[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASSACHUSETTS]

Preparation, Spectra and Electronic Structures of Tetrahedral Nickel(II) Complexes Containing Triphenylphosphine and Halide Ions as Ligands

BY F. A. COTTON, O. D. FAUT AND D. M. L. GOODGAME

The preparation and structural characterization of salts of the tetrahedral nickel(II) anions, $[Ni((C_6H_5)_3P)Br_3]^{-1}$ and $[Ni((C_6H_5)_3P)I_3]^{-1}$ are reported. It is shown or suggested that compounds containing these or analogous tetrahedral anions have been prepared before but not recognized. Magnetic data and electronic spectra for these anions and for the complexes $[Ni((C_6H_5)_3P)_2X_2]$, X = Cl, Br, I, are reported and their interpretation in terms of the symmetry and strength of the ligand fields are discussed.

Introduction

Two general types of tetrahedral nickel(II) compounds are now known. These are first the truly tetrahedral ones, $[NiX_4]^{-2}$ where all four ligands are the same. Those of this type which have been isolated to date include the tetrahalo anions, made by Gill and Nyholm[1] and others[2-4] and also various substances wherein Ni(II) ions are trapped in tetrahedral holes in host lattices.[5-7] The second general class embraces those which may be called pseudotetrahedral. They have four ligands at about or perhaps by chance exactly at the apices of a tetrahedron surrounding the Ni(II) ion, but two or more different kinds of ligand are present. Of the three cases involving 2 kinds of ligands which are in principal possible, viz., $[LNiX_3]^-$, $[L_2NiX_2]$ and $[L_3NiX]^{+1}$, where L is a neutral ligand and X an anion, only the second has previously been realized.

We have recently reported the compounds $[((C_6H_5)_3PO)_2NiX_2]$, X = Cl, Br, I[8] and $[((C_6H_5)_3AsO)_2NiX_2]$, X = Cl, Br[9] and shown that their spectra and magnetic moments, at room temperature at least, do not show any significant deviation from the behavior expected by analogy[1-6] or from theoretical consideration[10] for truly tetrahedral complexes. Deviations must, in principal, be expected in such compounds since the symmetry of the ligand field cannot but accidentally be fully tetrahedral but is instead C_{2v}. Evidently, the difference in the contributions of the oxygen in triphenylphosphine oxide and of the halide ions do not differ sufficiently to permit the C_{2v} component of the ligand field to manifest itself noticeably in the spectra or the magnetic moments at room temperature. This is of course encouraging as it makes the spectral and magnetic criteria for truly tetrahedral Ni(II) complexes applicable to at least some pseudotetrahedral ones as well.

The purpose of the study reported here is to see how far this approximation of treating a pseudotet- rahedral Ni(II) complex as a tetrahedral one with an average ligand field may be extended. We have therefore examined the compounds $[((C_6H_5)_3P)_2 NiX_2]$, X = Cl, Br, I,[11,12] in which the two kinds of ligands concerned are well separated in the spectrochemical series. Venanzi[13] and Garton, Powell and Venanzi[14] have demonstrated quite conclusively that these compounds are true pseudotetrahedral Ni(II) complexes, on the basis of X-ray studies and other supporting evidence. In addition, we report the preparation and characterization of several members of another class of pseudotetrahedral nickel(II) complexes,[15] viz., those containing the anions $[(C_6H_5)_3PNiBr_3]^{-1}$ and $[(C_6H_5)_3PNiI_3]^{-1}$. The spectral and magnetic properties of these new compounds have also been studied in order to determine the effect of a strong low symmetry (here C_{3v}) component in the ligand field upon the electronic states of the nickel(II) ion.

Experimental

Bis-(triphenylphosphine)-dihalonickel(II) Complexes.— The compounds $Ni((C_6H_5)_3P)_2X_2$, (X = Cl, Br, I), were prepared by the methods of Venanzi.[13] In the case of $Ni((C_6H_5)_3P)_2Cl_2$ it was found preferable to add $NiCl_2 \cdot 6H_2O$ (2.38 g.) dissolved in water (2 ml.) to the triphenylphosphine dissolved in glacial acetic acid (75 ml.) rather than to use the mixture of water and acetic acid for the nickel chloride as described by Venanzi.

Tetraethylammonium Triphenylphosphinetribromonickelate(II).—A solution of tetraethylammonium bromide (2.10 g., 0.01 mole) and triphenylphosphine, (2.62 g., 0.01 mole), in hot n-butanol, (30ml.), was added to a solution of nickel bromide, (2.19 g., 0.01 mole), also in hot butanol (50 ml.). As the deep green solution cooled clusters of fine, blue-green needles formed. These were filtered, washed with n-butanol and dried in vacuo. The yield was 4.51 g. (65%). The compound melted at 266°.

Anal. Calcd. for $C_{26}H_{35}Br_3NNiP$: C, 45.19; H, 5.11; N, 2.03; Ni, 8.49; P, 4.48. Found: C, 44.80; H, 4.98; N, 2.07; Ni, 8.61; P, 4.74.

The compound is decomposed by hot water and is insoluble in benzene, chlorobenzene and chloroform. It is soluble in nitromethane and acetone to form green solutions.

Tetra-n-butylammonium Triphenylphosphinetri-iodonickelate(II).—A solution of tetra-n-butylammonium iodide, (2.46 g., 0.0066 mole) and triphenylphosphine (1.74 g., 0.0066 mole), in hot n-butanol, (25 ml.), was added to a solution of nickel iodide (2.08 g., 0.0066 mole), also in hot n-butanol (55 ml.). A deep red solution was obtained, the color of which faded considerably on cooling. No solid product separated from the solution on standing

(1) N. S. Gill and R. S. Nyholm, *J. Chem. Soc.*, 3997 (1959).

(2) F. A. Cotton and R. Francis, THIS JOURNAL, **82**, 2986 (1960).

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(12) K. Yamamoto, *Bull. Chem. Soc. Japan*, **27**, 501 (1954).

(13) L. Venanzi, *J. Chem. Soc.*, 719 (1958).

(14) Unpublished observations, quoted by Venanzi in ref. 13.

(15) For a preliminary report of these compounds, see F. A. Cotton and D. M. L. Goodgame, THIS JOURNAL, **82**, 2967 (1960).

overnight. The volume of the solution was reduced to about 20 ml. by heating on a steam-bath under reduced pressure (water pump). The very dark red needles which formed were filtered, washed twice with *n*-butanol and dried *in vacuo*. The yield was 1.21 g. (19%). The compound melted at 132.5°.

Anal. Calcd. for $C_{34}H_{51}I_2NNiP$: C, 43.25; H, 5.44; N, 1.48; P, 3.28. Found: C, 42.92; H, 5.01; N, 1.64; P, 3.04.

The compound is decomposed by water, dimethylformamide and the lower alcohols. It is insoluble in ligroin (b.p. 90–100°), cyclohexane and ether. Red solutions are formed in chloroform, chlorobenzene, carbon tetrachloride, acetone, methyl ethyl ketone, nitromethane and 2-nitropropane. The compound is readily soluble in cold acetonitrile and slightly soluble on heating in benzene, toluene, xylene and dioxane, forming red-brown solutions in each case.

t-Butyltriphenylphosphonium Triphenylphosphinetribromonickelate(II).—This compound was prepared by a modification of the method given by Yamamoto.[12] A mixture of triphenylphosphine (5.2 g., 0.02 mole), nickel bromide (2.2 g., 0.01 mole) and tert-butyl bromide (1.4 g., 0.01 mole) was heated in a sealed tube at 150° for 2 hr. The dark green crystalline product was washed out of the tube with benzene and unreacted triphenylphosphine removed by trituration with hot benzene. The solid product was then recrystallized from *n*-butanol, (150 ml.). Short, dark green needles were obtained, which were filtered and dried in a drying-pistol, *in vacuo* at ~95°, for several hours. The yield was 1.0 g., (11%). The compound melted at 221°.

Anal. Calcd. for $C_{40}H_{39}Br_3NiP_2$: C, 54.58; H, 4.47. Found: C, 54.88; H, 4.38.

Bis-(tetraphenylphosphonium)-tetrabromonickelate(II).— A mixture of triphenylphosphine (10.0 g., 0.038 mole), nickel bromide (4.0 g., 0.018 mole) and bromobenzene (15.0 g., 0.1 mole) was heated in a sealed tube at 250° for 2 hr. The dark blue crystalline product was washed out of the tube with bromobenzene and the excess reactants removed by trituration with hot bromobenzene. The blue crystals were filtered and dried *in vacuo* at ~130°, in a drying-pistol, for two days. The yield was 12 g. (63%). On heating the compound becomes green at ~260° and melts at 273°.

Anal. Calcd. for $C_{48}H_{40}Br_4NiP_2$: C, 54.53; H, 3.81. Found: C, 54.34; H, 3.79.

Attempts to prepare other Anions of the Type $[LNiX_3]^{-1}$.— When equimolar quantities of tetramethylammonium chloride, nickel chloride and triphenylphosphine were mixed in a hot mixture of 2 parts of *n*-butanol to 1 part ethanol, buff-pink needles of $[Me_4N][NiCl_3]$ were obtained in 83% yield.

Anal. Calcd. for $C_4H_{12}Cl_3NiN$: C, 20.08; H, 5.06; N, 5.85. Found: C, 20.24; H, 4.79; N, 5.78.

A similar experiment carried out in glacial acetic acid, (the nickel chloride being dissolved in ~2 ml. water), yielded a mixture of $[Me_4N][NiCl_3]$ and $[Ni((C_6H_5)_3P)_2Cl_2]$. The latter compound was isolated for characterization.

Anal. Calcd. for $C_{36}H_{30}Cl_2NiP_2$: C, 66.09; H, 4.62. Found: C, 66.25; H, 4.68.

Attempts to react $[Me_4N][NiCl_3]$ with triphenylphosphine in various solvents were unsuccessful, the former compound being very insoluble.

Evaporation of a butanol/ethanol solution of equimolar quantities of nickel chloride, triphenylphosphine and tetraphenylarsonium chloride, and treatment of the blue residue with hot benzene yielded a compound of m. p. 199.5°. Analytical results indicated that the compound was $[(C_6H_5)_4As]_2[NiCl_4]$.

Anal. Calcd. for $C_{48}H_{40}As_2Cl_4Ni$: C, 59.61; H, 4.17. Found: C, 59.04; H, 3.80.

An attempt to prepare $[Et_4N][Ni(C_6H_5)_3P(SCN)_3]$ by mixing equimolar quantities of tetraethylammonium thiocyanate, triphenylphosphine and nickel thiocyanate in *l*-butanol gave only the red crystalline compound $[Ni((C_6H_5)_3P)_2(SCN)_2]$ previously described by Venanzi.[14]

Anal. Calcd. for $C_{38}H_{30}S_2N_2NiP_2$: C, 65.25; H, 4.32. Found: C, 64.58; H, 4.19.

Attempts to prepare $[Me_4N][Ni(Cy_3P)Cl_3]$, $[Bu(C_6H_5)_3P]$-$[Ni(Cy_3P)Br_3]$ and $[Bu_4N][Ni(Cy_3P)I_3]$, (where Cy = cyclohexyl), by mixing equimolar quantities of tris-(cyclohexyl)-phosphine, and the respective ammonium or phosphonium salts and nickel salts in alcohol were also unsuccessful. The compounds $[Ni(Cy_3P)_2X_2]$, (X = Cl, Br, I) were obtained from the reaction mixtures. The chloro complex has been reported previously by Issleib and Brack,[16] and the chloro and bromo complexes have been studied by Turco, *et al.*[17,18] The red compound $[Ni(Cy_3P)_2Cl_2]$ had an uncorrected melting point of 235° [lit. m.p. 227°[17]]; olive-green $[Ni(Cy_3P)_2Br_2]$ melted at 206° [lit. m.p. 204°[16,17]]; the green compound $[Ni(Cy_3P)_2I_2]$ melted at 214°.

The only products which could be isolated from an ethanolic solution of equimolar quantities of tetramethylammonium chloride, nickel chloride and tri-*n*-butylphosphine were buff-pink $[Me_4N][NiCl_3]$ and a blue, very hygroscopic compound the analytical figures for which suggested that it was impure $[Me_4N]_2[NiCl_4]$.

Anal. Calcd. for $C_8H_{24}Cl_4NiN_2$: C, 27.55; H, 6.93. Found: C, 28.88; H, 6.97.

Blue crystals were obtained on evaporation of an ethanolic solution of equimolar quantities of tetraethylammonium bromide, nickel bromide and triphenylphosphine oxide. However the product was found to be $[Et_4N]_2[NiBr_4]$.

Electrolytic Conductances.—Electrolytic conductance measurements were carried out using a Serfass bridge and a conventional cell, previously calibrated with an aqueous solution of potassium chloride. The results are given in Table I.

TABLE I

MOLAR CONDUCTANCES OF THE NEW COMPOUNDS

	Solvent	1×10^{-3} M	5×10^{-4} M	T, °C.
$[Et_4N][Ni((C_6H_5)_3P)Br_3]$	CH_3NO_2	79.8	83.3	25.2
$[Bu^t(C_6H_5)_3P][Ni((C_6H_5)_3P)Br_3]$	$C_6H_5NO_2$	23.3	a	26.1
$[Bu_4^nN][Ni((C_6H_5)_3P)I_3]$	CH_3NO_2	71.6	a	26.0
$[(C_6H_5)_4P]_2[NiBr_4]$	$C_6H_5NO_2$	61.7	a	26.9

Molar conductance ohm^{-1}

a Not measured.

Magnetic Measurements.—Bulk susceptibility measurements at room temperature for the compounds $[Et_4N]$-$[Ni((C_6H_5)_3P)Br_3]$ and $[Bu_4^nN][Ni((C_6H_5)_3P)I_3]$ were made using the Gouy method as previously described.[19] Mohr's salt and copper sulfate pentahydrate were used to calibrate the Gouy tubes. Duplicate determinations were carried out. The results are given in Table II.

TABLE II

MAGNETIC DATA FOR THE NEW COMPLEXES

	T, °K.	X^n corr. $\times 10^6$	Diamagn. corr. $\times 10^6$	μ_{eff}, B.M.
$[Et_4N][Ni((C_6H_5)_3P)Br_3]$	300.4	5584	−372	3.68 ± 0.05
$[Bu_4^nN][Ni((C_6H_5)_3P)I_3]$	300.0	4942	−516	3.46 ± 0.05

The magnetic susceptibility of the compound $[Et_4N]$-$[Ni((C_6H_5)_3P)Br_3]$ was kindly determined for us, over the temperature range 79–291°K., by Mr. Frank Mabbs and Dr. J. Lewis, University College, London. The results are shown in Table III.

L. T. Reynolds[20] has studied the magnetic susceptibilities of the compounds $[Ni((C_6H_5)_3P)_2X_2]$, (X = Cl, Br, I), over the temperature range 196–301°K. His results are shown in Table IV.

Spectral Measurements.—The reflectance spectra of the solid compounds were measured with a Beckman DU spectrophotometer, using a standard reflectance attachment and magnesium carbonate as the reference. In the

(16) K. Issleib and A. Brack, *Z. anorg. u. allgem. Chem.*, **277**, 258 (1954).

(17) A. Turco, V. Scatturin and G. Giacometti, *Nature*, **183**, 601 (1959).

(18) A. Turco and G. Giacometti, *Ricerca sci.*, **29**, 1057 (1959).

(19) R. H. Holm and F. A. Cotton, *J. Chem. Phys.*, **31**, 788 (1959).

(20) L. T. Reynolds, unpublished observations, Harvard University, 1955–1956.

TABLE III

VARIATION WITH TEMPERATURE OF THE MAGNETIC SUS-
CEPTIBILITY OF [Et$_4$N][Ni((C_6H_5)$_3$P)Br$_3$]

T, °K.	$x_{Ni}^{corr.} \times 10^6$	$\mu_{eff.}$ B. M.
290.8	5511	3.60
265.8	5949	3.57
240.7	6480	3.55
216.9	7167	3.54
193.1	7953	3 52
169.4	8952	3.50
146.3	10195	3.47
122.1	12028	3.44
104.5	13858	3.42
79.4	17608	3.36

case of [Ni((C_6H_5)$_3$P)$_2$I$_2$], a 1:1 mixture of the compound with magnesium carbonate was used, since the absorption in the blue is too intense to measure using pure [Ni((C_6H_5)$_3$P)$_2$I$_2$].

A Beckman DU spectrophotometer was also used to measure the solution spectra of the compounds [Bu^t(C_6H_5)$_3$-P][Ni((C_6H_5)$_3$P)Br$_3$] and [(C_6H_5)$_4$P]$_2$[NiBr$_4$]. The other solution spectra were measured with a Beckman DK2 recording spectrophotometer. No suitable solvent could be found for the measurement of [Ni((C_6H_5)$_3$P)$_2$Cl$_2$] in solution.

The results are shown in Figs. 1–6 and in Table V.
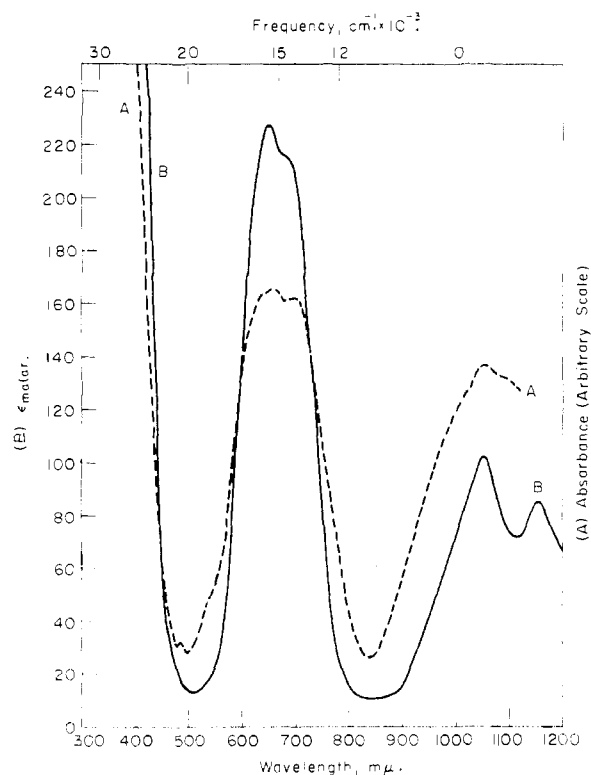
Fig. 1.—The electronic absorption spectrum of [(t-C$_4$H$_9$)(C_6H_5)$_3$P][(C_6H_5)$_3$PNiBr$_3$]: A, reflectance spectrum of the solid; B, transmission spectrum of a 3 $\times$ 10^{-3} M solution in nitromethane.

Discussion

Preparation of Compounds.—Several salts of the anions [(C_6H_5)$_3$PNiBr$_3$]$^{-1}$ and [(C_6H_5)$_3$PNiI$_3$]$^{-1}$ have been prepared by allowing them to crystallize from solutions of the components, namely, the cation salt (R$_4$PX or R$_4$NX) triphenylphosphine and the nickel halide in mole ratio of 1:1:1. The compounds prepared in this way were thoroughly
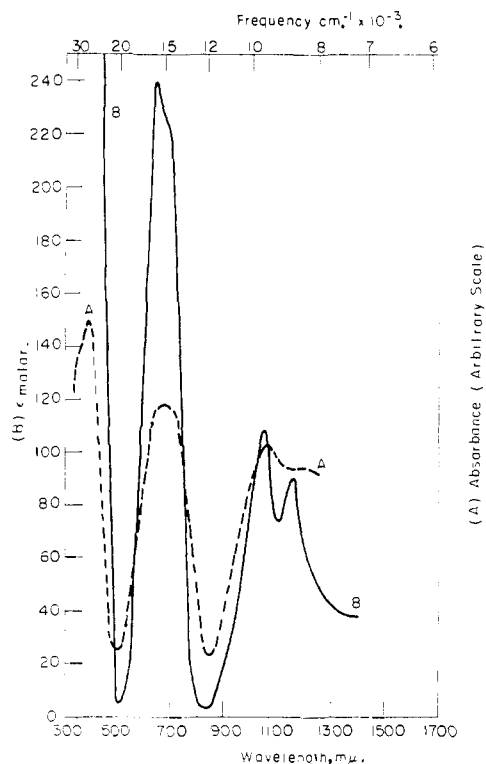

Fig. 2.—The electronic absorption spectrum of [(C_2H_5)$_4$N][(C_6H_5)$_3$PNiBr$_3$]: A, reflectance spectrum of the solid; B, transmission spectrum of a 5 $\times$ 10^{-3} M solution in nitromethane.

characterized analytically, by electrolytic conductance, magnetic properties and spectra. These data leave scarcely any room for doubt that they are correctly formulated as R$_4$P$^+$ and R$_4$N$^+$ salts of the tetrahedral anions.

TABLE IV

VARIATION WITH TEMPERATURE OF THE MAGNETIC SUS-
CEPTIBILITIES OF [Ni((C_6H_5)$_3$P)$_2$X$_2$] (DATA OF REYNOLDS)[20]

	T, °K.	$x_{corr}^M \times 10^6$	$\mu_{eff.}$ B. M.
[Ni((C_6H_5)$_3$P)$_2$Cl$_2$]	300	4800	3.41
	273	5200	3 39
	230	6100	3 37
	196	7130	3.36
[Ni((C_6H_5)$_3$P)$_2$Br$_2$]	300	4410	3.27
	273	4770	3.24
	226	5700	3.23
	196	6530	3.22
[Ni((C_6H_5)$_3$P)$_2$I$_2$]	301	4450	3.28
	273	4870	3.27
	236	5620	3.27
	206	6440	3.27

With this much established, it became evident that certain compounds prepared some years ago by Reppe and Schweckendiek[11] and Yamamoto[12] and recently brought to our attention by a note of Matsunaga[21] could most likely be formulated as salts containing [R$_3$PNiX$_3$]$^{-1}$ tetrahedral anions.[15] We can now offer definite proof of this surmise. Following the general procedures indicated by

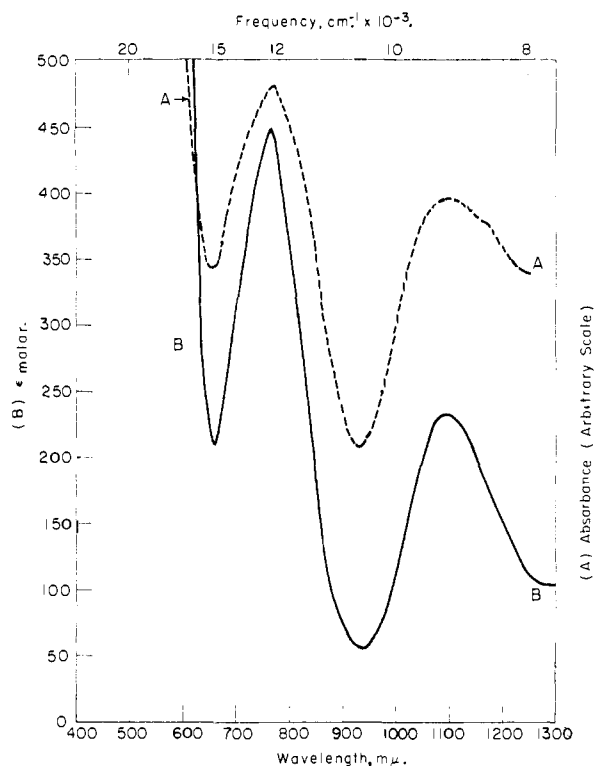(21) Y. Matsunaga, *Cand. J. Chem.*, **38**, 621 (1960).

Fig. 3.—Electronic absorption spectrum of [(n-C$_4$H$_9$)$_4$-N][(C$_6$H$_5$)$_3$PNiI$_3$]: A, reflectance spectrum of the solid; B, transmission spectrum of 1.5×10^{-3} M solution in benzene.

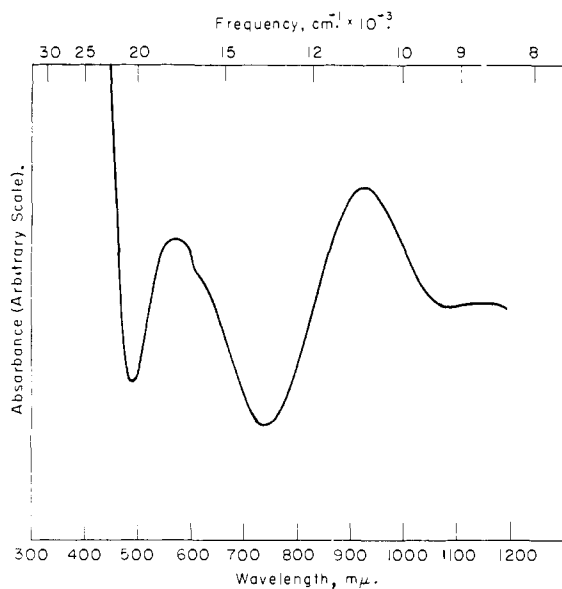Fig. 4.—Reflectance spectrum of Ni[(C$_6$H$_5$)$_3$P]$_2$Cl$_2$.

Reppe and Schweckendiek and Yamamoto, triphenylphosphine, tert-butyl bromide and nickel chloride, in mole ratio of 2:1:1 were heated in a sealed tube at 150° for 2 hr. After workup the dark green crystalline product was shown by analysis, conductance and direct comparison of its spectrum (Fig. 1) with the spectrum of [(C$_2$H$_5$)$_4$N][(C$_6$H$_5$)$_3$-PNiBr$_3$] that it is correctly formulated as [(t-C$_4$H$_9$)-(C$_6$H$_5$)$_3$P](C$_6$H$_5$)$_3$PNiBr$_3$].
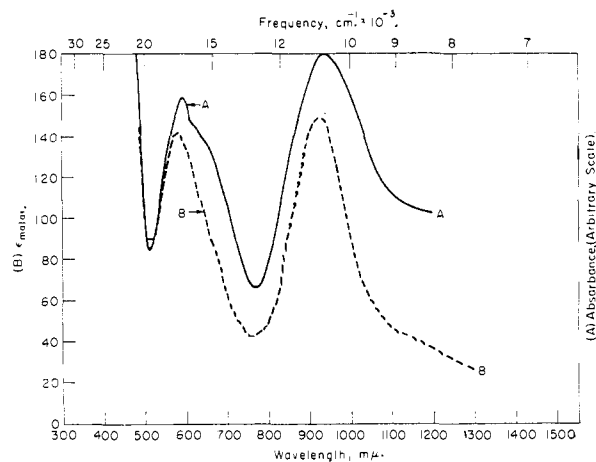
Fig. 5.—The electronic absorption spectrum of Ni-[(C$_6$H$_5$)$_3$P]$_2$Br$_2$: A, reflectance spectrum of the solid; B, transmission spectrum of 1.07×10^{-3} M solution in acetone.

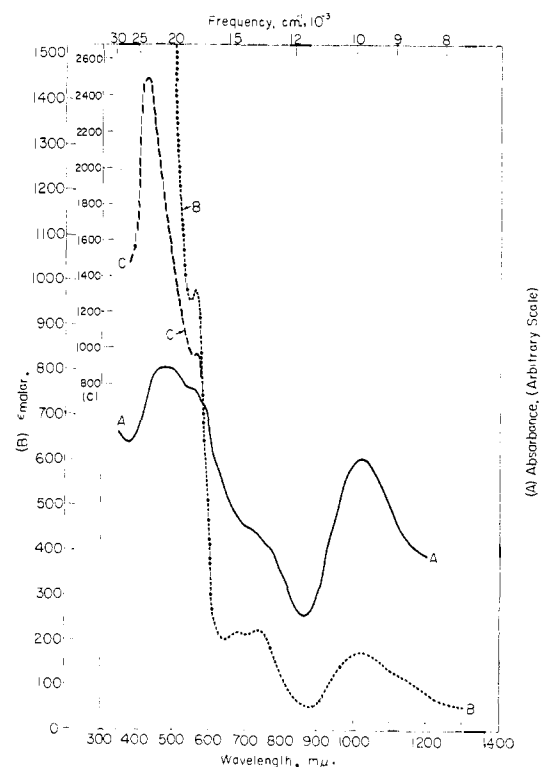Fig. 6.—The electronic absorption spectrum of Ni-[(C$_6$H$_5$)$_3$P]$_2$I$_2$: A, reflectance spectrum of the solid; B and C, transmission spectrum of 1×10^{-3} M solution in 2-butanol. (Note separate ϵ_{molar} scale for C.)

Similarly, we have prepared a compound representative of the "disolvates" of [(C$_6$H$_5$)$_3$P]$_2$NiBr$_2$, as they were formulated by Reppe and Schweckendiek, Yamamoto and Matsunaga, following the general preparative method they describe. When triphenylphosphine and nickel bromide in 2:1 mole ratio are heated in a sealed tube with an excess of bromobenzene, a dark blue crystalline mass whose analysis corresponds to the empirical formula 2(C$_6$H$_5$)$_3$P·NiBr$_2$·2C$_6$H$_5$Br is obtained. Its molar conductivity and comparison of its spectrum with the reported spectrum of the tetra

TABLE V

ELECTRONIC ABSORPTION SPECTRA OF THE COMPLEXES

Compound	State	Absorption maxima		Molar extinc.
		mμ	Cm.$^{-1}$	
Ni((C$_6$H$_5$)$_3$P)$_2$Cl$_2$	Solid	567	17,600	..
		~615(sh)	~16,300	..
		930	10,800	..
Ni((C$_6$H$_5$)$_3$P)$_2$Br$_2$	Solid	590	16,900	..
		~615(sh)	~16,300	..
		~640(sh)	~15,600	..
		935	10,700	..
	1.07 × 10^{-3} M in acetone	577	17,300	142
		~630(sh)	~15,900	..
		~665(sh)	~15,000	..
		925	10,800	149
Ni((C$_6$H$_5$)$_3$P)$_2$I$_2$	Solid	~470(broad)	~21,300	..
		~550(sh)	~18,200	..
		~585(sh)	~17,100	..
		~620(sh)	~16,100	..
		~700(sh)	~14,300	..
		~755(sh)	~13,300	..
		1020	9,800	..
	1 × 10^{-3} M in 2-butanone	425	23,500	2500
		557	18,000	975
		685	14,600	215
		740	13,500	220
		1020	9,800	166
		~1150(sh)	~ 8,700	..
[Bu^t(C$_6$H$_5$)$_3$P][Ni((C$_6$H$_5$)$_3$P)Br$_3$]	Solid	485	20,600	..
		~645(sh)	~15,500	..
		660	~15,100	..
		700	14,300	..
		~1015(sh)	~ 9,860	..
		1055	9,480	..
		1145	8,730	..
	3 × 10^{-3} M in nitromethane	~400	~25,000	CTB^a
		650	15,400	227
		~685(sh)	~14,600	213
		1050	9,520	102
		1155	8,660	85
[Et$_4$N][Ni((C$_6$H$_5$)$_3$P)Br$_3$]	Solid	385	26,000	..
		~675(broad)	~14,800	..
		1060	9,430	..
		~1150(sh)	~ 8,700	..
	5 × 10^{-3} M in nitromethane	386	26,000	3040
		640	15,600	240
		~675(sh)	~14,800	227
		1050	9,520	108
		1150	8,700	90
		~1700(sh)	~ 5,880	41
[Bu$_4$^{n}N][Ni((C$_6$H$_5$)$_3$P)I$_3$]	Solid	<600	>16,700	CTB
		770	13,000	..
		1100	9,090	..
		~1165(sh)	~ 8,580	..
	1.5 × 10^{-3} M in benzene	<600	>16,700	CTB
		765	13,100	450
		1095	9,130	233
[(C$_6$H$_5$)$_4$P]$_2$[NiBr$_4$]	Solid	475	21,000	..
		555	18,000	..
		725	13,800	..
		775	12,900	..
		960	10,400	..
	3 × 10^{-3} M in nitromethane	~385	~26,000	CTB
		~615(sh)	~16,300	..
		~685(sh)	~14,600	..
		720	13,900	217

[Me₄N][NiCl₄]	Solid	770	13,000	188

770	13,000	188
~1250(v. broad)	~8,000	22
327	30,600	..
475	21,100	..
~535(sh)	~18,700	..
~555(sh)	~18,000	..
~715(sh)	~14,000	..
~755(sh)	~13,200	..
~830(sh)	~12,000	..
925	10,800	..

[Me₄N][NiCl₄]   Solid

ᵃ CTB = charge transfer band (presumed).

hedral $[NiBr_4]^{-2}$ ion leave no doubt that this compound is $[(C_6H_5)_4P]_2[NiBr_4]$.

Chatt and Shaw[22] have recently reported that treatment of the compound $Ni[(C_2H_5)_2(C_6H_5)P]_2$ (1-naphthyl)Br, $C_{30}H_{37}P_2NiBr$, with bromine or chlorine leads to compounds with the formulas $C_{30}H_{37}P_2NiBr_3$ and $C_{30}H_{37}P_2NiBrCl_2$. They suggested the possibility that these compounds could be complexes of nickel(IV). We do not think that their description of the compounds (deep or bright blue, molar conductances typical of 1:1 electrolytes, and magnetic moments of 3.4 and 3.8 B.M., respectively) lends support to this suggestion; in fact, the magnetic data seem entirely incompatible with the presence of Ni(IV). We observe however that the reported properties are consistent with the presence of tetrahedrally coordinated Ni(II), and we suggest the following structures containing tetrahedral anions: $[(1-naphthyl)(C_6H_5)(C_2H_5)_2P]$ $\{[(C_6H_5)(C_2H_5)_2P]NiBr_3\}$, and $[(1-naphthyl)(C_6H_5)(C_2H_5)_2P]\{[(C_6H_5)(C_2H_5)_2P]NiBrCl_2\}$.

We do not believe that any salt of the ion $[(C_6H_5)_3PNiI_3]^{-1}$ or any other ion of the type $[LNiI_3]^{-1}$ has been reported before. We have isolated it as the tetra-n-butylammonium salt by direct crystallization from a solution of $(n-C_4H_9)_4NI$, $(C_6H_5)_3P$ and NiI_2 in 1:1:1 mole ratio in 1-butanol. The proposed structure is supported by conductance, magnetic susceptibility and spectral data.

Attempts to prepare salts of the $[(C_6H_5)_3PNiCl_3]^{-1}$ ion (see Experimental section for details) were unsuccessful. The only compounds isolated were salts of $[NiCl_4]^{-2}$, the compound $[(CH_3)_4N][NiCl_3]$ or a mixture of the latter with $[(C_6H_5)_3P]_2NiCl_2$. Compounds of the types M^INiCl_3 and M^INiBr_3, where M^I is a relatively large unipositive cation, have recently been studied by Asmussen and co-workers.[23,24] Comparison of the reflectance spectrum of $[(CH_3)_4N][NiCl_3]$, Fig. 7, with the published spectra of the compounds studied by Asmussen and Bostrup leaves no doubt that it belongs to the same class; it thus presumably contains the Ni(II) ion in an octahedral environment and is of no further interest here.

Attempts to prepare salts of the $[R_3PNiX_3]^{-1}$ anions where R = cyclohexyl or n-butyl were also unsuccessful.

Spectral and Magnetic Studies.—We now wish to consider in detail the magnetic and spectral data for all of the tetrahedral complex nickel(II) species containing both triphenylphosphine and halide ions

(22) J. Chatt and B. J. Shaw, *J. Chem. Soc.*, 1718 (1960).

(23) R. W. Asmussen and H. Soling, *Z. anorg. u. allgem. Chem.*, **283**, 3 (1956).

(24) R. W. Asmussen and O. Bostrup, *Acta Chem. Scand.*, **11**, 745 (1957).

as ligands. These include the compounds $[(C_6H_5)_3P]_2NiX_2(X = Cl, Br, I)$ for which no spectral data and only fragmentary magnetic data have previously been reported[13] as well as the new species, $[(C_6H_5)_3PNiX_3]^{-1}$ (X = Br, I). Calculations by Liehr and Ballhausen[10] have provided the necessary basis for interpretation of the spectra of the nickel (II) ion in environments of regular tetrahedral symmetry. It has also been shown that their results are applicable to complexes of the type L_2NiX_2, where L = $(C_6H_5)_3PO^8$ and $(C_6H_5)_3AsO^9$ and X =
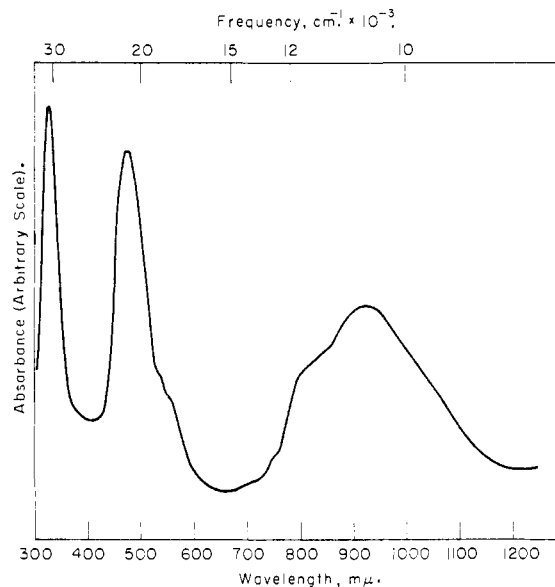

Fig. 7.—The reflectance spectrum of $[(CH_3)_4N][NiCl_3]$.

Cl, Br or I; this may be attributed to the fact that the oxygen and halogen ligand atoms make only slightly different contributions to the ligand field. Thus the C_{2v} component of the ligand field does not, in these compounds, have sufficient intensity to perturb the energy level pattern from the arrangement dictated by the major tetrahedral component to an extent detectable in the spectra.

In the phosphine complexes, however, there is reason to expect larger low-symmetry components in the ligand fields. It has been shown[25] that phosphines lie well to the strong end of the spectrochemical series at a position comparable to that of the nitrogen-bonded thiocyanate ion, when they are members of the coordination sphere of tetrahedral Co(II) complexes of the types $[Co(R_3P)_2X_2]$ and $[Co(R_3P)X_3]^{-1}$.[25] This means that they differ

(25) F. A. Cotton, O. D. Faut, D. M. L. Goodgame and R. H. Holm, THIS JOURNAL, **83**, in press (1961).

considerably from the halide ions in their contributions to the ligand field of the Co(II) ion. We might assume that their behavior in the analogous tetrahedral nickel(II) complexes would be essentially similar.

Let us consider first the magnetic data (Tables II, III, IV) for they are easiest to interpret, at least to the extent that we shall undertake to do so. The moments of the $[Ni((C_6H_5)_3P)_2X_2]$ compounds in the range 200–300°K. are well below the range (3.9–4.2 B.M.) predicted by theory[26] and repeatedly found experimentally[1,2,8,9] for nickel(II) in environments having rigorous or nearly rigorous T_d symmetry. This presumably means that the low symmetry component of the ligand field in these cases is sufficiently strong to split further some of the components of the multiplet produced by the action of spin-orbit coupling on the $^3T_{1g}$ orbital ground state. We believe a splitting of as little as 1000 cm.$^{-1}$ could cause the observed moments. It will be noted that the chloro complex has moments significantly higher than those of the bromo and iodo complexes. These latter moments are equal within experimental error. This relationship is to be expected since chloride ion must be closer to $(C_6H_5)_3P$ in the spectrochemical series than the bromide or iodide ions. The magnetic moments of the new $[Ni((C_6H_5)_3P)-Br_3]^-$ and $[Ni((C_6H_5)_3P)I_3]^{-1}$ ions, particularly that of the former, are not so far below the range for rigorous or nearly rigorous tetrahedral species. Evidently the low symmetry component of the ligand field in these complexes does not produce a splitting of the ground state multiplet exceeding the order of some hundred of wave numbers. It may be noted also that the iodo compound has the lower moment as the relative positions of the bromide and iodide ions in the spectrochemical series would seem to require. Table III shows the temperature variation of the effective magnetic moment for $[Ni((C_6H_5)_3P)Br_3]^{-1}$ from 80 to 291°K. In addition to confirming the independent measurement recorded in Table II, these data show that the magnetic behavior of this mixed complex is in rough qualitative accord with theoretical expectation[26] for regular tetrahedral nickel(II) complexes although there are significant quantitative discrepancies. Further theoretical and experimental work on the temperature dependence of the moments in tetrahedrally coordinated nickel(II) is in progress elsewhere.[27]

The spectra of the complexes are shown in Figs. 1–6 and the energies and extinction coefficients of the major absorption maxima are recorded in Table V. It may be noted first that in all cases save one it has been possible to obtain spectra of the complexes in solution as well as by reflectance from the solid. In all five cases there are no significant differences. Since the compound $[Ni((C_6H_5)_3P)_2Br_2]$ has been shown conclusively[13,14] to have a tetrahedral configuration in the solid state, we may infer that it retains this configuration in solution. Moreover the remarkable similarity of the solution and solid state spectra of the other two $[Ni((C_6H_5)_3P)_2X_2]$ compounds to those of the bromo compound provides strong evidence that all of these molecules

have the tetrahedral configuration both in the crystal and in solution. Additional evidence for this comes from the high extinction coefficients of the absorption bands. This, as has been noted previously,[1-3,8,9] is especially characteristic of tetrahedral nickel(II) complexes.

Similar comments may be made regarding the spectra of the $[Ni((C_6H_5)_3P)X_3]^{-1}$ complexes. In addition, comparison of Figs. 1 and 2 shows that the spectrum of the $[Ni((C_6H_5)_3P)Br_3]^{-1}$ ion is independent of the cation with which it is associated. Thus the incipient splitting of one of the bands and the well-resolved splitting of the other must be regarded as genuine features of the spectrum of this ion.

It remains now to consider how well the energies of the observed bands may be correlated with theoretical expectations. For this purpose, we begin with the nomograph of Liehr and Ballhausen, Fig. 1 of ref. 10, which gives the calculated dependence of eigenstates of nickel(II) in a field of T_d symmetry upon the strength of the field. It appears that the experimental data may be fitted to this nomograph fairly well for all of the complexes except $[Ni((C_6H_5)_3P)Br_3]^{-1}$. If in each case the absorption at 15000–18000 cm.$^{-1}$ is assigned to the $^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)$ absorption then the lower energy absorption bands occur within $\pm 10\%$ of the energies required for the $^3T_{1g}(F) \rightarrow {}^3A_{2g}$ transitions. The remaining expected transition, $^3T_{1g}(F) \rightarrow {}^3T_{2g}(F)$, should, according to the nomograph, lie beyond the range of our observations for these compounds, and, in fact, no other peaks are observed. Thus, it is possible to interpret the observed spectra in four of the five cases assuming that the low symmetry components of the ligand field have no pronounced effect upon the spectra. This would require that splitting of upper states caused by these low symmetry components could not exceed ~ 2000 cm.$^{-1}$. We have already seen that splittings of the ground state of perhaps 1000 cm.$^{-1}$ (or more) are indicated by the magnetic data. Thus the spectral and magnetic data do not appear to be inconsistent. Also, the order of magnitude of the splittings in the nickel compounds is comparable to that of the splittings in the analogous Co(II) complexes.[25]

There is one feature of the $[Ni((C_6H_5)_3P)_2X_2]$ spectra which is not typical of the spectra for truly tetrahedral Ni(II) complexes, and that is the intensity of the lower energy band (ν_2) relative to that of the upper one (ν_3). Normally ν_2 is weaker than ν_3 and this finds a ready explanation since ν_2 is, in the strong field limit, a two-electron change, which makes it somewhat more forbidden than ν_3 which is a one electron change regardless of field strength. However, in view of the often great sensitivity of intensities to wave function symmetries,[28] we do not feel that this feature of the spectra vitiates the suggested assignments.

In the complex $[Ni((C_6H_5)_3P)Br_3]^{-1}$ there is one feature which we are unable to explain, namely, the appearance of two maxima in the region of ν_2. The upper state for the $^3T_{1g} \rightarrow {}^3A_{2g}$ transition cannot be split by any ligand field since it is an or-

(26) B. N. Figgis, Nature, 182, 1568 (1958).

(27) J. Lewis and B. N. Figgis, University College, London, private Communication.

(28) One may think for example of how the introduction of a substituent in benzene increases the intensity of the $^1A_{1g} \rightarrow {}^1B_{1u}$ transition by an order of magnitude while changing m.o. energies by only a few per cent.

bital singlet. This problem has disturbed us for some time and caused us to consider whether there might not be some assignment for the spectra of all of the compounds which is quite different from the fairly obvious one described above. However, on the evidence at hand we have been unable to invent an acceptable alternative.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASSACHUSETTS]

The Donor–Acceptor Properties of Isonitriles as Estimated by Infrared Study

BY F. ALBERT COTTON AND FRANCO ZINGALES[1]

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A number of complexes of isonitriles with metal atoms and ions have been prepared and their infrared spectra measured. The results provide information about the extent of metal to isonitrile dative pi bonding as a function of the oxidation state of the metal and of the nature of the other ligands, if any, also attached to the metal. In compounds having only isonitrile molecules attached to zero-valent metal atoms, back donation seems to be about as extensive as it is in the corresponding metal carbonyl compounds. Breakdown of the selection rules for the NC stretching modes in $(RNC)_6M$ and $(RNC)_4M$ compounds is believed to indicate that significant back donation causes significant bending of the RNC chains; this in turn spoils what would otherwise be O_h or T_d symmetry in the $(-NC)_6M$ and $(-NC)_4M$ groups. When isonitriles are attached to mono- and dipositive metal ions, however, little or no back donation occurs and the NC stretching frequencies actually rise as a result of the inductive effect of the electrophilic metal ion. The preparation of the new compounds $(RNC)_3M(CO)_3$, where M = Cr, Mo and R = p-tolyl and methyl is described.

Introduction

Two extreme types of donor–acceptor behavior are generally recognized in ligands. At one extreme are ligands which are pure donors, such as aliphatic amines and ethers. The first row atoms, N and O, unless incorporated into a molecular system which as a whole can function as π-orbital acceptor (e.g., N in pyridine) are restricted to the single function of being donors by their intrinsic lack of the empty orbitals necessary for them to behave as pi acceptors. In the other direction (which we refrain from calling *an* extreme since there is no sharply defined limit here) are ligands which are only moderately good or even poor donors but which are good π-acceptors. Ligands such as CO and PX_3 are good representatives of this class. These two kinds of ligands, for reasons stemming from the electroneutrality principle taken in a qualitative but not necessarily quantitative sense, generally seek different kinds of acceptors. Considering here only metal atoms as acceptors, pure donor ligands combine well with cations because they can fulfill their single function of transferring electronic charge to the acceptor to a degree sufficient to form a strong ligand-metal bond without causing a net negative charge to appear on the acceptor. Ligands of the second type have little tendency to combine with cationic acceptors since their donor properties alone are insufficient to form strong ligand-metal bonds while their ability to supplement the bonding by pi acceptance is ineffectual when the cation has no significant pi donor properties. Conversely, the second kind of donor combines well with zero-valent or negative-valent (e.g., Co in $Co(CO)_4^-$) metal atoms because it can use synerically its sigma donor and pi acceptor functions, whereas pure donor bonding of

which alone the first class of ligands are capable cannot proceed far enough to give stability because of the poor acceptor powers of the zero-valent metal. Ligands of the first type can form reasonably stable bonds to zero-valent metal atoms when ligands of the second type are also present, e.g., in $(amine)_3Mo(CO)_3$ compounds, because the latter can assume the entire burden of draining negative charge from the metal atom.

Examination of the literature on isonitrile complexes[2] indicates that these ligands combine with zero-valent metals both with and without the presence of additional ligands of the second type and also with mono- and dipositive metal ions. This unusual capacity to combine with the entire range of metal atom acceptor types, excepting only the extremes of metal atoms in formally negative oxidation states and those in a tripositive state, suggested to us that isonitriles have the capacity to function as good sigma donors alone, as sigma donors and good pi acceptors simultaneously or to exhibit any intermediate behavior. In order to test this hypothesis, isonitrile complexes representative of all of the basic types known have been prepared and their infrared spectra in the NC stretching region carefully measured using both rock salt and fluorite prisms. The results support the hypothesis.

Experimental

Tri-(p-tolyl isonitrile)-molybdenum Tricarbonyl-(p-CH$_3$-C$_6$H$_4$NC)$_3$Mo(CO)$_3$.—1.4 g. (0.012 mole) of p-CH$_3$C$_6$H$_4$NC (see below for preparation of the isonitriles) was added to a solution of C$_7$H$_8$Mo(CO)$_3$[3,4] (0.82 g., 0.003 mole) in benzene (5 ml.). After a few minutes, the red color of the cycloheptatriene complex had completely disappeared. The

(1) On leave from Instituto di Chimica Generale dell'Universita di Milano.

(2) L. Malatesta, *Prog. Inorg. Chem.*, **1**, 283 (1959).

(3) E. W. Abel, M. A. Bennett, R. Burton and G. Wilkinson, *J. Chem. Soc.*, 4559 (1958).

(4) E. W. Abel, M. A. Bennett and G. Wilkinson, *ibid.*, 2323 (1959).