The stoichiometry of the complexes was determined at −64° where separate resonances are observed for the 4-picoline 1-oxide protons in the paramagnetic and diamagnetic environments (slow exchange). For the $\mathrm{Ni(AcAc)_2P_2}$ complex, the integrated areas under the paramagnetic and diamagnetic 3-H and 4-$\mathrm{CH_3}$ peaks ($P_{\mathrm{m}} = 0.35$–0.61) give a 4-picoline 1-oxide, P, to $\mathrm{Ni(AcAc)_2}$ ratio of (1.9 ± 0.2):1. The area under the acetylacetonate methyl resonance (a broad peak centered at −4.90 ppm) also indicates a $\mathrm{P{:}Ni(AcAc)_2}$ ratio of (2.0 ± 0.2):1.

The resonances for uncomplexed 4-picoline 1-oxide show concentration and temperature variations indicating some changes in orientation in the solvent. For example at 37° the 2-H, 3-H, and 4-$\mathrm{CH_3}$ resonances are found at −8.11, −7.12, and −2.36 ppm while at −53° they are found at −8.22, −7.24, and −2.44 ppm. However, under slow exchange conditions these diamagnetic resonance positions are found to be unaffected by the added paramagnetic complex. It was therefore assumed that the presence of the nickel complex in the intermediate and fast-exchange regions also has no effect on the diamagnetic resonance positions and the isotropic shifts were calculated using the proton resonance positions of the ligand in the absence of complex. The ratios of the spin densities at the various ligand nuclei were also observed to shift with temperature. For $\mathrm{Ni(AcAc)_2P_2}$ at −64° (slow-exchange region) the isotropic shifts (ppm) are as follows: 2-H, +27.5; 3-H, −14.4; 4-$\mathrm{CH_3}$, −39.2. These yield ratios (normalized to the 3-H resonance) of +1.9:1.0:−2.8 while at 37° the corresponding ratios are +1.8:−1.0:−2.35. The latter (fast-exchange ratios) are in agreement with those previously reported[7] and when compared with the low-temperature data may reflect a contribution to the isotropic shifts of a second geometrical isomer or a more subtle change in structure of the 2:1 complexes. The formation of adducts having less than 2:1 stoichiometry is also a possibility. However, since for a given complex the rates calculated from the shifts of the different ligand protons are all the same within experimental error, this complication does not affect the semiquantitative interpretation of the present data.

Discussion

Previous studies have shown that, all other factors being equal, the rate of ligand exchange in octahedrally coordinated nickel(II) chelates decreases as the substituents on the chelate rings become more electronegative.[4,16] This electron withdrawal from the central metal atom can be interpreted in terms of an incremental increase in its effective oxidation number. The resulting increased binding of the ligand in the ground state relative to the transition state produces the observed decrease in exchange rate. The relative magnitudes of this effect have been correlated with substituent parameters of the Hammett or Taft variety thus confirming its electronic origin.

While results of the present study support this general conclusion, they also suggest that steric factors play a more significant role in the 4-picoline 1-oxide–$\mathrm{Ni(AA)_2}$ systems than in the 4-picoline–$\mathrm{Ni(AA)_2}$ systems. Faster than expected rates of 4-picoline 1-oxide exchange are observed for both $\mathrm{Ni(BzAc)_2P_2}$ and $\mathrm{Ni(DMP)_2P_2}$, both of which contain bulky groups (R = phenyl or *tert*-butyl). The difference in behavior between these and the corresponding 4-picoline complexes can be accounted for by the angular structure[11] of coordinated 4-picoline 1-oxide. The Ni–O–N bond angle of approximately 120° allows the ligand ring to extend laterally in space and interact sterically with the chelate ring substituents R_1 and R_2. Such steric destabilization of the ground state relative to the transition state increases the exchange rate. On the other hand, the cylinder of steric influence generated by coordinated 4-picoline in $\mathrm{Ni(AA)_2L_2}$ does not extend as far as the R_1, R_2 groups and mere variation in their size apparently has negligible effect on the exchange rate except as it may inhibit solvation in the ground and/or transition state. A second factor which may affect the rate of exchange, a variation in the ratio of trans to cis isomers in solution with the change in R_1 and R_2, cannot be evaluated at this time.

Two additional generalizations become apparent from this study. (a) The rates of the 4-picoline 1-oxide exchange are greater than those for the comparable 4-picoline systems. This is probably due to a combination of factors including the lower basicity and the greater steric interaction of 4-picoline 1-oxide with the chelate ring. (b) The rates of exchange in the cobalt(II) complexes are faster than those of the corresponding nickel(II) complexes. This order of lability for hexacoordinate complexes of $\mathrm{Ni^{2+}}$ and $\mathrm{Co^{2+}}$ has been observed in many other cases and is in agreement with simple ligand field stabilization arguments.[17]

Acknowledgment.—Support of this research by the Rutgers University Research Council and the National Science Foundation through Grants GY-5795 and GP-6321 is acknowledged.

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Infrared and Mass Spectral Studies on Azaferrocene (π-Cyclopentadienyl-π-pyrrolyliron)

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After the synthesis of azaferrocene,[1,2] little attention has been devoted to its physicochemical properties.

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[1] K. K. Joshi, P. L. Pauson, A. R. Qazi, and W. H. Stubbs, *J. Organometal. Chem.*, **1**, 471 (1964).

[2] R. B. King and M. B. Bisnette, *Inorg. Chem.*, **3**, 796 (1964).

The more relevant peaks of the infrared spectrum were already reported,[1,2] but no detailed vibrational study is yet available. By contrast, such a study seems to be of interest in order to determine the influence of the heteroatom in this sandwich structure and to analyze the modifications of the infrared spectrum on going from ferrocene to azaferrocene.

The mass spectrum of azaferrocene was already known,[3,4] but no ionization or appearance potential studies were yet available. It was of interest to determine these properties also in order to have some insight into the iron–pyrrolyl bond dissociation energy.

In the present paper, the infrared spectra of azaferrocene and of pyrrolyl anion are reported. These spectra are compared with those of ferrocene[5-7] and of cyclopentadienyl anion.[8,9] The concurrent mass spectrometric study of azaferrocene is also reported.

Experimental Section

$C_4H_4N^-K^+$ and azaferrocene were obtained following literature methods.[1,10] The last sample was purified by high-vacuum sublimation; its purity was checked by mass spectrometric analysis.

Infrared Studies.—Good infrared spectra were obtained both in KBr pellet and in hexachlorobutadiene mull. Azaferrocene is rather unstable in solution even if an oxygen-free solvent is used. In any case, it was sufficiently stable in CCl_4 to allow good infrared spectra to be obtained.

The spectrum of potassium pyrrolide was taken just after its preparation, reducing the contact with air and humidity.

The measurements were performed with a Perkin-Elmer Model 521 grating spectrometer. For the solution spectra 0.5-mm KBr cells were used. The frequency scale was standardized with H_2O vapor and indene. The accuracy in the reported frequencies was estimated to be ±1 cm^{-1}. The frequency values of azaferrocene obtained in KBr, hexachlorobutadiene, and CCl_4 are reported in Table I.

Mass Spectral Studies.—An Atlas CH4 mass spectrometer, with a direct-introduction system (E4B), was used for the measurements. Xenon was used for calibration of the electron energy scale and was introduced through the conventional gas inlet system (MOL). The rod with the sample was kept to about 2.5 cm from the ionization region, to avoid appreciable modification of the fields (the Xe^+ intensity remained unchanged by inserting the rod until this distance, then dropped drastically). It was checked that around 2.5 cm the distance of the rod from the ionization chamber was not a critical factor in IP and AP measurements. By convenient regulation of the rod temperature, a constant vaporization of the sample could be obtained. In these conditions the peak intensities were constant during the measurement time. A reproducibility of ±0.2 eV in the AP value was obtained. For the other experimental conditions see ref 11.

Results and Discussion

Infrared Spectra.—The infrared spectra, in the range 4000–300 cm^{-1}, of azaferrocene and ferrocene are reported in Figure 1. The comparison of the two spectra shows that azaferrocene has many more bands than ferrocene. In addition, several azaferrocene bands arise at the same frequency as the corresponding ones of ferrocene.

TABLE I

INFRARED SPECTRUM[a] (CM^{-1}) OF AZAFERROCENE

KBr pellet	Hexachlorobutadiene mull	CCl_4 soln
3930 vw		
3106 w	3099 sh	3103 sh
3090 w	3090 m	3090 w
3080 w	3075 sh	
3048 sh	3043 sh	
2940 vw	2943 vw	
	1993 m	1996 w
1978 w	1983 sh	
1949 vw	1952 m	1956 w
1772 sh	1777 w	1780 w
1765 w	1765 sh	1765 w
1689 vw		1690 vw
1530 vw		
1408 m	1407 m	1411 sh
1404 sh		1405 m
1382 m	1385 m	1388 sh
1351 sh	1354 sh	
1343 m	1345 m	
1266 sh	1268 sh	
1257 m	1260 m	
1189 sh	1190 w	
1184 m		
1107 s		1110 m
1104 sh		
1083 sh		1083 vw
1054 m	1057 w	
		1014 sh
1003 s	1005 m	1008 m
995 sh		993 sh
853 w		845 w
815 vs		818 m
806 sh	806 w	
778 w		
628 s		
601 w		
572 vw		
546 vw		
492 vs		
472 vs		
385 m		
308 w		

[a] Abbreviations: v, very; s, strong; m, medium; w, weak; sh, shoulder.

Table II reports the frequency values and the assignments of the ferrocene vibrational spectrum. The frequency values and the assignments now proposed (see below) for the ir modes of azaferrocene are also given. A comparison of these data shows that almost all the additional infrared bands of azaferrocene correspond to Raman shifts or to inactive modes[12] of ferrocene.

The above results can be interpreted by assuming that the pyrrolyl ring in the azaferrocene molcule tends to behave almost as a cyclopentadienyl ring. The influence of the heteroatom seems, however, sufficient

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(12) Among these, particularly intense are those at 1257 and 628 cm^{-1}.

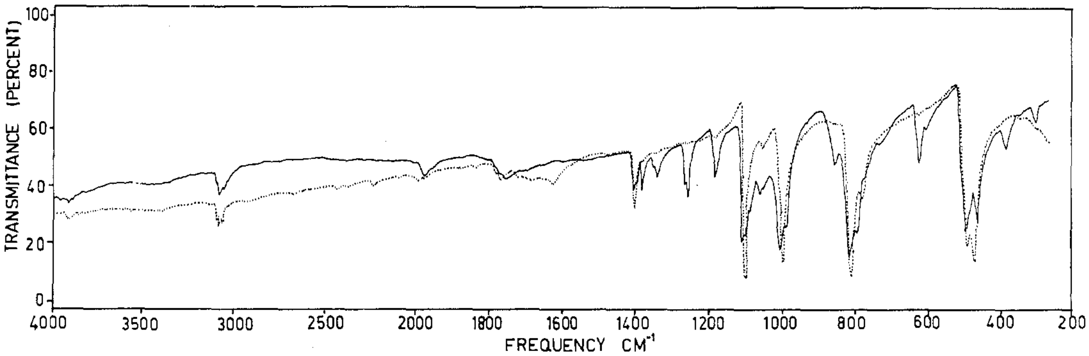

Figure 1.—Infrared spectra of azaferrocene (solid line) and ferrocene (dotted line) in a KBr pellet.

TABLE II

COMPARISON OF THE INFRARED SPECTRUM OF AZAFERROCENE WITH THE VIBRATIONAL ONE OF FERROCENE

Azaferrocene[a]		Ferrocene[b]		
ν_1[c]	3106	A_{1g}(R)	ν_1	3110
ν_2	806		ν_2	1105 (804)[d]
ν_3	1104		ν_3	1390, 1105[d]
ν_4	308		ν_4	306
ν_5	1266	A_{1u}(i)[e]	ν_5	(1253)
ν_6	. . .		ν_6	. . .
ν_7	1257		ν_7	(1249)
ν_8	3080	A_{2u}(ir)	ν_8	3086
ν_9	815		ν_9	1104, 811[d]
ν_{10}	1107		ν_{10}	1408, 1108[d]
ν_{11}	472		ν_{11}	478
ν_{12}	3090	E_{1g}(R)	ν_{12}	3089
ν_{13}	995		ν_{13}	998
ν_{14}	806		ν_{14}	818
ν_{15}	1404		ν_{15}	1412
ν_{16}	385		ν_{16}	390
ν_{17}	3080	E_{1u}(ir)	ν_{17}	3086
ν_{18}	1003		ν_{18}	1004
ν_{19}	815		ν_{19}	814
ν_{20}	1408		ν_{20}	1408
ν_{21}	492		ν_{21}	490
ν_{22}	. . .		ν_{22}	(170)
ν_{23}	3048	E_{2g}(R)	ν_{23}	3045
ν_{24}	1382		ν_{24}	1361
ν_{25}	1184		ν_{25}	1184
ν_{26}	1530		ν_{26}	1527
ν_{27}	1054		ν_{27}	1054
ν_{28}	601		ν_{28}	591
ν_{29}	. . .		ν_{29}	(3035)
ν_{30}	1351	E_{2u}(i)	ν_{30}	(1351)
ν_{31}	1189		ν_{31}	(1188)
ν_{32}	. . .		ν_{32}	. . .
ν_{33}	1054		ν_{33}	(1054)
ν_{34}	628		ν_{34}	(567)

[a] Present work. [b] Reference 5. [c] The present frequency numbering has been done by analogy with the ferrocene, as from ref 5. [d] Reference 6. [e] Inactive mode.

to make several Raman or inactive modes of ferrocene infrared active; *i.e.*, the nitrogen atom substitution causes a lowering of the D_{5d} symmetry of the ferrocene molecule, acting almost as an isotopic substitution of a carbon atom.

In order to see if such effects could be found also in a molecular situation simpler than that of a "sandwich" structure, the infrared spectra of the pyrrolyl and cyclopentadienyl anions have been also compared. Table III reports the frequency values for the vibrational spectrum of $C_5H_5^-$ [8,9] compared with the infrared one of the pyrrolyl anion, now obtained from its potassium salt; in the same table the vibrational spectrum of pyrrole[13,14] is also reported.

TABLE III

COMPARISON OF THE INFRARED SPECTRUM OF PYRROLYL ANION WITH THE VIBRATIONAL ONES OF $C_5H_5^-$ AND C_4H_5N

Cyclopentadienyl anion[a]			Pyrrolyl anion[b]	Pyrrole[c]		
A_1'(R)	ν_1	3099		A_1(R, ir)	ν_1	711
		3043[d]	3050 sh		ν_2	1076
	ν_2	1105	1060 m		ν_3	1144
					ν_4	1237
A_2''(ir)	ν_4	811	813 w		ν_5	1384
					ν_6	1467 (1582)
E_1'(ir)	ν_{12}	3085	3077 m		ν_7	3100
	ν_{13}	1411	1408 w		ν_8	3133
	ν_{14}	1002	1007 sh		ν_9	3400
				B_1(R, ir)	ν_{10}	647 (869)
E_2'(R)	ν_{15}	3085			ν_{11}	1015
	ν_{16}	1560	1572 m		ν_{12}	1046
	ν_{17}	1178	1197 w		ν_{13}	1146
	ν_{18}	885	884 s		ν_{14}	1418
		1447[d]	1447 s		ν_{15}	1530
		1020[d]	1018 w		ν_{16}	3111
		565[d]	552 w		ν_{17}	3133
				A_2(R)	ν_{18}	510
					ν_{19}	711
					ν_{20}	868 (652)
				B_2(R, ir)	ν_{21}	565
					ν_{22}	768 (735)
					ν_{23}	838
					ν_{24}	1046

[a] Reference 8, unless otherwise indicated. [b] Present work. [c] References 13 and 14. [d] Reference 9.

First of all, we wish to remark that the pyrrolyl anion ir spectrum is intermediate between those of pyrrole and $C_5H_5^-$. In particular, it shows many fewer bands than pyrrole; furthermore, the frequency values of several bands observed for these two heteroaromatic rings are somewhat different. By contrast, all the pyrrolyl anion infrared bands can be found in the cyclopentadienyl anion vibrational spectrum, except for a couple of cases. This indicates that, as for the above-considered sandwiches, also in the two free anions the molecular symmetries are very similar and that the nitrogen atom causes a failure of the D_{5h} selection rules. In this regard, it is to be noted that Mirone[13] and Lord and Miller[14] have interpreted some features of the pyrrole vibrational spectrum assuming

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(14) R. C. Lord, Jr., and F. A. Miller, *J. Chem. Phys.*, **10**, 328 (1942).

a failure of the C_{2v} selection rules and a partial D_{5h} behavior. It is reasonable to think that this failure should become more evident on going from pyrrole to pyrrolyl anion.[15]

In the light of these considerations the above interpretation of the infrared spectrum of azaferrocene seems to be supported. In particular, when the five electrons of the pyrrolyl ring are symmetrically involved in the dπ–pπ bond with the iron atom in azaferrocene, the symmetry of the pyrrolyl ring should increase and the C_{2v} local symmetry should tend toward a D_{5h} one (C_{5v} when referred to the π-C_4H_4NFe moiety).

The infrared spectra of $(C_4H_4N)Mn(CO)_3$ and $(C_5H_5)Mn(CO)_3$ give additional support to the above arguments. The cyclopentadienyl compound has been widely studied by infrared and Raman spectroscopy; a rather complete vibrational assignment has been proposed[16] for the ring and for the inorganic grouping modes. When this spectrum is compared with the infrared one of $(C_4H_4N)Mn(CO)_3$ reported in ref 1, one can see that almost all the relevant infrared bands of the pyrrolylic complex correspond, at about the same frequency, to vibrational modes of the cyclopentadienylic compound.

The above points and the previously reported assignments[5,6] of ferrocene allow us to propose with some confidence an assignment of the infrared spectrum of azaferrocene (see Table II). The table shows that the present attributions follow Fritz's assignments for ferrocene, except for a few cases. In particular, for the ν_2, ν_3, ν_9, and ν_{10} modes, Lippincott's assignments have been preferred, since the frequency range seems to be more appropriate to the nature of the corresponding vibrations.

Mass Spectral Studies.—The most peculiar feature of the mass spectrum[3,4] of azaferrocene is the very low abundance of the $C_4H_4NFe^+$ fragment. The peaks corresponding to the parent ion and to $C_5H_5Fe^+$ are instead very intense.

It has been therefore possible to determine the appearance potential (AP) of $C_5H_5Fe^+$ ion and the ionization potential (IP) of azaferrocene. Table IV gives these values, compared with those for ferrocene.[17,18] For the fragmentation processes giving $C_5H_5Fe^+$ from azaferrocene, it is possible to write the equation

TABLE IV

IONIZATION POTENTIALS (IP) AND APPEARANCE POTENTIALS (AP) (EV)

	Azaferrocene	Ferrocene
IP	7.17 ± 0.1	6.99 ± 0.1,[a] 7.05 ± 0.1[b]
AP[$C_5H_5Fe^+$]	12.6 ± 0.2	12.8 ± 1,[a] 14.38 ± 0.3[b]

[a] Reference 17. [b] Reference 18.

$$\mathrm{AP}[C_5H_5Fe^+]^{\mathrm{I}} = \mathrm{IP}[C_5H_5Fe] + D[C_5H_5Fe\text{–pyrrolyl}] + \mathrm{EE}^{\mathrm{I}} \quad (1)$$

while in the case of the $C_5H_5Fe^+$ formation from ferrocene it can be written

$$\mathrm{AP}[C_5H_5Fe^+]^{\mathrm{II}} = \mathrm{IP}[C_5H_5Fe] + D[C_5H_5Fe\text{–}C_5H_5] + \mathrm{EE}^{\mathrm{II}} \quad (2)$$

By subtracting eq 1 from 2 one has

$$\mathrm{AP}[C_5H_5Fe^+]^{\mathrm{II}} - \mathrm{AP}[C_5H_5Fe^+]^{\mathrm{I}} = D[C_5H_5Fe\text{–}C_5H_5] - D[C_5H_5Fe\text{–pyrrolyl}] + (\mathrm{EE}^{\mathrm{II}} - \mathrm{EE}^{\mathrm{I}}) \quad (3)$$

Neglecting in eq 3 the term relative to the difference in the excess energy (EE) one can see that the difference of the AP's is equal to the difference of the bond dissociation energies reported in eq 3. The AP values of Table IV suggest therefore that the $D[C_5H_5Fe\text{–pyrrolyl}]$ is lower than the $D[C_5H_5Fe\text{–}C_5H_5]$. However, due to both the large error encountered in the AP measurements for ferrocene and the above approximation regarding the EE term, this result should be used with caution.

For the fragmentation processes giving $C_5H_5Fe^+$ from azaferrocene, one can also write

$$\mathrm{AP}[C_5H_5Fe^+] \geqslant \mathrm{IP}[\text{azaferrocene}] + D[C_5H_5Fe^+\text{–pyrrolyl}]$$

By using the AP and IP values from Table IV, a value $\geqslant 125$ kcal/mol for the $D[C_5H_5Fe^+\text{–pyrrolyl}]$ is found. Even allowing for some excess energy in the AP value, it is evident that this bond dissociation energy in azaferrocene cation is much greater than that for the corresponding bond in the neutral molecule. From the above conclusion indeed the $D[C_5H_5Fe\text{–pyrrolyl}]$ value cannot be certainly higher than 69.5 kcal/mol (thermochemical value[19] for $D[C_5H_5Fe\text{–}C_5H_5]$). So, as in ferrocene, the less firmly bound electron of azaferrocene is therefore an antibonding one. In fact it has to be said that a great excess energy term might be involved in the fragmentation process leading to $C_5H_5Fe^+$, since it could require a large activation energy owing to its multicenter nature. It seems, however, unlikely that such activation energy could reach the value of at least 60 kcal/mol, which would question the last conclusion.

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[15] By using a $C_{2v} \rightarrow D_{5h}$ correlation table, the decrease of infrared activity on going from pyrrole to pyrrolyl anion can be easily explained.

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Icosahedral Carboranes. XV. Monomeric Carboranylenesiloxanes[1,2]

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In recent years the chemistry of the icosahedral car-

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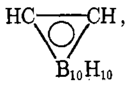
[1] Preceding communication: J. S. Roscoe, S. Kongpricha, and S. Papetti, *Inorg. Chem.*, **9**, 1561 (1970).

[2] Nomenclature of the closo boron–carbon hydrides is discussed by R. Adams, *ibid.*, **2**, 1087 (1963), and appropriate rules approved by the Council of the American Chemical Society are presented in *ibid.*, **7**, 1945 (1968). The terms *o*-, *m*-, and *p*-carborane are used to designate 1,2-, 1,7-, and 1,12-dicarba-*closo*-dodecaborane. In accord with current practice, the following symbols are employed for representation of these isomers in formulas, tables, etc.



, $HCB_{10}H_{10}CH$, and