spectra and to get information on the stereochemistry of the ground state. Further it was of interest to examine the temperature dependence of the ligand field bands and compare the results to those found for other pentacoordinate d^8 complexes.

On the basis of these results, the particular influence of $SbMe_3$ in stabilizing pentacoordinate Ni(II) complexes will be discussed.

Experimental Section

(A) Preparation of the Compounds. Trimethylstibine was prepared as reported in ref 7 and stored as $Sb(CH_3)_3Br_2$, which is a crystalline, stable, white powder. The stibine was regenerated by heating a mixture of this complex with an excess of powdered zinc and water under nitrogen. The distilled $Sb(CH_3)_3$ (yield 70%) was stored in a tightly stoppered ampule. All metal salts were reagent grade and were used without further purification.

Dichloromethane was dried and redistilled from $CaCl_2$; 2-methyltetrahydrofuran, from $LiAlH_4$.

$NiI_2(SbMe_3)_3$. A 2-ml (18-mmol) sample of $SbMe_3$ was added dropwise to a suspension of $NiI_2{\cdot}6H_2O$ (2 g; 4.7 mmol) in 10 ml of dichloromethane under nitrogen. A dark green color developed immediately. The solution was stirred for several hours and then filtered to remove the unreacted nickel iodide. Concentration of the solution in vacuo yielded dark green crystals. These were recrystallized from dichloromethane containing an excess of $SbMe_3$; yield ≃80%. Anal. Calcd for $NiI_2Sb_3C_9H_{27}$: C, 13.29; H, 3.34; Ni, 7.22; Sb, 44.92. Found: C, 13.14; H, 3.20; Ni, 7.20; Sb, 44.50.

$NiBr_2(SbMe_3)_3$. Dark green crystals of $NiBr_2(SbMe_3)_3$ were obtained by the same method when 3.5 ml (31.5 mmol) of $SbMe_3$ was added to 2.45 g (9 mmol) of $NiBr_2{\cdot}3H_2O$ in 10 ml of dichloromethane; yield ≃80%. Anal. Calcd for $NiBr_2Sb_3C_9H_{27}$: C, 15.03; H, 3.78; Ni, 8.16; Sb, 50.79. Found: C, 15.34; H, 3.76; Ni, 8.14; Sb, 50.59.

$NiCl_2(SbMe_3)_3$. A dark blue solution was obtained after 24 h when 1.3 g (10 mmol) of anhydrous nickel chloride was stirred with 3.5 ml (31.5 mmol) of $SbMe_3$ in dichloromethane (5 ml). No solid could be precipitated from this solution. Concentration of the solution or addition of diethyl ether, pentane, or hexane (in which such complexes are insoluble) led to decomposition and precipitation of $NiCl_2$. The formula $NiCl_2(SbMe_3)_3$ was thus attributed to the blue species in solution on the basis of spectroscopic and conductometric evidence.

$Ni(CN)_2(SbMe_3)_3$. Addition of 3 ml (27 mmol) of $SbMe_3$ to a suspension of anhydrous $Ni(CN)_2$ (0.99 g, 9 mmol) in dichloromethane (10 ml) under nitrogen led to an orange-red solution, from which only a red oil could be obtained by concentration in vacuo. Addition of pentane caused precipitation of a light orange solid which was only partly soluble in dichloromethane. This material was impure and remained so on recrystallization. No acceptable analysis could be obtained from these products.

$[Ni(SbMe_3)_5](BF_4)_2$. A 9-g (54-mmol) sample of $SbMe_3$ was added to 1 g (3 mmol) of $Ni(BF_4)_2{\cdot}6H_2O$ dissolved in ethanol and the mixture was stirred vigorously for 3 days. The violet solid which precipitated was isolated by filtration and used without further recrystallization; yield ≃80%. Anal. Calcd for $NiSb_5C_{15}H_{45}BF_4$: C, 16.87; H, 4.25; Ni, 5.50; Sb, 57.08. Found: C, 16.68; H, 4.11; Ni, 5.85; Sb, 56.81.

(B) Physical Measurements. All ultraviolet and visible spectra were obtained with a Cary 14 spectrophotometer equipped with a low-temperature Dewar. Solution spectra were measured in 10.00- and 1.00-mm silica cells, using dichloromethane and 2:1 mixtures of 2-methyltetrahydrofuran and ethanol as solvents. Calculation of molar extinction coefficients was based on the total metal present and they were corrected for volume contraction at 77 K. The spectra of the solid complexes were examined by using a thin film of poly(vinyl acetate) as a support.

Magnetic susceptibilities of the solid complexes were determined by the Faraday method using a Setaram MTB 10-8 microbalance coupled with an Alpha electromagnet. Experimental values are the mean of three determinations at 295 K. They are corrected for the diamagnetism of the ligands.[8] Conductivities of 10^{-3} M solutions of the complexes were measured using a Beckmann RC-18 conductivity bridge. To prevent decomposition of these complexes, excess stibine was added after checking that the conductivity of the solvent did not change with excess ligand present. Molecular weights were determined by cryoscopy in nitrobenzene. Gaussian analyses were performed on the spectra using a Du Pont Model 310 curve resolver.

Elemental microanalyses were carried out by the Service Central de Microanalyse du CNRS à Paris.

Results

$NiX_2(SbMe_3)_3$ (X = Cl, Br, I). The physical properties of these complexes are listed in Table I. The band maxima and the extinction coefficients of the electronic absorption spectra are given in Table II.

$NiI_2(SbMe_3)_3$ and $NiBr_2(SbMe_3)_3$ are dark green crystalline pentacoordinate complexes. They are nonelectrolytes in nitromethane. Whereas $NiI_2(SbMe_3)_3$ is diamagnetic, $NiBr_2(SbMe_3)_3$ has the unusual magnetic moment 1.5 μ_B (averaged over three individually prepared samples) a value which is intermediate between those of high-spin and low-spin Ni(II) complexes. Similar magnetic moments have been reported for $NiI_2(HPPh_2)_3$ (μ_{eff} = 1.48 μ_B)[9] and $NiI_2(PR_3)$

Table II. Electronic Absorption Spectra of the Complexes $NiX_2(SbMe_3)_3$ in the Presence of Excess Ligand [ν, μm^{-1} (ϵ)]

	Solid state (film)		CH_2Cl_2 soln		EPA or 2-MeTHF–EtOH soln	
Compd	295 K	77 K	295 K	176 K	295 K	77 K
NiI_2L_3	1.57	1.63	1.57 (1170)	1.64 (2240)	1.57 (980)	1.69 (2620)
	1.95[a]	2.00	1.95 (350)[a]	1.95 (400)[a]	1.95 (240)[a]	2.00 (465)
		2.60		2.53 (2840)		2.63 (2960)
	3.64	3.64				
		3.78				
$NiBr_2L_3$	1.55	1.67	1.59 (1230)	1.67	1.59 (615)	1.70 (1640)
		2.00			2.00 (125)[a]	2.00 (360)
	2.67	2.76	2.67 (4500)	2.76 (6400)		
	3.64	3.78				
$NiCl_2L_3$			1.62	1.87		
			2.70			
$NiL_5(BF_4)_2$			1.84 (655)	1.91 (990)		
			3.08 (4550)	3.08 (5600)		
			3.38 sh	3.98 sh		
$Ni(CN)_2L_3$			2.38	2.41		
			3.84	3.92		

[a] Value obtained from gaussian analysis.

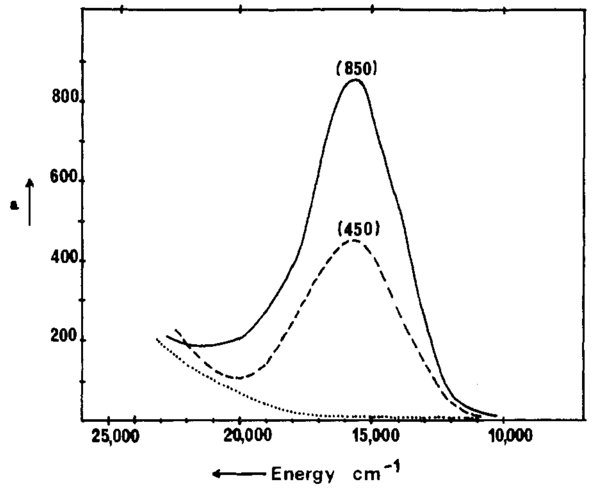


Figure 1. Room-temperature absorption spectra for 2-MeTHF–EtOH solutions of $NiBr_2(SbMe_3)_3$: ····, without excess $SbMe_3$; - - -, with excess $SbMe_3$ (Sb:Ni $\simeq$ 1000); —, with excess $SbMe_3$ (Sb:Ni $\simeq$ 8000).

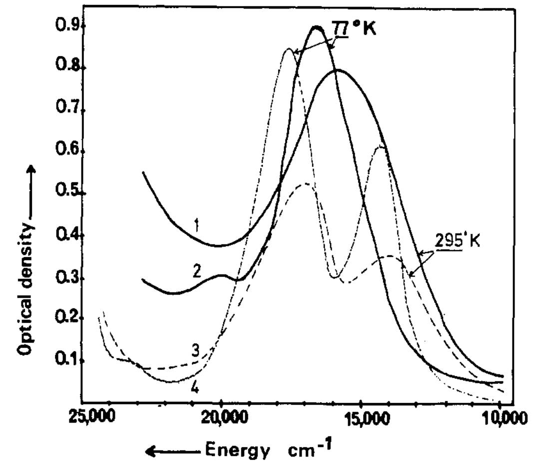


Figure 2. Temperature dependence of the solid-state electronic spectrum of $NiBr_2(SbMe_3)_3$ (as thin films of poly(vinyl acetate)) (curves 1 and 2) and of $NiBr_2(PMe_3)_3$ (curves 3 and 4).

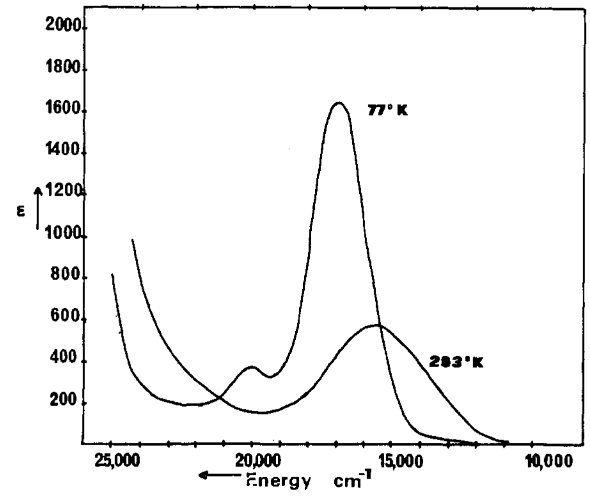


Figure 3. Temperature dependence of the electronic spectrum of $NiBr_2(SbMe_3)_3$ in 2-MeTHF–EtOH (with $SbMe_3$ in excess, Sb:Ni $\simeq$ 1000).

(PR_3 = 9-substituted 9-phosphofluorenes).[10] However, further studies of the magnetic properties of $NiBr_2(SbMe_3)_3$ have shown that the magnetic moment is independent of both temperature (4–300 K) and magnetic field (4200–5600 Oe). Thus equilibrium between high- and low-spin forms does not occur and ferromagnetic impurities are absent. No signal could be resolved in the Ni(I) range by ESR, thus suggesting the absence of a reduced Ni(I) paramagnetic species. The origin of the observed moment still remains uncertain and may be due to some undetermined paramagnetic species.

Cryoscopic measurements in nitrobenzene show that $NiI_2(SbMe_3)_3$ and $NiBr_2(SbMe_3)_3$ are monomeric. However, they readily dissociate in solution at concentrations of the order of 10^{-3} M. A colorless, slightly cloudy solution is observed when they are dissolved in organic solvents. These solutions become green and clear when excess $SbMe_3$ is added. Typical spectra of $NiBr_2(SbMe_3)_3$ in the presence of a large excess of $SbMe_3$ in 2-MeTHF–EtOH solution at ambient temperature are shown in Figure 1. Comparison with the solid-state spectrum (Figure 2) shows that the absorption maximum at 15 900 cm^{-1} can be assigned to the species $NiBr_2(SbMe_3)_3$. Thus, dissociation still occurs at room temperature in the presence of a 1000-fold excess of $SbMe_3$. Since we have observed in previous studies on similar phosphine and arsine complexes of Ni(II) that the unstable pentacoordinate species are preserved in solution at low temperature, we have reported in Figure 3 the 77 K electronic spectrum of $NiBr_2(SbMe_3)_3$ (with excess $SbMe_3$) in 2-MeTHF–EtOH solutions. The similarity of the spectra obtained in the solid state and in solution, at ambient and low temperatures, indicates that the pentacoordinate species is stabilized when the temperature is lowered.

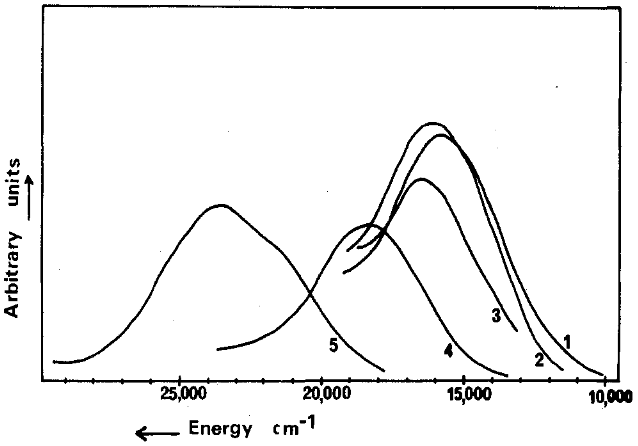
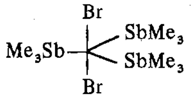


Figure 4. Low-temperature (176 K) electronic spectra of NiX$_2$(SbMe$_3$)$_3$ complexes with excess SbMe$_3$ (Sb:Ni $\simeq$ 1000) in CH$_2$Cl$_2$ solution: 1, NiI$_2$L$_3$; 2, NiBr$_2$L$_3$; 3, NiCl$_2$L$_3$; 4, [NiL$_5$](BF$_4$)$_2$; 5, Ni(CN)$_2$L$_3$.

At 295 K, NiBr$_2$(SbMe$_3$)$_3$ and NiI$_2$(SbMe$_3$)$_3$ exhibit a broad, slightly asymmetric ligand field band at 15 900 cm^{-1} (for X = Br) and 15 700 cm^{-1} (for X = I), together with a weaker band on the high-energy side at 20 000 cm^{-1} (for X = Br) and 19 750 cm^{-1} (X = I), resolved by a Gaussian curve analysis. On cooling, an increase in intensity and a slight shift toward higher energies are observed for the main transition, accompanied by improved resolution in the weaker transition at about 20 000 cm^{-1} (Figure 3). These ligand field spectra are very similar in shape and band position to those of pentacoordinate Ni(II) complexes known to be of trigonal-bipyrimidal structure with D_{3h} or C_{3v} symmetry.[11] Hence, the trimethylstibine–nickel(II) complexes NiBr$_2$(SbMe$_3$)$_3$ and NiI$_2$(SbMe$_3$)$_3$ are trans isomers with TBP geometry; i.e., the two bromine or iodine atoms occupy the axial position of the trigonal bipyramid.



The two low-energy transitions are therefore assigned to the symmetry-allowed ligand field transition $^1A'_1 \rightarrow {}^1E'$ and symmetry-forbidden transition $^1A'_1 \rightarrow {}^1E''$.

This result is particularly interesting since similar pentacoordinate TBP structures are known for monodentate secondary and tertiary phosphine–nickel(II) complexes and monodentate tertiary arsine–nickel(II) compounds, but with a cis TBP stereochemistry (the two halides being in equatorial positions). For these complexes, the low-energy asymmetric band is replaced by two distinct, intense bands, the ϵ values of which increase when the temperature is lowered (Figure 2).

The calculation of the oscillator strength values of the ligand field bands $^1A'_1 \rightarrow {}^1E$, in accordance with the relation $f \simeq 4.6 \times 10^{-6}\epsilon_{max}\bar{\nu}_{1/2}$, where ϵ_{max} is the extinction coefficient of the maximum absorbance and $\bar{\nu}_{1/2}$ is the half-width of the band, shows that $f_{295K} = 0.010 \pm 0.005$ and $f_{77K} = 0.017 \pm 0.005$ for NiBr$_2$(SbMe$_3$)$_3$ and that f_{295}K = 0.019 ± 0.005 and $f_{77K} = 0.023 \pm 0.005$ for NiI$_2$(SbMe$_3$)$_3$. Thus f is nearly temperature independent, as expected for the electronically allowed $^1A'_1 \rightarrow {}^1E'$ transition. Its smaller value at room temperature may be due to the fact that the pentacoordinate complexes are still dissociated under these conditions.

The charge-transfer spectra of NiBr$_2$(SbMe$_3$)$_3$ and NiI$_2$(SbMe$_3$)$_3$ show a similar transition at 36 400 cm^{-1} (37 800 cm^{-1} at 77 K). This band is present in all of the stibine complexes and can be definitively assigned to a L → M (Sb → Ni) charge-transfer band. Finally the transition at 26 700 cm^{-1} in NiBr$_2$(SbMe$_3$)$_3$ and 26 000 cm^{-1} in NiI$_2$(SbMe$_3$)$_3$ can be reasonably assigned to pπ X → Ni charge transfer.

Attempts to isolate a solid pentacoordinate nickel(II) chloride complex were unsuccessful. However, mixing of trimethylstibine and nickel(II) chloride in 3:1 and higher (5:1 and 10:1) molar ratios, in dichloromethane, led to the formation of dark blue solutions. The conductance of these dichloromethane solutions is decidedly lower than expected for an univalent electrolyte and is consistent with the presence of a molecular species.

The characterization of the species is made by electronic spectroscopy. The ambient-temperature spectrum consists of a large asymmetric ligand field band at about 16 200 cm^{-1}, i.e., in the same energy range as found for NiI$_2$(SbMe$_3$)$_3$ and NiBr$_2$(SbMe$_3$)$_3$. A trans TBP structure may thus be assumed for this species in solution. However, lowering of the temperature leads to a marked change in the color of the solution, which turns from blue to violet. Similarly, the energy of the ligand field band shifts from 16 200 to 18 700 cm^{-1} in the temperature range 295–176 K. Moreover, the pπ → Ni transition at 27 000 cm^{-1} disappears on cooling. These observations suggest that a new species is present in solution at 176 K.

These results are consistent with the fact that NiCl$_2$ is less effective than NiBr$_2$ and NiI$_2$ in stabilizing pentacoordination with "soft" ligands such as PR$_3$, AsR$_3$, and SbR$_3$.[12] For example, in the series PMe$_3$, AsMe$_3$, and SbMe$_3$, no stable crystalline pentacoordinate complexes have been isolated at ambient temperature: the more stable NiCl$_2$(PMe$_3$)$_3$ immediately evolves PMe$_3$,[2] NiCl$_2$(AsMe$_3$)$_3$ can only be prepared at low temperature (−50 °C), and NiCl$_2$(SbMe$_3$)$_3$ is characterized only in solution.

No tetracoordinate NiX$_2$(SbMe$_3$)$_2$ (X = halide) complexes have been isolated. This may be due to the greater stability of the pentacoordinate species relative to the tetracoordinate species.

Ni(CN)$_2$(SbMe$_3$)$_3$. Since cyanide ion shows a particular tendency to stabilize pentacoordination in the nickel–phosphine complexes,[12,13] it was of interest to examine the reaction of SbMe$_3$ with Ni(CN)$_2$. Mixing of the anhydrous nickel salt with excess SbMe$_3$ (molar ratio 3:1 or higher) leads to an orange-red solution from which only a red oil could be obtained by concentration in vacuo. Several attempts to precipitate a solid yielded only an impure compound which is slightly soluble in dichloromethane. Its infrared spectrum clearly shows three sharp cyanide modes at 2176, 2120, and 2105 cm^{-1}. This result is compatible with the presence of a polymerized cyanide species such as that described by Coskran et al.[14] for nickel(II)–trimethyl phosphite complexes. But contamination by Ni(CN)$_2$ can reasonably be postulated by the presence of its characteristic cyanide band at 2176 cm^{-1},[15] thus suggesting decomposition. We have repeated the reaction several times, with the same result.

The infrared spectrum of the solution, on the contrary, showed only one band in the cyanide region at 2100 cm^{-1}, which strongly favors the presence in solution of a monomeric, symmetrical species. The very low conductance of the solution, measured at various concentrations, confirms the presence of a molecular complex. However, the existence of a pentacoordinate complex of trans TBP geometry (the two CN groups being in axial positions) is shown unambiguously in the electronic spectrum, by the presence of an intense asymmetric ligand field band at 23 800 cm^{-1}. This band can be resolved by a Gaussian analysis at room temperature into two components at about 20 900 and 24 000 cm^{-1}. At 190 K, only a small increase in band intensity and a slight shift toward higher energy are observed. Similar transitions have been found at 25 600 cm^{-1} for $Ni(CN)_2(PMe_3)_3$,[13] at 24 000 and 27 500 cm^{-1} for $Ni(CN)_2(PPh(OEt)_2)_3$, and at 21 700 and 24 100 cm^{-1} for $Ni(CN)_2(PPhMe_2)_3$,[34] which are known to have a slightly distorted trans TBP structure.[16] This asymmetric band can thus be attributed to the $^1A'_1 \rightarrow {}^1E'$ ligand field transition.

The charge-transfer transition which is observed at 38 400 cm^{-1} in the "$Ni(CN)_2(SbMe_3)_3$" species and which is present with nearly the same energy in the halide complexes can reasonably be attributed to σ $SbMe_3 \rightarrow Ni$ charge transfer. However a $Ni \rightarrow CN$ π transition cannot be ruled out.

Thus in the trimethylstibine–nickel(II) complexes, the cyanide anion is not as effective as the halides in stabilizing pentacoordination. For tertiary phosphine–nickel(II) complexes, the stability of the NiX_2L_3 species follows the order[2,12,13,24] $CN \gg I > Br > Cl \sim NO_2 \sim NCS > PMe_3$ whereas for stibine–nickel(II) complexes, the experimental order of stabilities is $I \sim Br \sim SbMe_3 \gg CN > Cl$. These results emphasize the importance of the particular properties of the two ligands X and L, which have to be of similar electronegativities in order to stabilize pentacoordinate complexes. Steric and electronic factors will be discussed later. Further support is provided by the fact that the stable cationic $NiSb_5^{2+}$ species can be isolated.

$[Ni(SbMe_3)_5](BF_4)_2$. The existence of this cationic complex was suspected during the investigation on the $NiCl_2$–$SbMe_3$ solution containing a large excess of $SbMe_3$ since a drastic change in the solution color was observed on cooling. Very few low-spin crystalline Ni(II) complexes with five monodentate ligands have been reported: $Ni(CN)_5^{3-}$,[17] $[Ni(P(OR)_3)_5](ClO_4)_2$.[18,19] For electronic and steric reasons, the $Ni(SbMe_3)_5^{2+}$ cation was somewhat unexpected. However, we were able to isolate $[Ni(SbMe_3)_5](BF_4)_2$ as a violet crystalline powder when $Ni(BF_4)_2 \cdot 6H_2O$ was vigorously stirred with excess $SbMe_3$ in ethanol. The complex is pentacoordinate, monomeric, and diamagnetic and is a 2:1 electrolyte in dichloromethane. It is soluble in dichloromethane but insoluble in methanol and ethanol. Its electronic spectrum at 295 and 176 K in dichloromethane with excess $SbMe_3$ exhibits the pattern expected for a TBP geometry (D_{3h}). There is a symmetrical ligand field band $^1A'_1 \rightarrow {}^1E'$ at 18 400 cm^{-1} (ϵ 655), which becomes more symmetrical and shifts slightly toward higher energy at low temperature. Further, the weaker symmetry-forbidden $^1A'_1 \rightarrow {}^1E''$ transition, which can be resolved by Gaussian analysis, is observed at 22 800 cm^{-1}. The lowest energy transition occurs in the same energy range as for $NiX_2(SbMe_3)_3$ (X = halide) and $[Ni(PMe_3)_5]Br_2$ (19 200 cm^{-1}).[2] The two bands at 30 800 and 39 800 cm^{-1} can reasonably be assigned to σ $Sb \rightarrow Ni$ charge transfer.

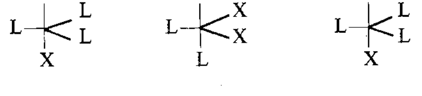
Discussion

To our knowledge these compounds are the first Ni(II) complexes reported which contain a soft monodentate tertiary stibine as ligand. Until now, the only known examples of Ni^{II}–Sb coordination are found in complexes with mixed Sb–As or Sb–P bidentate or tripod ligands such as (*o*-dimethylarsinophenyl)dimethylstibine, (*o*-diphenylphosphinophenyl)diphenylstibine, (*o*-diphenylarsinophenyl)diphenylstibine, tris(3-dimethylarsinopropyl)stibine, or tris(*o*-dimethylarsinophenyl)stibine.[20] In these complexes, the chelating and steric properties of the ligand play an important role in stabilizing the pentacoordinate species. In general, trivalent antimony behaves as a good ligand when it reacts with class "B" metals such as Pd(II) and Pt(II) or with the first-row metals in their lower oxidation state (Ni^0, Fe^0).[5,6] Since nickel is reported by Ahrland et al.[21] to be a "borderline" metal, it can act either as a class "A" or a class "B" metal. If, following these authors, a metal can be characterized as behaving as a class A metal when the stability order of its halides is $F < Cl > Br > I$ and a class B metal when the order is $F \ll Cl < Br < I$, Ni(II) acts as a typical B or "soft" metal in the pentacoordinate complexes of PR_3, AsR_3, and SbR_3. The stability order of the complexes NiX_2L_3 is always $I > Br \gg Cl$. Hence, this class B character of pentacoordinated Ni(II) explains why the formation of a relatively stable Ni^{II}–SbR_3 bond can occur. On the contrary, a class A character is observed for Ni(II) in the tetracoordinate complexes of trimethylphosphine,[22,23] since the observed stability order of the complexes NiX_2L_2 is $Cl > Br \gg I$.

The qualitatively observed thermodynamic stabilities of the trimethylstibine nickel(II) complexes follow the order $I > Br > SbMe_3 \gg CN > Cl$, which agrees with the one found by Dahl,[24] Alyea and Meek,[12] and Dawson et al.[2] for low-spin, pentacoordinate Ni(II) complexes with tertiary phosphines. The only difference is the position of the cyanide anion. For the trimethylstibine–nickel(II) complexes, we have shown that CN^- is a very poor ligand whereas it is known to be an exceptionally good ligand, giving very stable pentacoordinate Ni(II) complexes by itself or with phosphorus ligands. The arguments ordinarily used to explain the particular role of CN^- (its high position in the spectrochemical series and its good σ-donor ability in the nephelauxetic series) still apply but are obviously not sufficient to explain the different stability of the complexes. The relative influence of the two ligands CN and L (i.e., unfavorable competition) has to be considered in view of the existence of such different complexes as $Ni(CN)_5^{3-}$, $Ni(CN)_2(PR_3)_3$, $Ni(SbMe_3)_5^{2+}$, and $Ni(CN)_2(SbMe_3)_3$, the first three of which have been characterized and isolated in the solid state. Hence, the stabilization of pentacoordinate complexes seems more effective with ligands of comparable polarizabilities. Thus CN^-, which is nearly equivalent to chlorine in the nephelauxetic series,[25] is no longer a good ligand in the presence of the very "soft" $SbMe_3$. The fact that high polarizability of the ligands (and consequently more covalent bonds) favors pentacoordination in Ni(II) is in agreement with the high molar extinction coefficients observed for the ligand field bands.

Our studies with analogous Ni(II) complexes of trimethylphosphine and trimethylarsine allow us to compare the three series of pentacoordinate Ni(II) complexes. First of all, trigonal-bipyramidal structures can be reported for all NiX_2L_3 and NiL_5^{2+} complexes ($L = PMe_3$, $AsMe_3$, $SbMe_3$). Thus, since the energy difference between a trigonal-bipyramidal and a square-pyramidal complex is known to be small, the trigonal bipyramid is shown to be the most stable structure for such complexes, that is, in the absence of steric or chelating effect of the ligands. This is in good agreement with the previously reported results for pentacoordinate Ni(II) complexes with monodentate ligands since very few square-pyramidal low-spin Ni(II) compounds are known.[17,26]

Moreover, we have been able to show that two different TBP isomers are present, following the nature of X and L: a "trans" isomer (two X in axial positions of the TBP) and a "cis" eq–eq isomer (two X in equatorial positions of the TBP).



"trans" "cis" "trans"

X = CN, NCS

eq–eq

X = Cl, Br, I

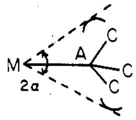
L = PMe_3, $AsMe_3$

X = Cl, Br, I, CN

L = $SbMe_3$

It was surprising to find only trans isomers of D_{3h} symmetry for $NiX_2(SbMe_3)_3$ complexes since trans and cis isomers are formed when NiX_2 reacts with PMe_3 or $AsMe_3$. Therefore it was tempting, at first, to assume that since the interligand

Table III. Comparative Cone Angle Calculation (2α) (As Defined by Tolman[24]) for d^8 Complexes Containing PMe_3, $AsMe_3$, and $SbMe_3$ Ligands (M = Ni, Fe; A = P, As, Sb)



Complexes	Ref	M–A, Å	A–C, Å	CAC, deg	Cone angle 2α, deg
$Br_2(PMe_3)_2Ni{-}PMe_3$	2	2.20	1.83 ± 4	102 ± 4	137
$(CO)_4Fe{-}AsMe_3$	28	2.30	2.06	104	126
$(CO)_4Fe{-}SbMe_3$	28	2.49	2.02	106	130

repulsions are lower in the equatorial plane of the TBP, the "bulky" $SbMe_3$ would occupy the equatorial sites in order to decrease the steric interactions. However, although van der Waals radii are in the order P < Br < As < I < Sb, the C–P–C, C–As–C, and C–Sb–C angles in the free ligands decrease in the order P > As > Sb. A cone angle 2α calculation[27] performed on the d^8 complexes $NiBr_2(PMe_3)_3$, $Fe(CO)_4(AsMe_3)$, and $Fe(CO)_4(SbMe_3)$, the structures of which are reported,[3,28] shows that 2α has approximately the same value for all three compounds (Table III). Thus the steric factor is not vital in determining the stereochemistry. This result is confirmed since the stable compound $[Ni(SbMe_3)_5](BF_4)_2$ with $SbMe_3$ ligands both in the equatorial and axial positions of the TBP can be isolated.

One may therefore conclude that the stereochemistries (cis or trans TBP isomers) adopted by the pentacoordinate NiX_2L_3 complexes can be correlated with electronic factors: that is, σ- and π-bonding properties of the ligands.

Until now, no satisfactory answer to the problem of the competition of ligands for the two substitution sites in a TBP has been proposed.

Muetterties' rule, generally used until now[29]—stating that the most electronegative substituent of a d^8 TBP prefers axial positions (based on the idea that metal d–ligand and ligand–ligand repulsions would be minimized when the negatively charged ligand is placed on the z axis facing the empty d_{z^2} orbital)—can be successfully used for the complexes $NiX_2(PMe_3)_3$ and $NiX_2(AsMe_3)_3$ (X = CN, NCS),[4,13] $Ni(CH_3)_2(PMe_3)_3$,[30] $Ni(CN)_2(P(OR)_3)_3$,[14] and $NiX_2(SbMe_3)_3$ but is violated for the halide complexes $NiX_2(PMe_3)_3$,[2] $NiX_2(AsMe_3)_3$,[4] $NiX_2(P(OMe)_3)_3$,[31] $NiX_2(PHPh_2)_3$.[9]

Very recently, Hoffmann[32] proposed an explanation based on an extended Hückel calculation. Its results agree with the experimental data for good σ-donor ligands (such as H^-, CH_3^-) which prefer the axial position or for good π-acceptor ligands (such as CO) which prefer the equatorial position. Moreover, he showed that for ligands which are both σ-donors and π-acceptors, an a priori preference cannot be set out.

Thus the choice between the substitution sites is a resultant of a preference set by both the σ and π properties of each ligand. This result points out an important problem, that is, the way of evaluation of the relative strength of σ- and π-bonding abilities of the ligands which still remains very often hazardous.

This is particularly explicit in the PMe_3, $AsMe_3$, and $SbMe_3$ series. The σ- and π-bonding abilities of these ligands have been investigated by Chatt et al.,[33] who have concluded from their experiments that the σ-donor properties follow the order $PMe_3 > AsMe_3 > SbMe_3$, while their π-bonding abilities must be nearly the same. Moreover, we have been able to show that their steric requirements are nearly identical. Hence, the major difference between PMe_3, $AsMe_3$, and $SbMe_3$ ought to be the decrease of their σ-donor ability from P to Sb, which does not explain the structural differences observed in the pentacoordinate Ni(II) complexes. Following Hoffmann's conclusion, however, it is tempting to conclude that the entering of $SbMe_3$ in the equatorial positions of the TBP is due to its weaker σ-donor but better π-acceptor properties. This argument gains a support from the comparable spectrochemical influence of $SbMe_3$ and PMe_3 in the two TBP cationic complexes of NiL_5^{2+},[2] which cannot be explained on σ ground alone.

Contrary to the observation of Gray et al.[34] on Ni(II), Pt(II), and Pd(II) complexes with tripod ligands, the electronic spectra of the trimethylstibine $NiX_2(SbMe_3)_3$ complexes show no marked change at low temperature. The observed increase of the *f* factor can reasonably be attributed to the stabilization of the pentacoordinate species when the temperature is lowered. The better resolution of the spectra (especially the ${}^1A'_1 \rightarrow {}^1E'$ transition) shows that the same pentacoordinate trans TBP species (D_{3h}) is present in solution and in the solid state at different temperatures.

In conclusion, we would point out that in pentacoordinate d^8 complexes NiX_2L_3 not only can two limiting geometries be present, the trigonal bipyramid and the square pyramid separated by a very small energy difference, but also inside one geometry—the TBP—two different isomers are isolated, following the nature of the ligands. Thus, one should be very cautious in interpreting factors responsible for pentacoordination and stabilities of the species. The predominant geometry, however, as far as monodentate phosphorus, arsenic, and antimony ligands are concerned, is a TBP geometry for NiX_2L_3 and NiL_5^{2+} complexes. Further discussions on this problem await results of other studies which are still in progress.

Registry No. $NiI_2(SbMe_3)_3$, 52393-91-6; $NiBr_2(SbMe_3)_3$, 52393-90-5; $NiCl_2(SbMe_3)_3$, 60117-14-8; $Ni(SbMe_3)_5(BF_4)_2$, 60909-15-1; $Ni(CN)_2(SbMe_3)_3$, 60245-87-6; NiI_2, 13462-90-3; NiBr2, 13462-88-9; $NiCl_2$, 7718-54-9; $Ni(CN)_2$, 557-19-7.

References and Notes

(1) R. Morassi, I. Bertini, and L. Sacconi, *Coord. Chem. Rev.*, **11**, 343 (1973).
(2) J. M. Dawson, T. J. MeLennan, W. Robinson, A. Merle, M. Dartiguenave, Y. Dartiguenave, and H. B. Gray, *J. Am. Chem. Soc.*, **96**, 4428 (1974).
(3) M.-F. Ludmann-Obier, M. Dartiguenave, and Y. Dartiguenave, *Inorg. Nucl. Chem. Lett.*, **10**, 147 (1974).
(4) C. D'Hem, M. Dartiguenave, and Y. Dartiguenave, *Inorg. Nucl. Chem. Lett.*, **10**, 1039 (1974), and unpublished work.
(5) G. O. Doak and L. D. Freedman, "Organometallic Compounds of Arsenic, Antimony and Bismuth", Wiley, New York, N.Y., 1970.
(6) J. C. Cloyd and C. A. McAuliffe in "Transition Metal Complexes of Phosphorus, Arsenic and Antimony Ligands", C. A. McAuliffe, Ed., Macmillan, New York, N.Y., 1973.
(7) G. O. Doak, G. G. Long, and M. E. Key, *Inorg. Synth.*, **9**, 92 (1967).
(8) G. Foex, "Constantes Sélectionnées–Diamagnétisme et Paramagnétisme", Masson et Cie, Paris, 1957.
(9) G. Hayter, *Inorg. Chem.*, **2**, 932 (1963).
(10) D. W. Allen and T. T. Millar, *J. Chem. Soc. A*, 1101 (1969).
(11) M. J. Norgett, J. H. M. Thornley, and L. M. Venanzi, *J. Chem. Soc. A*, 540 (1967); G. S. Benner and D. W. Meek, *Inorg. Chem.*, **6**, 1399 (1967); J. R. Preer and H. B. Gray, *J. Am. Chem. Soc.*, **92**, 7306 (1970); M. Ciampolini, *Inorg. Chem.*, **5**, 35 (1966); C. A. McAuliffe and D. W. Meek, *Inorg. Chim. Acta*, **5**, 270 (1971).
(12) E. C. Alyea and D. W. Meek, *J. Am. Chem. Soc.*, **91**, 5761 (1969).
(13) P. Rigo and A. Turco, *Coord. Chem. Rev.*, **8**, 175 (1972); B. B. Chastain, E. A. Rick, R. L. Pruett, and H. B. Gray, *J. Am. Chem. Soc.*, **90**, 3994 (1968); A. Merle, M. Dartiguenave, Y. Dartiguenave, J. W. Dawson, and H. B. Gray, *J. Coord. Chem.*, **3**, 199 (1974).
(14) K. J. Coskran, J. M. Jenkins, and J. G. Verkade, *J. Am. Chem. Soc.*, **90**, 5437 (1968).
(15) D. M. Adams, "Metal-Ligand and Related Vibrations", E. Arnold, London, 1967, p 172.
(16) J. K. Stalick and J. A. Ibers, *Inorg. Chem.*, **8**, 1090 (1969).
(17) K. N. Raymond, P. W. Corfield, and J. A. Ibers, *Inorg. Chem.*, **7**, 1362 (1968).
(18) T. J. Huttemann, B. M. Foxman, C. R. Sperati, and J. G. Verkade, *Inorg. Chem.*, **4**, 950 (1965); E. F. Riedel and R. A. Jacobson, *Inorg. Chim. Acta*, **4**, 407 (1970).
(19) M.-F. Ludmann, M. Dartiguenave, and Y. Dartiguenave, *Bull. Soc. Chim. Fr.*, 2771 (1974).
(20) W. Levason and C. A. McAuliffe, *Inorg. Chim. Acta*, **11**, 33 (1974), and references therein.

(21) S. Ahrland, J. Chatt, and N. R. Davies, *Q. Rev., Chem. Soc.*, **19**, 267 (1958).
(22) A. Merle, M. Dartiguenave, and Y. Dartiguenave, *J. Mol. Struct.*, **13**, 413 (1972).
(23) K. A. Jensen and O. Dahl, *Acta Chem. Scand.*, **22**, 1044 (1968).
(24) O. Dahl, *Acta Chem. Scand.*, **23**, 2342 (1969).
(25) C. K. Jorgensen, "Absorption Spectra and Chemical Bonding in Complexes", Pergamon Press, Elmsford, N.Y., 1962, p 138.
(26) H. M. Powell, D. J. Watkin, and J. B. Wilford, *J. Chem. Soc. A*, 1803 (1971).
(27) C. A. Tolman, *J. Am. Chem. Soc.*, **92**, 2956 (1970).
(28) J. J. Legendre, C. Girard, and M. Huber, *Bull. Soc. Chim. Fr.*, **6**, 1998 (1971).
(29) E. L. Muetterties and R. A. Schunn, *Q. Rev., Chem. Soc.*, **20**, 245 (1966).
(30) H. F. Klein and H. H. Karsch, *Chem. Ber.*, **105**, 2628 (1972); **107**, 537 (1974).
(31) L. J. Vande Griend, J. C. Clardy, and J. G. Verkade, *Inorg. Chem.*, **14**, 710 (1975); D. S. Milbrath, J. P. Springer, J. C. Clardy, and J. G. Verkade, *ibid.*, **14**, 2655 (1975).
(32) A. R. Rossi and R. Hoffmann, *Inorg. Chem.*, **14**, 365 (1975), and references herein.
(33) J. Chatt, *J. Chem. Soc. A*, 652 (1961); J. Chatt and R. G. Wilkins, *J. Chem. Soc.*, 4300 (1952).
(34) J. W. Dawson, H. B. Gray, J. E. Hix, Jr., J. R. Preer, and L. M. Venanzi, *J. Am. Chem. Soc.*, **94**, 2979 (1972).

Contribution from the Department of Petroleum Chemistry,
Faculty of Engineering, Osaka University, Suita, 565, Japan

Aryl(pentachlorophenyl)nickel(II) Complexes. Lack of Free Rotation about Tolyl–Nickel Bonds and Lack of "Ortho Effect" in Carbonylation

MASANORI WADA,* KOJI KUSABE, and KEISUKE OGURO

Received July 26, 1976 AIC60522X

A series of complexes of the type *trans*-$R(C_6Cl_5)Ni(PPhMe_2)_2$ (where R = aryl) was prepared. Their ^1H NMR spectra indicate that both R = *o*-tolyl and *m*-tolyl groups are oriented perpendicularly to the nickel coordination plane. Reaction of carbon monoxide with these complexes gave, under mild conditions, $R(C_6Cl_5)CO$ for R = aryl groups including *o*-tolyl but not for 2-furyl and its analogues. The *o*-tolyl complex was exceptionally stable toward thermal reductive elimination in tetrachloroethylene under air. Factors affecting the relative reactivities of these complexes are discussed, based mainly on the early explanation for the so-called "ortho effect".

Introduction

Since the initial discovery of σ-bonded alkyl and aryl transition metal complexes, the criteria for their stability have evolved considerably. In organonickel chemistry, complexes of types *trans*-$X(R)Ni(PR'_3)_2$ and *trans*-$R_2Ni(PR'_3)_2$ (X = anionic ligand such as halogen; R′ = alkyl or aryl) have been shown to have considerable stability when R is an ortho-substituted aryl group.[1-3] This so-called "ortho effect"[2] has been accounted for originally by Chatt and Shaw[1] by a combination of steric and electronic factors, but the detailed evidence seems to be quite scanty, especially for those nickel complexes with an ortho-unsubstituted aryl group.[3]

The pentachlorophenyl group is of interest in organonickel chemistry not only because of the great overall stability of pentachlorophenyl–nickel bond but also because of its ability to stabilize the nickel–carbon bond trans to the group. In fact, MacKinnon and West have shown that the pentachlorophenyl–nickel bond in *trans*-$Cl(C_6Cl_5)Ni(PPh_3)_2$ (X = halogen) is thermally stable up to 240 °C, although above 160 °C at 10^{-2} mm pressure the triphenylphosphine sublimes from the complexes,[4] and Rausch and Tibbetts have reported that, in spite of the repeated failures by Chatt and Shaw to isolate methylnickel complexes of the type *trans*-$X(CH_3)Ni(PR_3)_2$ (X = halogen),[1] the pentachlorophenyl analogue ($X = C_6Cl_5$) is stable enough to be isolated and characterized.[5] In contrast, some facile decompositions of pentachlorophenylnickel complexes have been reported recently. We have observed previously the formation of pentachlorobenzene as a by-product in the reaction of *trans*-$Cl(C_6Cl_5)Ni(PPhMe_2)_2$, **1**, and crotylmagnesium chloride, which probably resulted from the β-hydrogen elimination of an intermediate followed by the reductive elimination of the resulting nickel hydride.[6] Coronas et al. have also reported the formation of pentachlorobenzene by the reaction of *trans*-$Cl(C_6Cl_5)Ni(PPh_3)_2$ and an excess of KCN[7] and the formation of hexachlorobenzene by the reaction of $Cl(C_6Cl_5)Ni(dpe)$ and molecular chlorine,[8] but they have not presented any explanation for these reactions.

In connection with our current research program on pentachlorophenylnickel complexes,[6,9] we have now studied the preparation and the spectral and chemical properties of a series of nickel complexes of the type *trans*-$R(C_6Cl_5)Ni(PPhMe_2)_2$, **2**, with an aim to obtain information about the steric and/or electronic effects of the aryl (R) group. We have also obtained additional examples of the facile decomposition of pentachlorophenylnickel complexes.

Experimental Section

The starting material, *trans*-$Cl(C_6Cl_5)Ni(PPhMe_2)_2$, **1**, was prepared as described previously.[9] IR spectra were recorded on a Hitachi 225 spectrophotometer or on a JASCO Model IR-G spectrophotometer over the range 4000–500 cm^{-1} and on a Hitachi EPI-L spectrophotometer over the range 700–200 cm^{-1} using Nujol mulls. ^1H NMR spectra were recorded on a JEOL Model JNM-PS-100 spectrometer operating at 100 MHz. Chemical shifts were measured relative to TMS as an internal standard. Electronic spectra were measured on a Hitachi two-wavelength double-beam spectrophotometer, Model 356. Mass spectra were measured on a Hitachi mass spectrometer, Model RMU-6E.

Preparations of *trans*-Aryl(pentachlorophenyl)bis(dimethylphenylphosphine)nickel(II) Complexes, *trans*-$R(C_6Cl_5)Ni(PPhMe_2)_2$, 2 [R = (a) C_6H_5, (b) *o*-$CH_3C_6H_4$, (c), *m*-$CH_3C_6H_4$, (d) *p*-$CH_3C_6H_4$, (e) *p*-ClC_6H_4, (f) *p*-$CH_3OC_6H_4$, (g) 2-furyl, (h) 5-methyl-2-furyl, (i) 2-thienyl]. These complexes **2a–i** were prepared essentially by the same procedures, so only representative examples are described. Percentage yields, melting points, and analytical data as well as ^1H NMR and electronic spectral data are summarized in Table I.

An ethereal solution of phenyllithium was prepared from bromobenzene (0.43 ml, 4.1 mmol) and a 15% *n*-pentane solution of *n*-butyllithium (2.48 ml, 4.0 mmol) in 10 ml of dry diethyl ether. The two reagents were mixed at 0 °C under a nitrogen atmosphere and the solution was stirred at room temperature for 1 h. The phenyllithium solution was cooled on an ice bath and a benzene (10 ml) solution of **1** (0.620 g, 1.0 mmol) was added. The mixture was stirred