Reactions of Bis(η-cyclopentadienyl)nickel with some Pyrazoles. Unusual Temperature Dependence of the Hydrogen-1 Nuclear Magnetic Resonance Spectrum of the Cyclopentadienyl Group

By **Antony B. Blake,* David F. Ewing, John E. Hamlin,** and **Joy M. Lockyer,** Department of Chemistry, The University, Hull HU6 7RX

Bis(η-cyclopentadienyl)nickel reacts with 3,5-dialkylpyrazoles in benzene to give dark red diamagnetic complexes [$\{Ni(\eta-C_5H_5)(N_2C_3HR_2)\}_2$] (R = Me, Et, or Pr^i). No reaction occurs when R = Bu^t. The position of the resonance of the η-C_5H_5 group in the ^1H n.m.r. spectrum is temperature dependent, moving *ca.* 1 p.p.m. upfield between 0 and 80 °C ; this behaviour is consistent with an equilibrium ($\Delta H^\ominus$ *ca.* 45 kJ mol^{-1}) between the dimer and a paramagnetic monomer. The reaction of [$Ni(\eta-C_5H_5)_2$] with pyrazole and with 3-methylpyrazole results in the displacement of both η-C_5H_5 groups and the formation of polymeric bis(pyrazolates).

ONE of the characteristic reactions of [$Ni(\eta-C_5H_5)_2$] is the displacement of η-C_5H_5 by σ-bonding ligands.[1] Replacement of one η-C_5H_5 by SR or PR_2 generally results in the formation of dimetallic complexes [$\{Ni(\mu-X)(\eta-C_5H_5)\}_2$],[2] which are diamagnetic and may be regarded as containing formally five-co-ordinate low-spin Ni^{II}. In five-co-ordinate nickel(II) complexes the spin state is strongly dependent on the nature of the donor atoms: with O or N as donors, high-spin paramagnetic complexes are usual, whereas complexes with ligand atoms such as C, P, or S are invariably diamagnetic.[3] It seems possible that complexes of the type [$\{Ni(\mu-X)(\eta-C_5H_5)\}_2$], in which the bridging ligand X co-ordinates through O or N atoms, could fall into either class or might possibly be close to the spin crossover. Since the pyrazolate ion is well known as a bridging N-donor ligand,[4] *e.g.* in [$\{Fe(CO)_3(N_2C_3H_3)\}_2$],[5] [$\{Pd(\eta^3-allyl)(N_2C_3H_3)\}_2$],[6] and [$\{Cu(pd)(N_2C_3H_3)\}_2$] (pd = pentane-2,4-dionate),[7] and is not particularly high in the spectrochemical series,[8,9] we have investigated the

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reactions of $[Ni(\eta\text{-}C_5H_5)_2]$ with pyrazoles, in the hope of preparing complexes of this type and studying their magnetic properties.

RESULTS

Bis(η-cyclopentadienyl)nickel reacted readily with pyrazole in benzene, precipitating an orange-yellow diamagnetic complex which, from its empirical formula and insolubility in all non-destructive solvents, appeared to be a polymeric nickel(II) pyrazolate containing *ca.* 4 mol % of $Ni(\eta\text{-}C_5H_5)_2$. [Nickel(II) pyrazolate has been previously described as a yellow insoluble solid.[4]] Under the microscope the solid appeared crystalline and homogeneous, and the strong band of $[Ni(\eta\text{-}C_5H_5)_2]$ at 1 005 cm^{-1} was not detectable in the i.r. spectrum. This suggests that the residual C_5H_5, whose presence is indicated by the analytical data, serves to terminate polymeric chains of the approximate average formula $(\eta\text{-}C_5H_5)[Ni(N_2C_3H_3)_2]_{25}Ni(\eta\text{-}C_5H_5)$. Because of its insolubility and involatility, however, the complex was not further investigated.

A similar reaction occurred between $[Ni(\eta\text{-}C_5H_5)_2]$ and 3-methylpyrazole, the product being orange and sparingly soluble. Extraction with hot benzene and crystallisation gave a solid for which analysis indicated the approximate composition $[Ni(N_2C_4H_5)_2]_9Ni(C_5H_5)_2$. This also appeared homogeneous and crystalline under the microscope, and free $[Ni(\eta\text{-}C_5H_5)_2]$ could not be detected in the i.r. spectrum. The mass spectrum showed peaks that could be assigned (on the basis of *m/e* and isotope patterns) to $[Ni(C_5H_5)_2]^+$, $[Ni_2X_2{}^+]$, $[Ni_3X_4]^+$, $[Ni_3X_5]^+$, and $[Ni_3X_6]^+$ ($X = N_2C_4H_5$). It seems likely that the sample consists of a mixture of oligomers, perhaps including a trimer as the most volatile component.

The reactions of $[Ni(\eta\text{-}C_5H_5)_2]$ with 3,5-dialkylpyrazoles differed from its reactions with pyrazole and 3-methylpyrazole, in that even with a four-fold excess of the ligand only one $\eta\text{-}C_5H_5$ group was displaced. The rate of the reaction diminished as the bulk of the substituent R was increased, so that, whereas with Me it was complete in a few minutes at room temperature, with Pr^i refluxing was necessary and with Bu^t no reaction was observed after several hours in boiling benzene. The products were dark red, crystalline, diamagnetic solids, readily soluble in benzene, chloroform, and hexane, but insoluble in water. Vapour-phase osmometry showed that the 3,5-dimethylpyrazolato-complex is dimeric in benzene at room temperature, and the mass spectra showed the dimeric parent ions in high abundance, together with the expected fragmentation products (including $[Ni_2X_2]^+$).

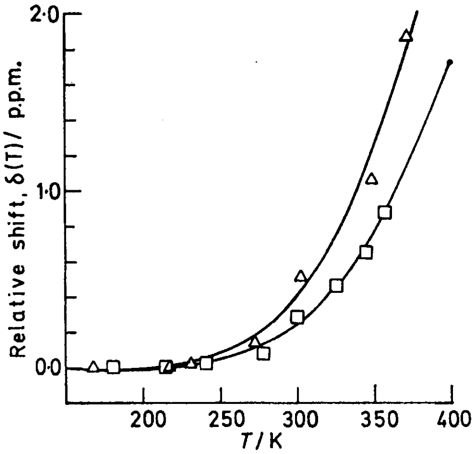
The ^1H n.m.r. spectra of the dimeric complexes are given in the Table. The C_5H_5 protons gave a single sharp resonance at all temperatures (−100 to 100 °C), indicating rapid rotation of the rings. The CH_3 signal of the 3,5-dimethylpyrazolato-complex was a singlet. For the 3,5-di-isopropylpyrazolato-complex the CH resonance appeared as a broad unresolved peak at room temperature and below, but at 76 °C the expected septet was resolved. The CH_3 resonances in this complex appeared as two doublets (*J ca.* 5 Hz, as in the unco-ordinated ligand), separated by *ca.* 0.30 p.p.m., this separation varying only slightly with temperature.

Hydrogen-1 n.m.r. spectra of $[\{Ni(\eta\text{-}C_5H_5)(N_2C_3HR_2)\}_2]$ in p.p.m. from $SiMe_4$ at 100 MHz in $CDCl_3$ at 27 °C

R = Me		R = $CHMe_2$	
C_5H_5	5.32 (s)	C_5H_5	5.11 (s)
C_3HN_2	5.48 (s)	C_3HN_2	5.57 (s)
CH_3	2.20 (s)	CH	3.20 (spt) *
		CH_3	1.05 (d) (*J* 5 Hz)
		CH_3	1.35 (d) (*J* 5 Hz)

* Broad; septet resolved at 76 °C.

The most interesting feature of the n.m.r. spectra is the way in which the position of the C_5H_5 resonance varied with temperature (Figure). As the temperature decreased, this peak moved to low field, its position becoming approximately constant below *ca.* −30 °C. The effect was particularly marked with the 3,5-di-isopropylpyrazolato-complex, the total shift being *ca.* 1.8 p.p.m. between 100 and −105 °C. Small changes also occurred in the positions of the other proton resonances, but these were mostly <0.1 p.p.m. and not consistently temperature dependent; the largest was that in the isopropyl CH resonance, *ca.* 0.3 p.p.m. over the 200 °C temperature range. Successive additions of $[Ni(\eta\text{-}C_5H_5)_2]$, up to a concentration $\{[Ni(\eta\text{-}C_5H_5)_2]$: complex *ca.* 2 : 1$\}$ sufficient to cause significant broadening of all the peaks, led to no detectable shift of the C_5H_5 resonance at constant temperature.



Temperature dependence of the C_5H_5 resonance in $[\{Ni(\eta\text{-}C_5H_5)(N_2C_3HR_2)\}_2]$: R = Me (□) or Pr^i (△). The resonance is given in p.p.m. upfield from the position in $CDCl_3$ at 300 K. Solvents used were as follows: 160—300 K, CS_2; 215—300 K, $CDCl_3$; 300—350 K, CCl_4; 300—375 K, $C_2H_2Cl_4$. To compensate for solvent effects, upfield shifts were decreased by 0.2 in CS_2 and by 0.05 in CCl_4 and $C_2H_2Cl_4$

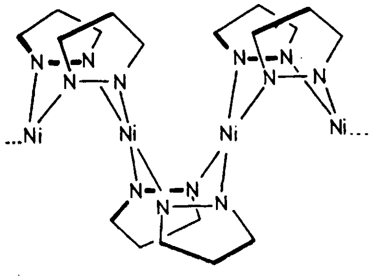
DISCUSSION

The reaction between $[Ni(\eta\text{-}C_5H_5)_2]$ and pyrazole or 3-methylpyrazole results in complete or very extensive replacement of $\eta\text{-}C_5H_5$ by the pyrazolate, whereas with 3,5-dialkylpyrazoles only one $\eta\text{-}C_5H_5$ is displaced and the tendency for reaction decreases rapidly as the substituents become more bulky. These observations seem to be adequately explained by steric interaction between the substituents and the C_5H_5 rings, although it is also possible that decreasing acidity of the imine function may contribute to the trend.

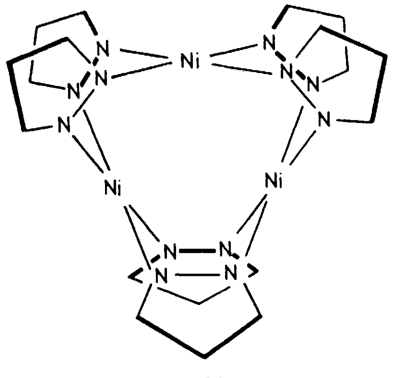
The low solubility of bis(pyrazolato)nickel(II) and bis(3-methylpyrazolato)nickel(II) suggests a polymeric (or at least oligomeric) structure, while their diamagnetism implies square-planar co-ordination of the nickel.

This is in contrast with bis(pyrazolato)cobalt(II), which also appears to be polymeric, but for which spectroscopic and magnetic evidence indicates pseudotetrahedral co-ordination.[9] The most likely structure for the nickel complexes is a zig-zag chain, (I), but a cyclic tri- or tetra-meric structure such as (II) is also possible and may represent a major component of the more soluble 3-methylpyrazole product in view of the appearance of $[\mathrm{Ni_3X}_n]^+$ ions in its mass spectrum. It may be noted that bis(3,4,5-tribromopyrazolato)copper(II) is tetrameric in benzene.[4]

Molecular models, of the framework type, indicate that structures (I) and (II) would be sterically difficult or impossible if both the 3 and 5 positions contained alkyl groups, and it is therefore understandable that in this case only 1 : 1 complexes of the type $[\mathrm{NiX}(\eta\text{-}C_5H_5)]$ are formed. The latter are evidently dimeric and their ^{1}H n.m.r. spectra are consistent with the symmetrical structure (III), analogous to that of $[\{\mathrm{Ni}(\eta\text{-}C_5H_5)(\mathrm{PPh_2})\}_2]$.[10]

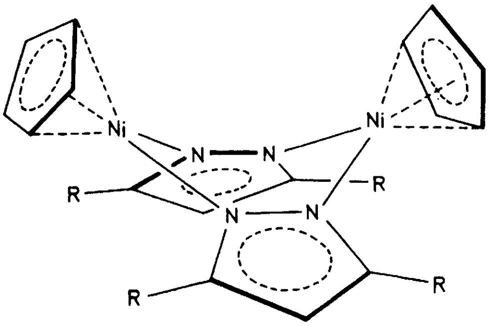


(I)



(II)

In the latter the $\mathrm{Ni_2P_2}$ ring is planar, but steric considerations suggest that the ring in (III) will be puckered. In the monomeric complexes $[\mathrm{NiX}(\eta\text{-}C_5H_5)(\mathrm{PPh_3})]$ ($X = CF_3$, Ph, or C_6F_5) the angle P–Ni–X is between 93 and 102°,[11] and in order to achieve a similar N–Ni–N angle in (III) the $\mathrm{Ni_2N_4}$ ring would need to adopt a boat conformation with a dihedral angle of *ca.* 135° between the pyrazole rings. The appearance of two methyl doublets in the n.m.r. spectrum of the 3,5-di-isopropyl- (but not the 3,5-dimethyl-) pyrazolato-complex supports this conclusion, since in such a structure the two methyl groups in each isopropyl unit are not equivalent. There is evidence for a similar puckering of the $\mathrm{M_2N_4}$ ring in bis[(3,5-dimethylpyrazolato)(η-2-phenylallyl)palladium] which also shows two methyl signals in the n.m.r.,* the asymmetry arising in this case from the η-allyl groups.[6] It is, of course, likely to be even more marked in $[\{\mathrm{Fe}(N_2C_3H_3)(CO)_3\}_2]$ which contains a metal–metal bond.[5]



(III)

The diamagnetism of the complexes $[\{\mathrm{Ni}(\eta\text{-}C_5H_5)(N_2C_3HR_2)\}_2]$ can be interpreted in two ways. Either (*a*) the energy levels available to the electrons of $\mathrm{Ni^{II}}$ as a result of bonding with η-C_5H_5 and the N atoms are such that these electrons are paired intra-atomically (*i.e.* low-spin d^8 in formal five-co-ordination), or (*b*) each $\mathrm{Ni^{II}}$ ion has two potentially unpaired electrons, but these become paired in the dimer as a result of strong superexchange or metal–metal bonding. The existence of a strong superexchange interaction through the pyrazolate ligands is rendered unlikely by the fact that in the complex bis{aqua[3,5-di(2-pyridyl)pyrazolato]-nitratonickel}, which contains six-co-ordinate $\mathrm{Ni^{2+}}$ ions bridged by pyrazolate groups, the exchange interaction is weak.[8] Also, in $[\{\mathrm{Ni}(\eta\text{-}C_5H_5)(N_2C_3HR_2)\}_2]$ each nickel atom already has 18 valence electrons, so that any metal–metal interaction would probably be at best nonbonding. We are thus led to conclude that the ligand environment of $\mathrm{Ni^{II}}$ in these complexes results in a low-spin d^8 configuration.

However, the marked reversible shift of the C_5H_5 proton resonance with changing temperature suggests that in solution there is a thermal equilibrium involving a small amount of a paramagnetic species. In order to account for this we have considered three possible mechanisms.

(*a*) Since $[\mathrm{Ni}(\eta\text{-}C_5H_5)_2]$ is paramagnetic, and its proton resonance shows a contact shift (*ca.* 251 p.p.m. upfield in benzene at 24 °C)[12] in the same direction as that

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* The coalescence of the two CH_3 signals of this complex on warming to 167 °C was attributed to rotation of the η-allyl groups rather than inversion of the boat conformation of the $\mathrm{Pd_2N_4}$ ring.[6] This interpretation is supported by the fact that the CH_3 signals in bis[(η-cyclopentadienyl)(3,5-di-isopropylpyrazolato)-nickel] remain sharp and distinct up to at least 100 °C.

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[12] H. P. Fritz, H. J. Keller, and K. E. Schwartzhans, *J. Organometallic Chem.*, 1967, **7**, 105.

observed with increasing temperature in our complexes, the most obvious possibility is disproportionation as in equation (1). This is ruled out, however, by the failure

$$[\{NiX(\eta\text{-}C_5H_5)\}_2] \rightleftharpoons NiX_2 + [Ni(\eta\text{-}C_5H_5)_2] \quad (1)$$

of added $[Ni(\eta\text{-}C_5H_5)_2]$ to affect the position of the C_5H_5 resonance in a solution of the dimer.

(*b*) A reversible dissociation of the dimer according to equation (2) could account for the observations: the monomer would be likely to be paramagnetic with spin

$$[\{NiX(\eta\text{-}C_5H_5)\}_2] \rightleftharpoons 2[NiX(\eta\text{-}C_5H_5)] \quad (2)$$

$S = 1$, since it can be regarded as formally pseudotetrahedral. If we let $(1 - \alpha)$ be the mol fraction of dimer and 2α that of the monomer, then for small degrees of dissociation α is approximately equal to $\exp(-\Delta G^\ominus/2RT)$, where $\Delta G^\ominus$ is the free energy of reaction (2). For the monomer we assume Curie-law behaviour {as for $[Ni(\eta\text{-}C_5H_5)_2]$ [13]}, so that its contact shift $\delta_M \propto T^{-1}$. If the interconversion (2) is rapid on the n.m.r. time scale, the observed shift (relative to pure dimer) at temperature T will be given by equation (3), where T_0 is some fixed

$$\begin{aligned}\delta(T) &= 2\alpha\delta_M(T) \\ &= [2T_0\delta_M(T_0)\exp(\Delta S^\ominus/2R)]T^{-1}\exp(-\Delta H^\ominus/2RT) \\ &= aT^{-1}\exp(-\Delta H^\ominus/2RT) \quad (3)\end{aligned}$$

temperature. By fitting equation (3) by least squares to the shifts of the C_5H_5 resonance over the experimental temperature range we can obtain the values of a and $\Delta H^\ominus$. The data and calculated curves are shown in the Figure. The parameters giving the best fit for $[\{Ni(\eta\text{-}C_5H_5)(N_2C_3HR_2)\}_2]$ are: R = Me, $a = (6.9 \pm 0.3) \times 10^5$ K and $\Delta H^\ominus = 45.8 \pm 0.4$ kJ mol^{-1}; Pr^i, $a = (7.6 \pm 0.6) \times 10^5$ K and $\Delta H^\ominus = 43.6 \pm 1.0$ kJ mol^{-1}.

If we assume that δ_M is approximately equal to the contact shift of $[Ni(\eta\text{-}C_5H_5)_2]$ itself we can estimate $\Delta S^\ominus$. We find $\Delta S^\ominus$ *ca.* 25 for the 3,5-dimethyl- and 27 J K^{-1} mol^{-1} for the 3,5-di-isopropyl-pyrazolato-complex, which are quite reasonable values for a dissociation of this type. The extent of dissociation implied by these results is quite small, the value of α at 84 °C being only *ca.* 0.002 for R = Me and 0.003 for R = Pr^i. The smaller $\Delta H^\ominus$ in the latter case is consistent with somewhat greater steric interaction between the Pr^i groups and the C_5H_5 rings.

(*c*) A third possible interpretation of the results is that within the dimer each Ni^{II} has an excited $S = 1$ state that is just thermally accessible in the temperature range studied. (This would accord with the hypothesis that the presence of N-donor ligands in $[\{NiX(\eta\text{-}C_5H_5)\}_2]$ should lead to some stabilisation of the high-spin state of five-co-ordinate d^8.) The effective shift will be proportional to the average z component of the spin, which (neglecting any coupling between the spins) is given by equation (4), where E is the energy of the $S = 1$ state. Thus, $\delta(T) = a'T^{-1}[f(-E/\boldsymbol{k}T)]$, which is similar in form to equation (3) if E is large compared to $\boldsymbol{k}T$. By a

$$\langle S_z\rangle = \frac{g\beta H}{\boldsymbol{k}T}\cdot\frac{4\exp(-E/\boldsymbol{k}T)}{1 + 3\exp(-E/\boldsymbol{k}T)} \quad (4)$$

least-squares fit of (4) to the experimental data we find for $[\{Ni(\eta\text{-}C_5H_5)(N_2C_3HR_2)\}_2]$: R = Me, $a' = (1.73 \pm 0.1) \times 10^5$ K and $E = 22.9 \pm 0.2$ kJ mol^{-1}; Pr^i, $a' = (1.93 \pm 0.15) \times 10^5$ K and $E = 21.8 \pm 0.5$ kJ mol^{-1}.

For the pure $S = 1$ state, $\langle S_z\rangle_T = 2g\beta H/3\boldsymbol{k}T$, and hence $\delta_T(T) = 2a'/3T$. The values obtained for δ_T at 25 °C are $+386 \pm 17$ for R = Me and $+431 \pm 36$ p.p.m. for R = Pr^i. These values are considerably greater than that of $[Ni(\eta\text{-}C_5H_5)_2]$ itself, and even if allowance is made for the possibility of a sizeable pseudocontact contribution we are inclined to think them improbably high. This interpretation of the observations is thus rather less satisfactory than the dissociative mechanism, (*b*), above.

We conclude therefore, that the most likely explanation of the unusual temperature dependence of the C_5H_5 proton resonance in $[\{Ni(\eta\text{-}C_5H_5)(N_2C_3HR_2)\}_2]$ is a slight degree of reversible dissociation to give paramagnetic pseudotetrahedral monomers, but that the alternative of a thermally accessible, paramagnetic, excited state (*ca.* 1 900 cm^{-1} above the ground state) cannot be ruled out.

It may be added that the much smaller temperature dependence of the other proton resonance positions in these complexes merely reflects the greater attenuation of the spin density in the paramagnetic species at nuclei four or more bonds distant from the nickel atom.

EXPERIMENTAL

Bis(η-cyclopentadienyl)nickel was prepared from hexa-amminenickel(II) chloride and sodium cyclopentadienide,[14] and purified by vacuum sublimation. Pyrazole and 3-methylpyrazole were purchased from Koch–Light. 3,5-Dimethylpyrazole was prepared by adding hydrazine hydrate, dissolved in ethanol, dropwise to a stirred solution of pentane-2,4-dione in diethyl ether. 3,5-Di-isopropyl- and 3,5-di-t-butyl-pyrazole were prepared by direct reaction (1 : 1) between $N_2H_4\cdot H_2O$ and the corresponding diketone, the latter being prepared by the method of Adams and Hauser.[15] The dialkylpyrazoles were recrystallised from benzene before use.

Reactions of the Pyrazoles with $[Ni(\eta\text{-}C_5H_5)_2]$.—All the reactions were carried out in benzene solution under nitrogen, in a flask fitted with a stirrer, reflux condenser, and tap funnel.

Pyrazole. The complex (1.9 g, 0.01 mol) and pyrazole (1.6—6.5 g, 0.01—0.04 mol) were placed in the flask and oxygen-free benzene (50 cm^3) was added. The solution was warmed to 60 °C and stirred for 1 h, and the orange-yellow microcrystalline precipitate was filtered off, washed with benzene, and dried in air {Found (typically): C, 38.25; H, 3.20; N, 27.85. Calc. for $Ni(N_2C_3H_3)_2$: C, 37.35;

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[13] M. F. Rettig and R. S. Drago, *J. Amer. Chem. Soc.*, 1969, **91**, 1361.

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[15] J. T. Adams and C. R. Hauser, *J. Amer. Chem. Soc.*, 1944, **66**, 1220; *cf.* ' Organic Reactions,' ed. R. Adams, Wiley, New York, 1954, vol. 8, p. 122.

H, 3.15; N, 29.05. Calc. for $[Ni(N_2C_3H_3)_2]_{25}Ni(C_5H_5)_2$: C, 38.4; H, 3.20; N, 27.9%}.

3-*Methylpyrazole*. The complex (0.95 g, 0.005 mol) was placed in the flask under nitrogen and 3-methylpyrazole (0.85 g, 0.01 mol) in oxygen-free benzene (50 cm^3) was added. The solution was stirred at room temperature for 1 h, the benzene was removed *in vacuo*, and the orange residue was extracted with boiling benzene and crystallised {Found: C, 45.45; H, 4.55; N, 23.2. Calc. for $Ni(N_2C_4H_5)_2$: C, 43.5; H, 4.55; N, 25.35. Calc. for $[Ni(N_2C_4H_5)_2]_9Ni(C_5H_5)_2$: C, 45.25; H, 4.65; N, 23.15%}.

3,5-*Dimethylpyrazole*. The complex (1.9 g, 0.01 mol) and 3,5-dimethylpyrazole (1.0 g, 0.01 mol) were placed in the flask and benzene (50 cm^3) was added. The dark red product was isolated as for the 3-methylpyrazolate {Found: C, 54.6; H, 5.45; N, 12.85%; *M* 455 ± 35. Calc. for $[Ni(C_5H_5)(N_2C_5H_7)]$: C, 54.85; H, 5.50; N, 12.8%; *M* 218.9}.

3,5-*Di-isopropylpyrazole*. The method was the same, but the reaction was carried out at reflux temperature {Found: C, 61.2; H, 7.45; N, 10.0. Calc. for $[Ni(C_5H_5)(N_2C_9H_{15})]$: C, 61.15; H, 7.35; N, 10.2%}.

3,5-*Di-t-butylpyrazole*. No reaction was observed after 1 h under reflux.

Apparatus.—Mass spectra were obtained with an A.E.I. MS902 spectrometer, i.r. spectra of Nujol mulls with a Perkin-Elmer 457, and n.m.r. spectra with a JEOL 100 MHz instrument using $SiMe_4$ as internal standard. Molecular weights in benzene were determined by vapour-phase osmometry, using a Hitachi–Perkin-Elmer 115 instrument.

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