Organonitrogen Groups in Metal Carbonyl Complexes. Part IX.[1] Amidino-derivatives of Some π-Cyclopentadienyl Compounds

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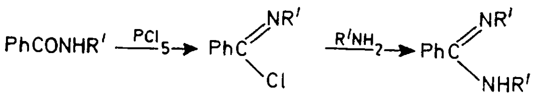
Lithioamidines, R′NC(R)NR′Li, react with $[(\pi\text{-}C_5H_5)M(CO)_3Cl]$ (M = Mo or W) to form the complexes $[(\pi\text{-}C_5H_5)\text{-}M(CO)_2\{R'NC(R)NR'\}]$ (R = Ph; R′ = H, Ph, or *p*-tolyl) in which the organonitrogen group acts as a bidentate 3-electron-donor ligand. Bidentate attachment of the amidino-ligand is considered to be of the σ,σ-type, unlike the isoelectronic allyl group. No corresponding amidino-complexes of carbonyl(π-cyclopentadienyl)iron could be isolated at room temperature and the complex $[(\pi\text{-}C_5H_5)Ni\{PhNC(Ph)NPh\}]$, obtained from $[(\pi\text{-}C_5H_5)Ni(PPh_3)Cl]$, appears to be polymeric, possibly through NCN bridges.

PREVIOUS papers in this series have been concerned with the synthesis and study of methyleneamino ($R_2C{:}N$, R = alkyl or aryl)[2] and 2-aza-allyl (R_2CNCR_2, R = aryl)[3] complexes. The two ligands behave as 3-electron donors and form complexes of the type $[(\pi\text{-}C_5H_5)M(CO)_2L]$ (M = Mo or W). Both series of complexes arise from the same reaction, *i.e.* treatment of $[(\pi\text{-}C_5H_5)M(CO)_3Cl]$ with the reagent $R_2C{:}NLi$, and the 2-aza-allyl ligand must result from a condensation of two methyleneamino-groups.[3] The 2-aza-allyl complexes adopt a π-allene-type configuration in the solid state,[4] but their observed[5] fluxional behaviour in solution is consistent with an equilibrium involving, at low temperatures, a σ,π-allylic-type structure. These observations have stimulated our interest in complexes containing these or related three-atom 3-electron-donor ligands. Further study of the 2-aza-allyl group has, however, been limited since the introduction of the preformed ligand has been relatively unsuccessful[6] and its synthesis *via* R_2CNLi reagents appears applicable only to π-cyclopentadienyl-molybdenum and -tungsten complexes. The present report concerns the amidino-group, R′NC(R)NR′, which is isoelectronic with both the allyl and the carboxylato-groups and may adopt bidentate or bridging bonding modes characteristic of both these latter groups. Few examples of amidine–transition-metal complexes are known. Hieber has prepared the cationic species $[(NO)_2MH_2NC(Ph){:}NPh]^+$ (M = Fe or Co)[7] while amidino-groups are thought[8] to have been formed by intramolecular condensation of one of the alkyl cyanide groups with an ammine ligand in the complexes $[Pt(RCN)_2(NH_3)_2][PtCl_4]$. In addition, various main-group compounds, particularly of silicon and tin, have been reported.[9]

RESULTS AND DISCUSSION

In the light of previous experience with $R_2C{:}N$ ligands, aryl-substituted amidines were considered most suitable for isolating stable products, and were prepared by the route:[10]



(I) R′ = Ph or *p*-tolyl

The di-*p*-tolylbenzamidine (I; R′ = *p*-tolyl) was intended in this work to provide a suitable ^1H n.m.r. monitoring group for structural studies. The amidines react readily with n-butyl-lithium in ether at sub-ambient temperatures to give yellow solutions and/or suspensions of the *N*-lithiated derivatives, R′NC(Ph)-NR′Li.

The lithioamidines react smoothly with $[(\pi\text{-}C_5H_5)\text{-}M(CO)_3Cl]$ (M = Mo or W) in ether at temperatures between 0 and 25 °C to form complexes of composition $[(\pi\text{-}C_5H_5)M(CO)_2\{R'NC(Ph)NR'\}]$ (II; M = Mo or W; R′ = Ph or *p*-tolyl), isolated as air-sensitive golden-yellow solids. Molecular-weight measurements, both by osmometry in 1,2-dichloroethane and by mass spectrometry, confirm the mononuclear formulation. In the mass spectrum, each of the ions $[(\pi\text{-}C_5H_5)M(CO)_x\text{-}\{R'NC(Ph)NR'\}]^+$ ($x = 0, 1,$ or 2) was observed and good agreement was obtained between the observed and theoretical isotope-combination patterns for each ion. Further spectroscopic data (i.r. and ^1H n.m.r., Table) confirm that these are dicarbonyl complexes in which the amidino-group is acting as a 3-electron-donor ligand. Only two ν_{CO} at characteristically[2,3,5] low frequencies are observed and there is no evident ν_{NH} or corresponding ^1H n.m.r. signal.

The amidino-group may fulfil its 3-electron-donor role by bonding through either (i) one nitrogen atom or (ii) more than one skeletal atom; the latter is preferred, however, for two reasons. In the first place, complexes of the type $[(\pi\text{-}C_5H_5)M(CO)_2NR'R'']$ (M = Mo or W) are not known and attempts to prepare them have failed.[11] Secondly the amidino-complexes (II) are found to have carbonyl stretching frequencies at positions close to those

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[3] H. R. Keable and M. Kilner, *J.C.S. Dalton*, 1972, 153.

[4] H. M. M. Shearer and J. D. Sowerby, personal communication.

[5] H. R. Keable and M. Kilner, *J.C.S. Dalton*, 1972, 1535.

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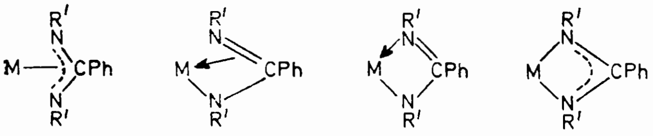
[11] M. Kilner, unpublished results.

Infrared and ^{1}H n.m.r. spectroscopic data for [(π-C_5H_5)M(CO)$_2${R′NC(R)NR′}] (II; M = Mo or W) complexes

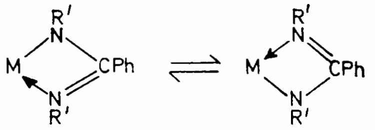
Complex	Form	ν(CO)str. frequencies/cm^{-1}	^{1}H N.m.r. (τ) *
[(π-C_5H_5)Mo(CO)$_2${PhNC(Ph)NPh}]	CCl_4	1970vs, 1890vs	3·5 (3),† 4·7 (1)
	Mull	1950vs, 1864sh, 1852vs	
[(π-C_5H_5)Mo(CO)$_2${(*p*-tolyl)NC(Ph)N(*p*-tolyl)}]	$(CH_2Cl)_2$	1956vs, 1868vs	*ca.* 3·0 (13),† 4·62 (5), 7·67 (6)
[(π-C_5H_5)Mo(CO)$_2${HNC(Ph)NH}] (*a*)	CH_2Cl_2	1962vs, 1874vs	
(*a*)	Mull	1968sh, 1955vs, 1875vs, 1860sh	
(*b*)	Mull	1958vs, 1853sh, 1833vs	
[(π-C_5H_5)W(CO)$_2${PhNC(Ph)NPh}]	Mull	1935vs, 1840vs	
	$(CH_2Cl)_2$	1965vs, 1877vs	
[(π-C_5H_5)W(CO)$_2${(*p*-tolyl)NC(Ph)N(*p*-tolyl)}]	$(CH_2Cl)_2$	1949vs, 1852vs	*ca.* 3·0 (13),† 4·48 (5), 7·67 (6)
[(π-C_5H_5)W(CO)$_2${HNC(Ph)NH}] (*a*)	CH_2Cl_2	1945vs, 1858vs	
(*b*)	Nujol	1941vs, 1839sh, 1820vs	

* In CS_2 solution. † Multiplet.

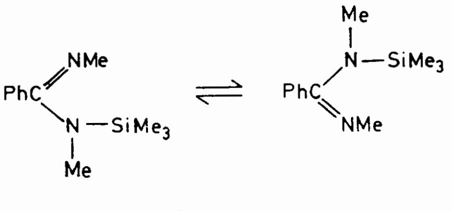


(A) (B) (C) (D)

of the 2-aza-allyl complexes [5] and at lower frequency than the methyleneamino-complexes,[12] indicative of the greater degree of electron donation expected from a bidentate ligand. It is proposed, therefore, that the amidino-group is bidentate, but the nature of its attachment is not clear. For the amidino-group, three modes of attachment are feasible. Structure (A) has a completely delocalised, pseudo-π-allylic arrangement, (B) has localised σ,π-bonding in which a M–N σ-bond is supported by olefinic-type bonding through the C=N double bond, (C) has the chelate ring completed by lone-pair donation from the second nitrogen atom, and (D) has a σ,σ-attached delocalised group with the metal lying in the NCN plane. Unfortunately, the choice of any specific mode is rendered difficult by the equivocal nature of the spectroscopic data. For instance, a medium intensity absorption is present at *ca.* 1630 cm^{-1} in the i.r. spectrum of each complex. This band is little removed from the position of ν_{NCN} of the free amidine,[13] and favours structures (C) and (D). Variable-temperature i.r. and ^{1}H n.m.r. data are, however, more consistent with structures (A) and (D). No change was observed in the ν_{CO} stretching region of the i.r. spectrum of [(π-C_5H_5)Mo(CO)$_2${PhNC(Ph)NPh}] in (CH_2Cl_2) solution between +50 and −40 °C. ^{1}H N.m.r. spectra for the complexes (II; R′ = *p*-tolyl) remained little changed over the range +40 to −90 °C (slight broadening at <−80 °C was probably due to precipitation of solid complex). It therefore appears that, throughout this temperature range, the environment of both N-substituents is identical, as implied by structures (A) and (D). Previous studies [1] with [Mn(CO)$_4$C(O)N(*p*-tolyl)C(Ph)N(*p*-tolyl)] also failed to detect differences between the environments of the *para*-methyl substituents, and such probes may well be insensitive to any electronic or steric differences between the two nitrogen atoms. This does, however, appear rather surprising in view of our successful studies [5] of *p*-tolyl-substituted 2-aza-allyl complexes, where chemical shift differences of 1—2 Hz were readily resolved, and Robinson's results on bis-*p*-tolyl triazene complexes for which separations of *ca.* τ 0·1 are reported.[14] If structure (B) is ruled out because of the i.r. band at *ca.* 1630 cm^{-1}, then a further possibility of a rapid equilibrium between structures of type (C) exists as shown below:



Worthy of mention in connection with such a process are the ^{1}H n.m.r. studies of Group IVB compounds [{MeN:C(Ph)N(Me)}M′(Me)$_3$] (M′ = Si or Sn), although in these derivatives the amidino-group is predominantly a 1-electron donor while in (π-C_5H_5)M(CO)$_2$ derivatives (M = Mo or W) it is a multidentate 3-electron donor. Equivalence of *N*-methyl groups at room temperature has been observed [9] but at −60 °C the *N*-methyl signal could be resolved into two components. This result was interpreted in favour of a very rapid equilibrium rather than the existence of one delocalised species, *i.e.*:



Further studies are continuing in an effort to resolve the nature of the bonding to the metal, although, in the light of findings with other 3-atom 3-electron-donor ligands,[15] structure (D) appears to us most likely and makes the ligand strictly comparable with bidentate carboxylate, carbonate groups, *etc.*

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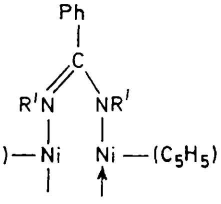
Studies using the lithio-derivative of benzamidine (I; $R^1 = H$) indicated that, as well as the monomeric complexes (II; M = Mo or W; R′ = H), a second type of complex was formed. The lower solubility of these materials in organic solvents and characteristic differences in the i.r. spectrum suggest that these complexes may be polymeric through amidino-bridges.

The diphenylbenzamidino-complexes (II; R′ = Ph) proved resistant to substitution or addition by triphenylphosphine and, on treatment of the molybdenum complex with iodine, only extensive decomposition occurred and no organometallic product could be isolated. These results are similar to those obtained using the 2-aza-allyl/allene complexes.[3,5]

Treatment of $[(\pi\text{-}C_5H_5)Ni(PPh_3)Cl]$ with PhNC(Ph)N(Ph)Li afforded a brown, almost insoluble, powder, the analysis for which was consistent with its formulation as $[(C_5H_5)Ni\{PhNC(Ph)NPh\}]$, (III). Mass spectral and molecular-weight measurements proved impossible owing to the involatility and insolubility of the complex which is probably polymeric in nature. If this is so, the complex is markedly different from the known monomeric π-allyl derivative, $[(\pi\text{-}C_5H_5)Ni(\pi\text{-}C_5H_5)]$.[16] The i.r. spectrum of the amidino-complex in the region 1600—600 cm^{-1} bears a close resemblance to that of $[Mo_2\{PhNC(Ph)N(Ph)\}_4]$ [17] which is known to have amidino-groups bridging two metal atoms in a cupric acetate-type structure. Structure (D) is therefore proposed as being consistent with the available data and with the retention of an 18-electron configuration for the nickel atom, but the degree of association is not known. Complex (III) was chemically very stable as evidenced during our study by its failure to dissolve in, and resistance to attack by, a variety of organic solvents, water, or warm dilute nitric acid (used to remove impurities).



(D)

The solid product of the reaction between $[(\pi\text{-}C_5H_5)Fe(CO)_2Cl]$ and R′NC(Ph)N(R′)Li (R′ = Ph or *p*-tolyl) proved to be extremely unstable at room temperature and no amidino-derivative could be characterised although it is probable that one was formed.

In conclusion, therefore, it appears that despite the electronic and structural resemblance of amidino- to carboxylato-groups, a sharp distinction between the two occurs also in the cyclopentadienyl series of compounds. For instance, the complexes $[(\pi\text{-}C_5H_5)Mo(CO)_3(OCOR)]$ [17] contain the carboxylate group as a unidentate 1-electron-donor ligand. Indeed, in low-valent complexes, the carboxylato-group generally prefers to adopt either a unidentate or a bridging conformation as in $[Mn(CO)_5(OCOR)]$ [18,19] and $[\{Rh(CO)_2(OCOR)_2\}]$[20] respectively. Those few examples of bidentate carboxylato-groups bonded to transition metals in low valent complexes are mostly confined to the heaviest members of the series, *e.g.* Ir or Os.[15] On the other hand, unidentate amidino-groups appear to be formed only with reluctance (*cf.* $[Mn(CO)_5\{N(Ph)C(Ph)NPh\}]$[1]) and in the present case not at all. Treatment of $[(\pi\text{-}C_5H_5)Mo(CO)_2\{PhNC(Ph)NPh\}]$ with carbon monoxide at 150 °C and 330 atm was followed spectroscopically using a high-pressure i.r. cell.[1,21] No evidence was obtained for a tricarbonyl amidino-species, the only products observed being, successively, $[\{Mo(CO)_3(\pi\text{-}C_5H_5)\}_2]$ and $[Mo(CO)_6]$. Bridging amidino-groups now appear to be fairly usual and their occurrence is suspected in some of the complexes described here.

EXPERIMENTAL

NN′-Diphenyl- and di-(*p*-tolyl)-benzamidine were prepared according to published procedures,[10,21] and $H_2NC(Ph)NH$ was obtained from a commercial sample of the hydrochloride using a method previously reported.[22] Tricarbonylchloro-π-cyclopentadienyl-molybdenum [23] and -tungsten,[23] tetracarbonyldi-π-cyclopentadienyldi-iron,[24] and chloro-π-cyclopentadienyltriphenylphosphinenickel [25] were synthesised by standard routes, and were recrystallised before use. Dicarbonylchloro-π-cyclopentadienyliron was prepared from $[\{\pi\text{-}C_5H_5Fe(CO)_2\}_2]$ in chloroform solution by irradiation with a 150 W u.v. lamp.[11] Commercial n-butyllithium (*ca.* 2·5M in hexane) was used without further purification. Hydrocarbon solvents and diethyl ether were dried over extruded sodium, and dichloromethane was freshly distilled from phosphorus pentoxide. All solvents were pumped to remove dissolved air, stored under nitrogen, and transferred by syringe against a counter flow of nitrogen. All reactions were performed with rigorous exclusion of oxygen.

Spectra.—I.r. spectra in the range 4000—250 cm^{-1} were recorded on a Perkin-Elmer 257 spectrophotometer, and ^1H n.m.r. spectra at 60 MHz with a Varian A56/60D spectrometer. Mass spectra were obtained with an A.E.I. MS9 instrument at 70 eV and an accelerating potential of 8 kV. Samples were inserted directly into the ion source between 80 and 220 °C.

Analyses.—Conventional combustion methods of elemental analysis, *e.g.* using a Perkin-Elmer 240 Elemental Analyser, proved unreliable, and results obtained on different

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[24] R. B. King, ' Organometallic Syntheses,' eds. J. J. Eisch and R. B. King, Academic Press, London, 1965 and refs. therein.

[25] G. E. Schroll, U.S.P. 3054815/1962 (*Chem. Abs.*, 1963, **58**, 1494).

batches of the same sample were widely different even though we were confident that samples were of high purity. This problem has been experienced previously with organonitrogen derivatives of molybdenum and tungsten and ascribed to the formation of highly stable carbides, nitrides, *etc.* Characterisation of the complexes has therefore been primarily based on mass spectral data. Molecular weights were determined osmometrically using a Mecrolab Osmometer.

Preparation of N-*Lithio*-NN′-*diphenylbenzamidine*.—A solution of n-butyl-lithium in hexane (1·5 ml; 2·5M) was added by syringe to a frozen solution containing *NN*′-diphenylbenzamidine (1·00 g, 3·68 mmol) in ether (50 ml) and the resulting mixture was allowed to warm to ambient temperature. The solution was then deeper yellow in colour and i.r. spectroscopy showed the disappearance of a band at *ca.* 1630 cm^{-1}, which is assigned to ν_{as} (NCN) of the amidines.

Other lithioamidines were prepared similarly, and used within 0·5 h after the solutions had reached room temperature.

Reaction of Tricarbonylchloro-π-cyclopentadienylmolybdenum with LiN(Ph)C(Ph)NPh.—A solution of the lithioamidine (3·68 mmol) in ether (*ca.* 50 ml) was transferred to a flask containing a cooled mixture of the carbonyl chloride (0·897 g, 3·20 mmol) and ether (80 ml). The resulting mixture was allowed to warm to room temperature and then stirred for 1·5 h. During this period a colour change from yellow to orange-yellow took place and some precipitation occurred. The resulting mixture was filtered and hexane (25 ml) was added to the filtrate. Concentration of the solution (20 °C, 0·01 mmHg) caused precipitation of [(π-C_5H_5)Mo(CO)$_2${PhNC(Ph)NPh}] as a yellow solid (1·50 g, 3·07 mmol; 96% yield) almost free of impurities. Analytical samples, m.p. 138—139 °C (decomp), were obtained by recrystallisation from dichloromethane–hexane at 20 °C [Found: C, 60·5, 57·95, 59·45, 58·5; H, 4·85, 4·2, 3·95, 3·9; N, 4·95, 4·85, 4·65, 4·8; Mo, 19·4%; *M*, 510, 502 (osmometry). $C_{26}H_{20}MoN_2O_2$ requires C, 63·93; H, 4·10; N, 5·74; Mo, 19·6%; *M*, 488]; *m/e* (P^+) 490, [P − CO]$^+$ 462, and (P − 2CO)$^+$ 434. The last peak given had the greatest intensity.

Attempted sublimation of the complex at 130—150 °C *in vacuo* (10^{-4} mmHg) caused decomposition and the only sublimate obtained, a purple solid, was identified by i.r. spectroscopy as [{π-C_5H_5Mo(CO)$_3$}$_2$].

Attempted reaction of [(π-C_5H_5)Mo(CO)$_2${PhNC(Ph)NPh}] *with* PPh$_3$.—The complex (50 mg, 0·1 mmol) and PPh$_3$ (0·25 g, 0·95 mmol) in light petroleum (b.p. 60—80 °C) were heated together under reflux for 1 h. No reaction was detected by i.r. spectroscopy.

Attempted reaction of [(π-C_5H_5)Mo(CO)$_2${PhNC(Ph)NPh}] *with Iodine*.—A solution of iodine (0·2 g, 0·79 mmol) in hexane (30 ml) was added dropwise at room temperature to the complex (0·277 g, 0·57 mmol) in ether (15 ml). The solution became brown, a brown solid separated, and gas was evolved. Evaporation of the solvent, and removal of iodine *in vacuo* (20 °C, 10^{-2} mmHg), yielded a dark brown decomposition product, which was not studied further.

Reaction of LiN(*p*-tolyl)C(Ph)N(*p*-tolyl) *with* [(π-C_5H_5)Mo(CO)$_3$Cl].—The reaction between the carbonyl chloride (0·802 g, 2·9 mmol) and the lithiated amidine, prepared from the amidine (0·900 g, 3·0 mmol), in ether (90 ml), proceeded as described previously for the reaction of *NN*′-diphenylbenzamidine. Fractional crystallisation of the product gave red-brown crystals identified by i.r. spectroscopy and analysis as [{π-C_5H_5Mo(CO)$_3$}$_2$], and a yellow powder. Analytical data on the yellow product proved unreliable, but the complex [(π-C_5H_5)Mo(CO)$_2${(*p*-tolyl)NC(Ph)N(*p*-tolyl)}] was characterised by mass spectrometry, and by comparison of spectroscopic data with those of the *NN*-diphenyl complex; *m/e* (P^+) 518, (P − CO)$^+$ 490, and (P − 2CO)$^+$ 462.

Reaction of LiN(Ph)C(Ph)N(Ph) *with* [(π-C_5H_5)W(CO)$_3$Cl].—The amidine (0·997 g, 3·7 mmol) was converted into the lithio-derivative as described previously and treated with the carbonyl chloride (1·22 g, 3·3 mmol) in ether (80 ml) at room temperature during 2·5 h. The yellow complex [(π-C_5H_5)W(CO)$_2${PhNC(Ph)NPh}] was characterised solely by mass spectrometry as a result of unsatisfactory analyses, *m/e* (P^+) 576, (P − CO)$^+$ 548, and (P − 2CO)$^+$ 520. The ions occurred in the relative abundances 30·3, 5·6, and 100 respectively. The *NN*′-di-*p*-tolylbenzamidino-complex was synthesised and characterised similarly; *m/e* (P^+) 604, (P − CO)$^+$ 576, and (P − 2CO)$^+$ 548.

Reaction of LiNHC(Ph)NH *with* [(π-C_5H_5)Mo(CO)$_3$Cl].—The lithium compound prepared from benzamidine (0·374 g, 3·12 mmol) in ether (80 ml) was added to a frozen solution of [(π-C_5H_5)Mo(CO)$_3$Cl] (0·875 g, 3·12 mmol) also in ether (150 ml) and the procedure described above followed. At the end of the reaction, as indicated by the consumption of all the carbonyl chloride as monitored by i.r. spectroscopy, the solvent was removed *in vacuo* (20 °C; 10^{-1} mmHg), and the residue extracted with dichloromethane (3 × 30 ml). Fractional crystallisation techniques enabled yellow crystals of complex (*a*) to be isolated. Washing of the residue with water to remove lithium chloride followed by drying *in vacuo* extraction with acetone (100 ml) yielded a yellow solution which on reduction to small bulk and addition of ether yielded a yellow powder (*b*). The two products differ in physical properties but are believed to have the same empirical formula based upon limited analytical data. A parent peak in the mass spectrum was detected for complex (I) at *m/e* 338, with an isotopic-distribution pattern consistent with the formulation [(π-C_5H_5)Mo(CO)$_2${HNC(Ph)NH}]; *m/e* (P^+) 338, (P − CO)$^+$ 310, and (P − 2CO)$^+$ 282.

Reaction of LiNHC(Ph)NH *with* [(π-C_5H_5)W(CO)$_3$Cl].—Two products (*a*) and (*b*) were obtained from stoicheiometric amounts of these reactants, and were separated as described for the corresponding molybdenum system. Mass spectral evidence was obtained for the identity of the most-soluble complex being [(π-C_5H_5)W(CO)$_2${HNC(Ph)NH}], *m/e* (P^+) 424, (P − CO)$^+$ 396, and (P − 2CO)$^+$ 368.

Reaction of [(π-C_5H_5)Ni(PPh$_3$)Cl] *with* LiN(Ph)C(Ph)NPh.—The lithio-reagent prepared from the amidine (1·01 g, 3·7 mmol) in ether (40 ml) was added to solid [(π-C_5H_5)Ni(PPh$_3$)Cl] (1·36 g, 3·2 mmol) at room temperature. An immediate reaction occurred and the characteristic colour of the chloride in solution failed to appear. After being stirred for 2 h, the reaction mixture was filtered to give a yellow solution, which on removal of the solvent gave an intractable viscous oil. The residue was washed with ether, warm dilute nitric acid (5%), water, and finally acetone to give [(π-C_5H_5)Ni{PhNC(Ph)NPh}]$_n$, as a brown powder (m.p. 318—319 °C dec. *in vacuo* in a sealed capillary) (Found: C, 72·6; H, 5·8; N, 8·05. $C_{24}H_{20}N_2Ni$ requires C, 73·0; H, 5·07; N, 7·99%).

Reaction of [(π-C_5H_5)Fe(CO)$_2$Cl] *with* LiN(Ph)C(Ph)NPh.—The lithio-reagent prepared from the amidine (0·995 g, 3·66 mmol) in ether (35 ml) was added at low temperatures (*ca.* 40 °C) to the carbonyl chloride (0·768 g, 3·62 mmol) also in ether (100 ml) and the mixture, after warming to room temperature, was stirred for 16 h. Addition of hexane (25 ml) followed by removal of the solvent (20 °C, 10^{-2} mmHg), yielded a brown residue comprising principally of the starting materials {amidine and [(π-C_5H_5)Fe(CO)$_2$Cl]} and a trace of [{(π-C_5H_5)Fe(CO)$_2$}$_2$]. No evidence for any possible amidino-complex was obtained.

Reaction of [(π-C_5H_5)Fe(CO)$_2$Cl] *with* LiN(*p*-tolyl)C(Ph)N-(*p*-tolyl).—The lithio-reagent, prepared from the amidine (0·985 g, 3·0 mmol) in ether (40 ml), was added to [(π-C_5H_5)-Fe(CO)$_2$Cl] (0·621 g, 2·9 mmol) in ether (50 ml) at low temperature; the mixture was then warmed and stirred at room temperature for 0·5 h, before being cooled to 0 °C. Green-black crystals separated but all attempts to isolate the product from the reaction mixture failed because of its thermal instability near room temperature.

We thank the S.R.C. for a research grant.

[4/2039 *Received, 4th October,* 1974]