Transition-metal Derivatives of Arenediazonium Ions. Part VII.[1] Fluorine-19 Nuclear Magnetic Resonance and Nitrogen-15 Infrared Labelling Studies on some Benzene-, *meta*-Fluorobenzene-, and *para*-Fluorobenzene-diazo-complexes of Iron, Molybdenum, Platinum, and Tungsten

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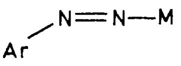
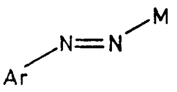
^{19}F N.m.r. spectra of fifteen different classes of *m*- and *p*-fluorobenzenediazo-complexes containing iron, molybdenum, platinum, or tungsten have been measured. The ^{19}F n.m.r. technique is shown to be a sensitive tool for determination of the degree of $M-N_2Ar$ π-bonding provided all complexes studied are of the same structural type. Direct evidence has been obtained for the view that the cation ArN_2^+ is a poorer π-acceptor than NO^+. The ν(NN) stretching frequencies of the ArN_2 complexes (Ar = Ph, *m*-FC_6H_4, or *p*-FC_6H_4) have been identified by $^{15}N^{14}N$ labelling. Many of these complexes show an unexpected multiplicity of bands associated with the N_2 chromophore.

ARENEDIAZO-LIGANDS may adopt two modes of co-ordination and at least two limiting geometric configurations. The ligands may behave either formally as ArN_2^+ (A; singly bent, substantial $M \rightarrow L$ π-bonding) [2] or ArN_2^- (B; doubly bent, with little $M \rightarrow L$ π-interaction).[3]



(A)



(B)

This co-ordinative versatility parallels the behaviour of the nitrosyl ligand and ν(NN), like ν(NO), covers a broad range of wavenumbers (1 440—2 095 cm^{-1}),[3,4] with considerable overlap of regions characteristic of the two co-ordination modes. Ibers and his co-workers [3] have recently derived a set of empirical rules for calculating a 'corrected' ν(NN) value more truly diagnostic of the co-ordination mode. A knowledge of the degree of $M \rightarrow N_2Ar$ π-interaction would advance our understanding of the relation between bonding and structure in these complexes. The ν(NN) stretching frequencies do not yield useful information on this point. Another area of ambiguity concerns the relative importance of π-bonding in analogous NO^+ and ArN_2^+ complexes. Chemical and i.r. evidence has been separately advanced to suggest that ArN_2^+ is the stronger [5,6] or weaker [1,7] π-acceptor of the two. We have applied the ^{19}F n.m.r. technique of Taft [8] to a study of both these problems. Since the position of ν(NN) was not known with certainty for most of the complexes studied, we have attempted to identify this absorption unambiguously using $^{15}N^{14}N$ labelling.

RESULTS AND DISCUSSION

Fifteen different classes of complex were examined and ^{19}F n.m.r.† and i.r. data are collected in Table 2. Before discussing the data as a whole, we direct attention to the results obtained for classes $[\{HB(pz)_3\}W(CO)_2(N_2Ar)]$ (II), $[\{HB(pz)_3\}Mo(CO)_2(N_2Ar)]$ (pz = pyrazol-1-yl) (IV), and $[(cp)Mo(CO)_2(N_2Ar)]$ (cp = η-cyclopentadienyl) (VI). ^{19}F N.m.r. spectra of these complexes were previously investigated by Trofimenko.[10] The results were inconclusive and cast doubts on the usefulness of the technique since the value of $(\delta_p - \delta_m)$ obtained seemed to depend on the conditions of measurement. Radically different results were obtained depending on whether an internal or external fluorobenzene standard was used. Having carefully reinvestigated the data using an external hexafluorobenzene reference, we conclude that Trofimenko's results are in error.

Table 1 summarises our data. Addition of fluorobenzene to acetone or CH_2Cl_2 solutions of *m*- or *p*-fluorobenzenediazo- (*m*- or *p*-FC_6H_4) derivatives of complexes (II) did produce shifts in the resonance positions of the fluorine atoms. However these shifts were small (*ca.* 0·46 p.p.m. maximum) and the effects on $(\delta_p - \delta_m)$ were still smaller (0·03—0·08 p.p.m.). Moreover our own data for complexes (II), (IV), and (VI) were in good agreement with those obtained by Trofimenko [10] using an *internal* fluorobenzene reference. The possibility of a specific interaction between the internal reference and substrate postulated by Trofimenko [10] may thus be discounted and the doubts he raised as to the validity of the technique dispelled. It is evident that Trofimenko's data with an *external* fluorobenzene reference are

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† In reporting ^{19}F chemical shifts we have used the sign convention suggested by Mooney,[9] *i.e.* signals which occur to higher frequency (lower field) of the reference are designated as positive in sign and *vice versa*. Where data have been quoted from the work of authors who adopted the opposite sign convention, signs have been corrected accordingly.

[1] Part VI, W. E. Carroll, F. A. Deeney, and F. J. Lalor, *J.C.S. Dalton*, 1974, 1430.

[2] (*a*) V. F. Duckworth, P. G. Douglas, R. Mason, and B. L. Shaw, *Chem. Comm.*, 1970, 1083; (*b*) G. Avitabile, P. Ganis, and M. Nemiroff, *Acta Cryst.*, 1971, **B27**, 725; (*c*) J. A. McArdle, A. J. Schultz, B. J. Corden, and R. Eisenberg, *Inorg. Chem.*, 1973, **12**, 1676; (*d*) B. L. Haymore and J. A. Ibers, unpublished work.

[3] A. P. Gaughan, jun., B. L. Haymore, J. A. Ibers, W. H. Myers, T. E. Nappier, jun., and D. W. Meek, *J. Amer. Chem. Soc.*, 1973, **95**, 6859.

[4] W. L. Bowden, W. F. Little, and T. J. Meyer, *J. Amer. Chem. Soc.*, 1973, **95**, 5084.

[5] B. L. Haymore, personal communication; B. L. Haymore and J. A. Ibers, *J. Amer. Chem. Soc.*, 1973, **95**, 3052.

[6] D. R. Fisher and D. Sutton, *Canad. J. Chem.*, 1973, **51**, 1697.

[7] W. E. Carroll and F. J. Lalor, *J.C.S. Dalton*, 1973, 1754.

[8] R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Anderson, and G. T. Davis, *J. Amer. Chem. Soc.*, 1963, **95**, 709.

[9] E. F. Mooney, 'An Introduction to ^{19}F N.m.r. Spectroscopy,' Heyden and Son Ltd., London, 1970, p. 2.

[10] S. Trofimenko, *Inorg. Chem.*, 1969, **8**, 2675.

anomalous, although it is not at all clear why this should be so.

Complexes [(cp)Mo(NO)(PPh_3)(N_2Ar)]$^+$, (XV), were insufficiently soluble in the solvent used (CH_2Cl_2) for their ^{19}F n.m.r. spectra to be measured under conditions directly comparable to the other complexes studied. [^{19}F N.m.r. spectra for these complexes were determined in *NN*-dimethylformamide (dmf), see below.] Data for complexes (I)—(XIII) are arranged in Table 2 in order of increasing ($\delta_p - \delta_m$), *i.e.* of decreasing relative shielding of the *p*-fluorine atom and hence of decreasing conjugative transfer of electron density from the metal atom along the ArN_2 chain. Of complexes (I) through (XIII), two, *i.e.* (IV)[2b] and [Fe(CO)$_2$(PPh_3)$_2$(N_2Ar)]$^+$ (XIII),[2d] are known to involve singly bent formal ArN_2^+ ligands. Similar structures may safely be inferred for all the other classes of complexes except (XIV), [PtCl(PEt_3)$_2$(N_2Ar)], which was included for reference purposes and is thought to involve a doubly bent formal ArN_2^- ligand.[3]

TABLE 1

Effect of solvent and reference on ^{19}F-resonance positions (p.p.m.)[a]

Complex	Solvent[a]	Reference	δ_p	δ_m	$(\delta_p - \delta_m)$	Source
(II)	CH_2Cl_2	C_6F_6 (ext.)	50·39	54·93	−4·54	*b*
	CH_2Cl_2 + C_6H_5F (int.)	C_6F_6 (ext.)	50·47	54·93	−4·46	*b*
	Me_2CO	C_6F_6 (ext.)	49·10	54·05	−4·95	*b*
	Me_2CO + C_6H_5F (int.)	C_6F_6 (ext.)	49·56	54·48	−4·92	*b*
	Me_2CO	C_6H_5F (int.)	−2·32	1·92	−4·24	*c*
	Me_2CO	C_5H_5F (ext.)	6·62	7·45	−0·83	*c*
(IV)	CH_2Cl_2	C_6F_6 (ext.)	51·72	55·30	−3·58	*b*
	Me_2CO	C_6H_5F (int.)	−1·13	2·30	−3·43	*c*
	Me_2CO	C_5H_5F (ext.)	7·90	7·86	0·04	*c*
(VI)	CH_2Cl_2	C_6F_6 (ext.)	53·04	55·24	−2·20	*b*
	Me_2CO	C_5H_5F (int.)	−0·39	2·20	−2·59	*c*
	Me_2CO	C_6H_5F (ext.)		7·75		*c*

[a] See Experimental section for conditions of measurement. [b] This work. [c] Ref. 10.

The sequence of ($\delta_p - \delta_m$) values is in excellent agreement with the ranking of $M\rightarrow N_2Ar$ π-bonding anticipated on the basis of the relative donor and acceptor power of the co-ligands and the formal oxidation state of the metal atom. Thus phosphine substitution of complexes (VI) or [(tpcp)Mo(CO)$_2$(N_2Ar)] (IX; tpcp = η-triphenylphosphoniocyclopentadienyl) results in a marked decrease in ($\delta_p - \delta_m$) reflecting the expected increase in π-bonding to the arenediazo-ligand. Again the similar values of ($\delta_p - \delta_m$) determined for complexes (VI) and [{HC(pz)$_3$}Mo(CO)$_2$(N_2Ar)]$^+$, (VII), indicate that the higher formal oxidation state in the latter is compensated for by the much greater electron-donor character of the tris(pyrazol-1-yl)methane ligand. It was somewhat unexpected to discover that $M\rightarrow N_2Ar$ π-bonding is more efficient in tungsten complexes (II) than in their molybdenum analogues, (IV). The more diffuse W 5*d* orbitals might have been expected to lead to the reverse trend. However a similar trend in π-bonding, W > Mo, has been determined for the hexacarbonyl complexes.[11] It may, however, be noted that the value of ($\delta_p - \delta_m$) for platinum complexes (XIV) suggests a similar degree of back bonding to the arenediazo-ligand as that which obtains in the cp molybdenum complexes, (VI). The probable differences in the mode of ArN_2 co-ordination render this unlikely. It appears therefore that the ^{19}F n.m.r. technique yields useful information on bonding trends within a particular structural group of ArN_2^+ complexes, but may not be used to compare the bonding in one structural group with that in another.

($\delta_p - \delta_m$) Values for the complexes [(cp)Mo(NO)Cl(N_2Ar)], (XII), and their tris(pyrazol-1-yl)borate analogues, (XI), show that the amount of back bonding to the ArN_2^+ ligand is almost identical for both. This may be compared with the data for complexes (IV) and (VI) which clearly demonstrate the greater overall electron-donor character of the tris(pyrazol-1-yl)borate ligand. It is evident that in the former pair of complexes the increased electron density on the metal atom on going from the cp to the HB(pz)$_3$ derivative is effectively absorbed by the NO^+ rather than the ArN_2^+ ligand, showing the former to be the more efficient π-acceptor. This conclusion was further reinforced by a separate experiment involving ^{19}F n.m.r. spectra obtained in dmf solution for the cations [(cp)Mo(PPh_3)(N_2Ph)($N_2C_6H_4F$)]$^+$, (X), and [(cp)Mo(PPh_3)(NO)($N_2C_6H_4F$)]$^+$, (XV) (see footnotes to Table 2). Here the ($\delta_p - \delta_m$) values clearly demonstrate that replacement of PhN_2^+ by NO^+ leads to withdrawal of π-electron density from the remaining arenediazo-ligand. This represents the first unambiguous evidence in favour of the suggestion previously made by us[1,7] that the π-acceptor character of the cation NO^+ is greater than that of ArN_2^+.

The results of the ^{15}N-labelling experiments are also collected in Table 2 and yield some puzzling results. Complexes (I)—(III), [Fe(NO)(CO)(PPh_3)(N_2Ar)] (VIII), (XIII), and (XIV) showed a single ν(NN) absorption shifted to lower wavenumber by an amount generally close to that predicted by theory. However the remaining nine classes showed *two* well separated (*ca.* 64—88 cm^{-1}) bands [three in the case of complexes (X) which, with two ArN_2^+ ligands, would be expected to show two ν(NN) bands], which were displaced to lower wavenumber by *ca.* 5—20 cm^{-1} on $^{15}N^{14}N$ substitution and which are therefore both associated with the ArN_2 chromophore. The only previous reports of multiple ν(NN) bands have concerned complexes involving the

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[11] D. R. Lloyd and E. W. Schlag, *Inorg. Chem.*, 1969, **8**, 2544.

TABLE 2

I.r. (cm^{-1}) and ^{19}F n.m.r. data (p.p.m.) for some aryldiazonium complexes [a]

Complex	Ar	Labelling	ν(NN)	Isotopic shift Found (calc.)	$\delta(^{19}F)$	$(\delta_p - \delta_m)$
$[(cp)Mo(CO)(PPh_3)(N_2Ar)]$ (I) [b]	Ph	$^{14}N^{14}N$	1 509s			
	Ph	$^{15}N^{14}N$	1 492s	17 (26)		
	m-FC_6H_4	$^{14}N^{14}N$	1 504s		53·88	
	p-FC_6H_4	$^{14}N^{14}N$	1 526s		48·86	−5·02
$[\{HB(pz)_3\}W(CO)_2(N_2Ar)]$ (II) [c]	Ph	$^{14}N^{14}N$	1 539s			
	Ph	$^{15}N^{14}N$	1 518s	21 (26)		
	m-FC_6H_4	$^{14}N^{14}N$	1 547s		54·93	
	p-FC_6H_4	$^{14}N^{14}N$	1 560s		50·39	−4·54
$[(tpcp)Mo(CO)(PPh_3)(N_2Ar)]$ (III) [d,e]	Ph	$^{14}N^{14}N$	1 527s			
	Ph	$^{15}N^{14}N$	1 505s	22 (26)		
	m-FC_6H_4	$^{14}N^{14}N$	1 530s		55·00	
	p-FC_6H_4	$^{14}N^{14}N$	1 543s		51·14	−3·86
$[\{HB(pz)_3\}Mo(CO)_2(N_2Ar)]$ (IV) [c]	Ph	$^{14}N^{14}N$	1 625m, 1 556s			
	Ph	$^{15}N^{14}N$	1 612w, 1 539s	13 (28), 17 (27)		
	m-FC_6H_4	$^{14}N^{14}N$	1 621w, 1 552s		55·30	
	p-FC_6H_4	$^{14}N^{14}N$	1 611m, 1 559s		51·72	−3·58
$[Mo(CO)_2OH(N_2Ar)]_4$ (V) [f]	Ph	$^{14}N^{14}N$	1 630m, 1 562s			
	Ph	$^{15}N^{14}N$	1 613m, 1 548s	17 (28), 14 (27)		
	m-FC_6H_4	$^{14}N^{14}N$	1 628m, 1 563s		55·72	
	p-FC_6H_4	$^{14}N^{14}N$	1 622s, 1 573s		52·85	−2·87
$[(cp)Mo(CO)_2(N_2Ar)]$ (VI) [b]	Ph	$^{14}N^{14}N$	1 620m, 1 549s			
	Ph	$^{15}N^{14}N$	1 605m, 1 529s	15 (28), 20 (27)		
	m-FC_6H_4	$^{14}N^{14}N$	1 622s, 1 551s		55·24	
	p-FC_6H_4	$^{14}N^{14}N$	1 613w, 1 564s		53·04	−2·20
$[\{HC(pz)_3\}Mo(CO)_2(N_2Ar)]^+$ (VII) [g]	Ph	$^{14}N^{14}N$ [h]	1 639s, 1 569s			
	Ph	$^{15}N^{14}N$ [h]	1 625m, 1 560s	14 (28), 9 (27)		
	m-FC_6H_4	$^{14}N^{14}N$ [e]	1 633m, 1 571s		56·66	
	p-FC_6H_4	$^{14}N^{14}N$ [e]	1 632s, 1 581m		54·55	−2·11
$[Fe(NO)(CO)(PPh_3)(N_2Ar)]$ (VIII) [i]	Ph	$^{14}N^{14}N$	1 664s			
	Ph	$^{15}N^{14}N$	1 641s	23 (28)		
	m-FC_6H_4	$^{14}N^{14}N$	1 658s		55·65	
	p-FC_6H_4	$^{14}N^{14}N$	1 658s		54·51	−1·14
$[(tpcp)Mo(CO)_2(N_2Ar)]^+$ (IX) [d]	Ph	$^{14}N^{14}N$ [e]	1 640s, 1 566s			
	Ph	$^{15}N^{14}N$ [e]	1 624m, 1 554s	16 (28), 12 (27)		
	m-FC_6H_4	$^{14}N^{14}N$ [h]	1 631m, 1 568s		54·37	
	p-FC_6H_4	$^{14}N^{14}N$ [h]	1 628s, 1 577m		56·23	−0·14
$[(cp)Mo(N_2Ph)(PPh_3)(N_2Ar)]^+$ (X) [e,j,k]	Ph	$^{14}N^{14}N$	1 655m, 1 621s, 1 547s			
	Ph	$^{15}N^{14}N$	1 645m, 1 612s, 1 536s	10 (28), 9 (28), 11 (27)		
	m-FC_6H_4	$^{14}N^{14}N$	1 651m, 1 622s, 1 546s		56·87[l]	
	p-FC_6H_4	$^{14}N^{14}N$	1 650m, 1 618s, 1 553s		58·09[l]	1·12[l]
$[\{HB(pz)_3\}Mo(NO)Cl(N_2Ar)]$ (XI) [m]	Ph	$^{14}N^{14}N$	1 642s, 1 573m			
	Ph	$^{15}N^{14}N$	1 627s, 1 563s	15 (28), 10 (27)		
	m-FC_6H_4	$^{14}N^{14}N$	1 641s, 1 580s		57·96	
	p-FC_6H_4	$^{14}N^{14}N$	1 641s, 1 572w		60·32	2·36
$[(cp)Mo(NO)Cl(N_2Ar)]$ (XII) [m]	Ph	$^{14}N^{14}N$	1 623s, 1 559m			
	Ph	$^{15}N^{14}N$	1 610s, 1 542m	13 (28), 17 (27)		
	m-FC_6H_4	$^{14}N^{14}N$	1 622s, 1 560s		57·33	
	p-FC_6H_4	$^{14}N^{14}N$	1 616s, 1 567m		59·74	2·41
$[Fe(CO)_2(PPh_3)_2(N_2Ar)]^+$ (XIII) [e,n]	Ph	$^{14}N^{14}N$	1 723s			
	Ph	$^{15}N^{14}N$	1 693s	30 (30)		
	m-FC_6H_4	$^{14}N^{14}N$	1 716s		56·36	
	p-FC_6H_4	$^{14}N^{14}N$	1 720s		61·15	4·79
$[PtCl(PEt_3)_2(N_2Ar)]$ (XIV) [o]	Ph	$^{14}N^{14}N$	1 440s [o]			
	m-FC_6H_4	$^{14}N^{14}N$	1 455s		53·56	
	p-FC_6H_4	$^{14}N^{14}N$	1 463s [o]		51·29	−2·27
	p-FC_6H_4	$^{15}N^{14}N$	1 440s [o]	23 (25)		
$[(cp)Mo(NO)(PPh_3)(N_2Ar)]^+$ (XV) [k]	Ph	$^{14}N^{14}N$	1 651s, 1 563m			
	Ph	$^{15}N^{14}N$	1 631s, 1 558m	20 (28), 5 (27)		
	m-FC_6H_4	$^{14}N^{14}N$	1 649s, 1 575s		*p*	
	p-FC_6H_4	$^{14}N^{14}N$	1 650s, 1 579w		*p*	*p*

cp = η-Cyclopentadienyl, pz = pyrazol-1-yl, and tpcp = η-triphenylphosphoniocyclopentadienyl.

[a] See Experimental section for conditions of measurement, *etc.* N.m.r. data for CH_2Cl_2 solutions unless stated otherwise. s = Strong, m = medium, and w = weak. [b] R. B. King and M. B. Bisnette, *Inorg. Chem.*, 1966, **5**, 300. [c] Ref. 10. [d] D. Cashman and F. J. Lalor, *J. Organometallic Chem.*, 1971, **32**, 351. [e] BF_4^- Salt. [f] F. J. Lalor and P. L. Pauson, *J. Organometallic Chem.*, 1970, **25**, C51. [g] S. Trofimenko, *J. Amer. Chem. Soc.*, 1970, **92**, 5118. [h] PF_6^- Salt. [i] W. E. Carroll and F. J. Lalor, *J. Organometallic Chem.*, 1973, **54**, C37. [j] W. E. Carroll, M. E. Deane, and F. J. Lalor, unpublished work. [k] The complex labelled with $^{15}N^{14}N$ groups in *both* arenediazo-groups showed two strong bands at 1 610 and 1 531 cm^{-1}. The medium-intensity peak, which appeared at 1 655 cm^{-1} in the unlabelled complex, was identifiable only as a shoulder (*ca.* 1 627 cm^{-1}) on the 1 610 cm^{-1} peak. [l] In dmf solution: $\delta_p = 56{\cdot}37$; $\delta_m = 55{\cdot}66$; and $(\delta_p - \delta_m) = 0{\cdot}71$ p.p.m. [m] M. Deane and F. L. Lalor, *J. Organometallic Chem.*, 1973, **57**, C61. [n] Ref. 7. [o] G. W. Parshall, *J. Amer. Chem. Soc.*, 1965, **87**, 2133; 1967, **89**, 1822. [p] In dmf solution: $\delta_p = 62{\cdot}50$; $\delta_m = 56{\cdot}67$; and $(\delta_p - \delta_m) = 5{\cdot}83$ p.p.m.

ArN_2^- co-ordination mode, where they were thought to arise from *cis–trans*-isomerism of the doubly bent structure, (B).[12] No such explanation is applicable to complexes involving structure (A). The presence of both singly and doubly bent isomers of the ArN_2 ligand, analogous to the linear and bent nitrosyl isomers[13] of the complexes $[CoCl_2(NO)L_2]$, seems improbable as it is doubtful whether the complexes could tolerate the 16-electron configuration which structure (B) would imply. Since all the data, excepting that for complexes (I), were obtained in solution, solid-state effects may be excluded. Neither is there any obvious relation between structure and the number of ν(NN) bands shown. Thus complexes (IV) showed two such bands but their tungsten analogues, (II), showed only one. Similarly, complexes (VI) and (IX) had two ν(NN) bands while their triphenylphosphine derivatives, $[(cp)Mo(CO)(PPh_3)(N_2Ar)]$ (I) and $[(tpcp)Mo(CO)(PPh_3)(N_2Ar)]$ (III), had only one. We note, however, that with but three exceptions, complexes (VII), (IX), and (X), one of the two ν(NN) bands remained strong on $^{15}N^{14}N$ or *m*- and *p*-fluoro-substitution while the other underwent major intensity changes. The most reasonable interpretation of the evidence involves assignment of the latter absorption to a ring skeletal vibration of the arenediazo-ligand which is relatively strongly coupled to the ν(NN) stretching vibration. The phenomenon is receiving further study.

Broadly speaking, a low degree of $M \rightarrow N_2Ar$ π-bonding [high positive values of $(\delta_p - \delta_m)$] corresponds to high values of ν(NN) and *vice versa*. There is, however, no evident systematic relation between $(\delta_p - \delta_m)$ and ν(NN). The shielding parameter $(\delta_p - \delta_m)$ is evidently a much more sensitive indicator of π-bonding effects than is ν(NN). The technique promises to be a very useful tool for studying these complexes and for assessing the overall bonding characteristics of various metal–co-ligand arrays. We are currently extending its use to a wider range of arenediazo-complexes.

EXPERIMENTAL

All starting materials and arenediazo-complexes were prepared by standard literature syntheses or by procedures recently developed in this laboratory which will be published shortly. Literature references are given in Table 2. Correct microanalytical data were obtained for all complexes studied.

I.r. spectra were obtained for *ca.* 2% solutions in CH_2Cl_2 except with complexes (I) for which thin-film spectra were recorded. No evidence was found for coupling of ν(NN) and ν(CO) stretching vibrations. In two cases, complexes (XII) and (XV), the ν(NO) absorptions, at 1 713 and 1 705 cm^{-1} respectively, were shifted by *ca.* 6 cm^{-1} to lower wavenumber on $^{15}N^{14}N$ substitution of the arenediazo-ligand indicating a slight coupling of ν(NN) and ν(NO). ^{19}F N.m.r. spectra were obtained with saturated solutions in CH_2Cl_2. A Perkin-Elmer–Hitachi R20A spectrometer with oscillator frequency of 56·456 MHz was used. Resonance positions were located using a Takeda–Aiken TR3824 frequency counter. All ^{19}F n.m.r. data are expressed in p.p.m. and are referred to external hexafluorobenzene. A negative value of $(\delta_p - \delta_m)$ indicates greater shielding for the *p*- than for the *m*-fluorine atom.

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[4/459 *Received, 8th March,* 1974]

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[12] K. R. Laing, S. D. Robinson, and M. F. Uttley, *J.C.S. Dalton,* 1973, 2713.

[13] C. P. Brock, J. P. Collman, G. Dolcetti, P. H. Farnham, J. A. Ibers, J. E. Lester, and C. A. Reed, *Inorg. Chem.*, 1973, **12**, 1304.