Inorganica Chimica Acta, 37 (1979) 181–185
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Five-coordinate Complexes of Iron(II) with Secondary Phosphines

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Received February 13, 1979

The reactions of iron(II) salts FeX_2 (X = Cl, Br, I) and $FeY_2\cdot 6H_2O$ (Y = BF_4, PF_6) with the secondary phosphines HPR_2 (R_2 = $(CH_3)Ph$, $(C_2H_5)Ph$, $(C_2H_5)_2$) in alcohol solution have been investigated. The five-coordinate complexes $[FeX(HPR_2)_4]Y$ and $[Fe(HPR_2)_5]Y_2$ have been isolated and characterised by elemental analysis, IR and visible spectra and conductivity and magnetic measurements. The $[FeX(HPR_2)_4]^+$ complexes are in a triplet ground state, while the magnetic moments at room temperature of the $[Fe(HPR_2)_5]^{2+}$ cations are found in the range 1.4–2.5 B.M. These five-coordinate complexes react with carbon monoxide to yield bis-carbonyl derivatives of the type $[FeX(CO)_2(HPR_2)_3]^+$ and $[Fe(CO)_2(HPR_2)_4]^{2+}$ respectively.

Introduction

During a systematic study [1] on the coordination behavior of the secondary phosphines HPR_2, we have reported on a series of complexes of cobalt(II) and nickel(II). In particular, the 'small' phosphines $HP(C_2H_5)_2$, $HP(C_2H_5)Ph$ and $HP(CH_3)Ph$ were found to stabilize a number of five-coordinate adducts of the type $[M(HPR_2)_5]^{2+}$ and $[MX(HPR_2)_4]^+$ (M = Co, Ni; X = halogen), containing respectively five and four molecules of phosphine bound to the metal atom.

We report here on the reactions of the secondary phosphines $HP(C_2H_5)_2$, $HP(C_2H_5)Ph$ and $HP(CH_3)Ph$ with Fe(II) salts. We find again that the small size of the ligands allows five-coordination with the formation of $[FeX(HPR_2)_4]^+$ and $[Fe(HPR_2)_5]^{2+}$ species.

A substantial number of five-coordinate iron(II) complexes have been synthetised in recent years, which contain bi-, tri- and tetradentate donor ligands comprised of nitrogen and phosphorus atoms. For these complexes, different spin ground-states (triplet or quintuplet) have been observed, depending on the overall nucleophilicity of the donor atoms [2]. Moreover, Sacconi [3, 4] showed that the complexes with tetradentate ligands having a P_4X (X = halogen) donor set, exhibit different spin-states, depending on the geometry of the tetraphosphines. So, whereas the complexes formed with the tripod-like ligands *QP* (tris-*ortho*-diphenylphosphinophenylphosphine) [5] or *PP*$_3$ (tris-2-diphenylphosphinoethylphosphine) [4] possess a triplet ground state, those formed with the linear ligand *P*$_4$ (hexaphenyl-1,4,6,10-tetraphosphadecane) exhibit a singlet–triplet equilibrium [4].

The novel five-coordinate complexes $[FeX(HPR_2)_4]^+$ here reported, which have the donor set P_4X and contain only monodentate ligands, together with the complexes $[Fe(HPR_2)_5]^{2+}$ [6], which possess the most nucleophilic donor set P_5, can be of some interest, in view of a better understanding of the factors affecting the spin state of iron(II).

Experimental

Microanalyses and magnetic measurements (by standard Gouy method) were performed by Mr. L. Turiaco, University of Padua. The published procedures were used to prepare the ligands. $Fe(BF_4)_2\cdot 6H_2O$ and anhydrous FeX_2 (X = Cl, Br, I) [7] were prepared starting from powdered iron and the corresponding aqueous acid. Infrared and visible spectra were recorded on Perkin Elmer 457 and Optica CF4RNI instruments respectively. Conductance data were obtained using a LKB conductance bridge. Reactions and handling of the compounds were carried out under dry nitrogen. Solvents were carefully purified and dried by standard methods.

$[FeX(HP(CH_3)Ph)_4]PF_6$ (X = Cl, Br, I)

Methylphenylphosphine (0.75 g = 6 mmol) in ethanol (5 ml) was added to a solution of anhydrous FeX_2 (1 mmol) in ethanol (10 ml). The resulting red mixture was filtered and to the clear solution was added dropwise NH_4PF_6 (0.16 g = 1 mmol), dissolved in little ethanol. The precipitated products were washed with ethanol. Only the chloro- and bromo-derivatives can be recrystallised from acetone–2-propanol in the presence of small amounts of free phosphine (yields 60–70%).

TABLE I. Analytical Data and Physical Constants.

Compound	Color	M.p.[a]	μ_{eff}[b]	Λ_M[c]	Anal., %					
					C		H		P	
					calcd.	found	calcd.	found	calcd.	found
$[FeCl(HP(CH_3)C_6H_5)_4]PF_6$	pink	70	3.01	70	45.77	45.68	4.93	5.16	21.41	20.9
$[FeBr(HP(CH_3)C_6H_5)_4]PF_6$	red	98	3.00	88	43.27	43.12	4.66	5.02	19.93	19.0
$[FeI(HP(CH_3)C_6H_5)_4]PF_6$	violet	115	3.00	. . .[d]	40.80	41.00	4.40	4.64	18.80	19.0
$[FeCl(CO)_2(HP(CH_3)C_6H_5)_3]PF_6$	orange	80	diam	69	45.38	45.82	4.47	4.89	–	–
$[FeBr(CO)_2(HP(CH_3)C_6H_5)_3]PF_6$	orange	90	diam	80	38.96	39.09	3.84	4.04	–	–
$[FeI(CO)_2(HP(CH_3)C_6H_5)_3]PF_6$	orange	109	diam	74	36.54	36.51	3.60	4.04	–	–
$[Fe(P(C_2H_5)C_6H_5)(HP(C_2H_5)C_6H_5)_3]_2(PF_6)_2$	violet	130	1.25	154[e]	51.08	50.35	5.76	5.97	20.58	21.9
$[Fe(P(C_2H_5)C_6H_5)(CO)_2(HP(C_2H_5)C_6H_5)_2]_2(PF_6)_2$	orange	168	diam	165	46.38	45.92	4.69	5.30	–	–
$[Fe(HP(C_2H_5)_2)_5](BF_4)_2$	yellow	175	1.81	190	35.33	36.02	6.52	6.37	–	–
$[Fe(HP(C_2H_5)_2)_5](PF_6)_2$	yellow	160	1.54	160	30.17	30.88	6.96	6.93	27.23	27.1
$[Fe(HP(CH_3)C_6H_5)_5](BF_4)_2$	yellow-brown	180	2.36	170	49.47	48.86	5.34	6.00	–	–
$[Fe(HP(CH_3)C_6H_5)_5](PF_6)_2$	yellow-brown	212	2.16	140	43.50	42.78	4.69	4.01	22.44	21.9
$[Fe(HP(C_2H_5)C_6H_5)_5](BF_4)_2$	yellow-brown	161	2.52	162	52.20	51.88	6.02	6.60	–	–
$[Fe(HP(C_2H_5)C_6H_5)_5](PF_6)_2$	yellow-brown	115	1.45	138	46.13	45.93	5.32	5.87	20.94	20.5
$[Fe(CO)_2(HP(C_2H_5)C_6H_5)_4](PF_6)_2$	yellow-orange	121	diam	138	42.61	42.90	4.63	4.37	–	–

[a] °C, in sealed tube under vacuum. [b] B.M., at 20 °C (mean values). [c] S cm^2 mol^{-1}, for 10^{-3} *M* nitromethane solutions at 25 °C. [d] Decomposes. [e] Plot of Λ_e *vs.* $N^{1/2}$ gives, according to the Onsager eq., $\Lambda_o = \Lambda_e + AN^{1/2}$, $\Lambda_o = 88$ S cm^2 equiv^{-1} and A = 380 S cm^2 equiv^{-1} $N^{-1/2}$.

TABLE II. Electronic (Visible) Spectra.[a]

Compound	Band max, 10^3 cm^{-1} (relative absorbance)
$[FeCl(HP(CH_3)Ph)_4]PF_6$	19.25(1), 27.00(1.5)
$[FeBr(HP(CH_3)Ph)_4]PF_6$	19.25(1), 25.00(1.2)
$[FeI(HP(CH_3)Ph)_4]PF_6$	18.50
$[Fe(HP(C_2H_5)_5](PF_6)_2$	23.80(1), 29.40(1.2)
$[Fe(HP(CH_3)Ph)_5](PF_6)_2$	22.10(1), 27.80(1.4)
$[Fe(HP(C_2H_5)Ph)_5](PF_6)_2$	21.75(1), 27.00(1.3)
$[Fe(P(C_2H_5)Ph)(HP(C_2H_5)Ph)_3]_2(PF_6)_2$	19.25(1), 27.00(1.3)

[a] Solid state (Nujol mull) at 25 °C, in the range 30,000–12,000 cm^{-1}.

$[FeX(CO)_2(HP(CH_3)Ph)_3]PF_6$ (X = Cl, Br, I)

A solution of $[FeX(HP(CH_3)Ph)_4]PF_6$ in acetone was stirred under an atmosphere of carbon monoxide at ambient conditions until the color turned yellow (*ca.* 2 hr). By adding 2-propanol, yellow-orange crystals precipitated, which were recrystallised from acetone–2-propanol (yields 30–40%).

$[Fe(HPR_2)_5]Y_2$ (R_2 = $(C_2H_5)_2$, $(C_2H_5)Ph$, $(CH_3)Ph$; Y = BF_4, PF_6)

The secondary phosphine (6 mmol), dissolved in 2-propanol (5 ml) was added to a 2-propanol mixture of $Fe(BF_4)_2 \cdot 6H_2O$ (0.34 g = 1 mmol) or of '$Fe(PF_6)_2$' (prepared by mixing stoichiometric amounts of $Fe(BF_4)_2 \cdot 6H_2O$ and NH_4PF_6 and then filtering off the precipitated NH_4BF_4). Yellow or yellow-brown crystals of the products slowly separated from the yellow solutions, which were removed by filtration and washed with 2-propanol (yields: 30% for the fluoborate derivatives, 60–70% for the hexafluorophosphate derivatives).

$[Fe(CO)_2(HP(C_2H_5)Ph)_4](PF_6)_2$

A solution of $[Fe(HP(C_2H_5)Ph)_5](PF_6)_2$ in acetone was shaken in an atmosphere of carbon monoxide at ambient conditions for *ca.* 8 hr. By concentrating and adding 2-propanol, yellow crystals of the compound separated (yield 10%).

$[Fe(P(C_2H_5)Ph)(HP(C_2H_5)Ph)_3]_2(PF_6)_2$

Ethylphenylphosphine (0.83 g = 6 mmol) in ethanol (5 ml) was added to FeX_2 (X = Cl, Br, I) in ethanol (1 mmol in 10 ml). The resulting violet mixture was filtered and to the clear solution was added NH_4PF_6 (0.16 g = 1 mmol). Violet crystals immediately separated, which were recrystallised from acetone–2-propanol (yield 60%).

$[Fe(P(C_2H_5)Ph)(CO)_2(HP(C_2H_5)Ph)_2]_2(PF_6)_2$

A solution of $[Fe(P(C_2H_5)Ph)(HP(C_2H_5)Ph)_3](PF_6)_2$ in acetone was shaken in an atmosphere of carbon monoxide at ambient conditions. After *ca.* 2 hr, the solution became yellow-orange and by addition of 2-propanol yellow-orange crystals of the product precipitated. The complex can be recrystallised from acetone–2-propanol (yield 30%).

Results and Discussion

Treatment of ethanolic solutions of anhydrous iron(II) halides with excess methylphenylphosphine gives red solutions, from which the red, pink or violet paramagnetic (3 B.M.) complexes $[FeX(HP(CH_3)Ph)_4]PF_6$ (X = Cl, Br, I) can be isolated by addition of NH_4PF_6 (Table I). The values of the magnetic moments are consistent with a triplet ground-state and are similar to those reported for a series of five-coordinate trigonal-bipyramidal complexes of iron(II) containing the same donor set P_4X, *i.e.* $[FeBr(PP_3)]^+$ [3,4] and $[FeX(QP)]^+$ (X = Cl, Br, I) [5].

The $[FeX(HP(CH_3)Ph)_4]PF_6$ complexes are reasonably stable in the solid state when stored under nitrogen, but slowly decompose in solution with formation of white deposits. The chloro- and bromo-derivatives, however, are stable in solution in the presence of an excess of phosphine. The conductivity data for freshly prepared 10^{-3} *M* nitromethane solutions indicate that both complexes are uni–univalent electrolytes (Table I).

Visible spectra in the 30,000–12,000 cm^{-1} region of the complexes $[FeX(HP(CH_3)Ph)_4]PF_6$ (X = Cl, Br) in the solid state (Nujol mull) are similar to each other and show two bands around 26,000 and 19,000 cm^{-1}. For the iodo-derivative, only the absorption at lower frequency is observed, the second being probably obscured by intense CT bands (Table II).

Solution spectra are complicated by the occurrence of decomposition processes and reliable data can be obtained only for concentrated (*ca.* 0.1 *M*) acetone solutions of the chloro- and bromo-derivatives and in the presence of free phosphine. For a molar ratio phosphine: complex = 1:1, the spectra of the $[FeX(HP(CH_3)Ph)_4]^+$ cations exhibit the same bands found in the corresponding solid state spectra, together with one well-defined absorption in the 6,100 cm^{-1} region. By increasing the amount of added phosphine (or by lowering the temperature), the intensity of this low-frequency band is strongly reduced, while the two absorptions at *ca.* 26,000 and *ca.* 19,000 cm^{-1} become sharper and gain in intensity.

The above spectroscopic data can be interpreted in terms of the dissociative equilibrium (1):

$$[FeX(HP(CH_3)Ph)_4]^+ \rightleftarrows [FeX(HP(CH_3)Ph)_3]^+ + HP(CH_3)Ph \qquad (1)$$

The four-coordinate species should be responsible for the absorption at 6,100 cm^{-1}, in agreement with the spectral patterns of known tetrahedral complexes of Fe(II), which exhibit one typical transition $^5E \rightarrow {}^5T_2$ in the range 3,000–7,000 cm^{-1} [8].

The complexes $[FeX(HP(CH_3)Ph)_4]PF_6$ readily react with carbon monoxide in acetone solution at ambient conditions, with formation of the carbonyl-derivatives $[FeX(CO)_2(HP(CH_3)Ph)_3]PF_6$. The compounds can be isolated in the solid state as yellow-orange crystals and have been characterised by elemental analyses and conductivity data (Table I). The i.r. spectra in CH_2Cl_2 show a strong ν_{CO} absorption at 1990 cm^{-1}, suggesting a mutual *trans*-position for the carbonyl groups. The band splits in the solid state (Nujol mull) into two distinct peaks of comparable intensities, at 1990 and 1970 cm^{-1}.

We were not able to isolate complexes of the type $[FeX(HPR_2)_4]^+$ with the other two phosphines investigated, *i.e.* ethylphenyl- and diethylphosphine [9]. In the case of ethylphenylphosphine, however, we find that the reaction between the ligand and anhydrous FeX_2 (X = Cl, Br, I) in ethanol and in the presence of NH_4PF_6, results in the formation of a unique violet compound, which does not contain the halogen. Elemental analysis data suggest a molar ratio Fe:phosphine:PF_6 approximately equal to 1:4:1. We tentatively propose a dimeric structure $[Fe(P(C_2H_5)Ph)(HP(C_2H_5)Ph)_3]_2^{2+}$, in which two $Fe(HPR_2)_3$ moieties are linked together by two ethylphenylphosphido bridges. The above formulation seems reasonable, in view of the well-known tendency of secondary phosphines to yield complexes derived from the anionic ligand PR_2^- [1e, 10]. The binuclear structure is confirmed by conductance data at variable concentrations (Hayter's method [11]), which indicate the uni–bivalent nature of the compound.

Carbon monoxide reacts with $[Fe(P(CH_3)Ph)(HP(CH_3)Ph)_3]_2(PF_6)_2$ without fission of the PR_2-bridges, to give the diamagnetic bis(carbonyl) derivative $[Fe(P(CH_3)Ph)(CO)_2(HP(CH_3)Ph)_2]_2(PF_6)_2$, in which the two carbonyl groups are in mutual *trans*-position (ν_{CO} at 1985 cm^{-1} in CH_2Cl_2 solution). It should be noted that the magnetic moment of the dimer $[Fe(P(CH_3)Ph)(HP(CH_3)Ph)_3]_2(PF_6)_2$, calculated for each five-coordinate iron atom is 1.25 B.M. at room temperature, which is clearly a value intermediate between those expected for a Fe(II) in a triplet and in a singlet ground state [12].

The addition of a six-fold excess of the phosphines HPR_2 (R_2 = $(C_2H_5)_2$, $(C_2H_5)Ph$ and $(CH_3)Ph$) to 2-propanol solutions of iron(II) salts containing weakly coordinating anions, leads to the formation of yellow (or yellow-brown) solids of composition $[Fe(HPR_2)_5]Y_2$ (Y = BF_4, PF_6). The compounds are fairly stable in the solid state in dry, inert atmosphere, but slowly decompose in solution, even in the presence of added phosphine, giving whitish deposits. Moreover, the complexes appear to be slightly soluble (less than 10^{-3} *M*) in the common organic solvents and highly sensitive to moisture, when dissolved.

I.r. spectra of the $[Fe(HPR_2)_5]Y_2$ complexes (Nujol mull) only show the typical absorptions of the phosphine ligands and of the non-coordinated anions, without evidence for the presence of solvent molecules (water, alcohol), which may possibly occupy the sixth coordination site of Fe(II).

Visible spectra in Nujol mull exhibit two well-developed bands in the 23,000 and 29,000 cm^{-1} regions, whose maxima produce the series $HP(C_2H_5)_2 > HP(CH_3)Ph \cong HP(C_2H_5)Ph$. The strong similarity of the solution spectra, recorded at –20 °C in acetone, with those in the solid state suggests that in these conditions the process of dissolution is not accompanied by significant structural changes [to avoid decomposition, solutions freshly prepared in pre-cooled (–25 °C) anhydrous acetone were used].

All the $[Fe(HPR_2)_5]Y_2$ complexes are found to be paramagnetic at room temperature and their magnetic susceptibilities are independent of field strength. However, the results are not entirely reproducible and variations of up to 0.5 B.M. of the values of μ_{eff} have been obtained for different samples of the same compound. It should be remembered that the complexes cannot be purified, owing to their low solubility and instability in solution and therefore there is the real possibility of contamination by paramagnetic impurities. For example, in a series of six samples of $[Fe(HP(C_2H_5)_2)_5]Y_2$, which were subjected to independent analyses and did not show significant differences in the physical properties, the following values of μ_{eff} were found: 1.90, 1.81, 1.74 (Y = BF_4) and 1.67, 1.58, 1.37 B.M. (Y = PF_6). For the corresponding ethylphenyl- and methylphenyl phosphine derivatives, μ_{eff} were in the range 1.36–2.54 B.M., the mean values being reported in Table I.

Because of the apparent presence of paramagnetic impurities in the samples [13], the true values of the magnetic moments of the complexes $[Fe(HPR_2)_5]Y_2$ remain uncertain, although clearly below those expected for a triplet ground state (*ca.* 3 B.M.). Thus, it seems hard to establish whether the complexes actually are in a singlet ground state or are involved in a triplet–singlet equilibrium.

It should be noted that in the case of the five-coordinate complexes $[FeX(P_4)]BPh_4$ (X = Cl, Br, I) reported by Sacconi *et al.* [4], unusual values of magnetic moments (1.3–1.6 B.M. at room temperature) have been found. For these compounds, on the basis of magnetic measurements at variable temperature [4, 14] and of Mössbauer studies [15], the occurrence of a spin equilibrium between a singlet ground state and a thermally accessible low-lying triplet state has been suggested.

The five-coordinate $[Fe(HP(C_2H_5)Ph)_5](PF_6)_2$ complex reacts with carbon monoxide yielding the diamagnetic bis(carbonyl) derivative $[Fe(CO)_2(HP(C_2H_5)Ph)_4](PF_6)_2$, which has been isolated in the solid state as yellow-orange crystals. I.r. spectra show a single ν_{CO} absorption at 1990 cm^{-1}, both in Nujol mull and in CH_2Cl_2 solution and are consistent with the presence of two carbonyl groups in equivalent *trans*-positions. The reaction of carbon monoxide was studied in a gas-buret apparatus, by following the CO-uptake at constant pressure at 20 °C. Experiments carried out in acetone, show an initial rapid absorption of *ca.* one mol of CO per mol of Fe, followed by a much slower uptake of another mol of CO. It seems likely that in the first step there is addition of one molecule of CO to the coordinatively unsaturated $[Fe(HPR_2)_5]^{2+}$ complex, followed by a slow substitution reaction with the formation of the bis(carbonyl) derivative, according to eq. (2):

$$[Fe(HP(C_2H_5)Ph)_5]^{2+} \xrightarrow{+CO} [Fe(HP(C_2H_5)Ph)_5(CO)]^{2+} \xrightarrow[-HP(C_2H_5)Ph]{+Co} [Fe(HP)C_2H_5)Ph)_4(CO)_2]^{2+} \qquad (2)$$

The corresponding diethyl- and methylphenylphosphine derivatives behave similarly in the presence of carbon monoxide, but crystalline samples have not been isolated.

Acknowledgment

The authors thank Mr. G. Gomiero for technical assistance.

References

1 (a) P. Rigo and M. Bressan, *Inorg. Chem., 11,* 1314 (1972); (b) P. Rigo and A. Turco, *Coord. Chem. Rev., 13,* 133 (1974); (c) M. Bressan and P. Rigo, *Inorg. Chem., 14,* 38 (1975); (d) P. Rigo and M. Bressan, *Inorg. Chem., 15,* 220 (1976); (e) M. Bressan and P. Rigo, *Inorg. Chem., 17,* 769 (1978); (f) P. Rigo and M. Bressan, *Inorg. Chim. Acta, 33,* 39 (1979); (g) definite evidence for $[M(HPR_2)_5]^{2+}$ has been obtained also in the case of M = Ni, but no solid products have been isolated. P. Rigo and M. Bressan, unpublished results.

2 (a) L. Sacconi, *J. Chem. Soc. A,* 248 (1970); (b) W. S. Kelly, G. H. Ford and S. M. Nelson, *J. Chem. Soc. A,* 388 (1971); (c) W. V. Dahlhoff and S. M. Nelson, *J. Chem. Soc. A,* 2184 (1971).

3 L. Sacconi and M. Di Vaira, *Inorg. Chem., 17,* 810 (1978).

4 M. Bacci, S. Midollini, P. Stoppioni and L. Sacconi, *Inorg. Chem., 8,* 1801 (1973).

5 M. T. Halfpenny, J. G. Hartley and L. M. Venanzi, *J. Chem. Soc.,* 627 (1967).

6 A five-coordinate $[Fe(P)_5]^{2+}$ adduct, with P = $P(OCH_3)_3$, has been briefly reported, for which a trigonal bipyramidal structure in solution has been proposed on the basis of ^{31}P n.m.r. spectra. E. L. Muetterties and J. W. Rathke, *Chem. Commun.,* 850 (1974).

7 G. Winter, *Inorg. Syntheses, 14,* 101 (1973).

8 W. Levason, C. A. McAuliffe, M. M. Khan and S. M. Nelson, *J. Chem. Soc. D,* 1778 (1975) and references therein.

9 Iron(II) chloride reacts with diethylphosphine in concentrated ethanol solution to give a red product of composition $[FeCl_2(HP(C_2H_5)_2)_2]$, which rapidly decomposes in solution. K. Issleib and G. Doell, *Z. anorg. Allg. Chem., 305,* 1 (1960).

10 R. G. Hayter and F. S. Humiec, *Inorg. Chem., 2,* 306 (1963).

11 R. G. Hayter, *J. Am. Chem. Soc., 84,* 3046 (1962).

12 B. N. Figgis, 'Introduction to Ligand Fields', Wiley, New York, 1966.

13 There is the possibility of the presence in the samples of some amount of four-coordinate high-spin species of the type $[Fe(HPR_2)_4]^{2+}$; in the case of the diphenylphosphine, indeed, the white complex $[Fe(HPPh_2)_4](PF_6)_2$ has been isolated in the solid state (although in crude form), which showed a magnetic moment over 5 B.M., typical of tetrahedral Fe(II) complexes.

14 M. Bacci and C. A. Ghilardi, *Inorg. Chem., 13,* 2398 (1974).

15 E. König, G. Ritter and H. A. Goodwin, *Chem. Phys. Letters, 31,* 543 (1975).