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TRANSITION METAL DERIVATIVES OF ARENE DIAZONIUM IONS

X *. FOUR-COORDINATE ARENEDIAZO DERIVATIVES OF IRON(—II) AND COBALT(—I)

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Summary

The first arenediazo derivatives of iron(—II), $Fe(N_2Ar)(NO)(CO)(PPh_3)$, have been synthesised and their properties are described. A linear relationship has been found between $\nu(CO)$ in these complexes and σ^- for the *para* substituent in the arenediazo aryl ring. The ^{57}Fe Mössbauer spectra of the complexes indicate that $[ArN_2]^+$ is a stronger σ-donor and weaker π-acceptor than $[NO]^+$. The relationship between ΔE_q and σ_p^- suggests that changes in ΔE_q with aryl substitution involve both substituent-specific and substituent-independent effects. The unstable cobalt(—I) compound $Co(N_2C_6H_5)(CO)_2(PPh_3)$, the first arenediazo derivative of cobalt, is also described.

Surprisingly few arenediazo complexes of first-row transition metals have been described in the literature. In the case of iron the only such complexes for which full details are available are two closely-related series of trigonal-bipyramidal derivatives of iron(0): $[Fe(N_2Ar)(CO)_2(PPh_3)_2]^+$ and $FeX(N_2Ar)(CO)(PPh_3)_2$, ($X = Cl, N_3$ etc.) [1—3]. We now report the preparation and characterisation of a third group of arenediazoiron complexes, neutral four-coordinate iron(—II) species of the type $Fe(N_2Ar)(NO)(CO)(PPh_3)$. A related complex of cobalt(—I), $Co(N_2Ar)(CO)_2(PPh_3)$, is also described. Some of the material in this communication has previously appeared in abbreviated form [4].

$$[Fe(NO)(CO)_3]^- \xrightarrow[\text{Acetone, }-70^\circ C]{[RC_6H_4N_2]^+} Fe(N_2C_6H_4R)(NO)(CO)_2$$

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* For part IX see ref. 17.

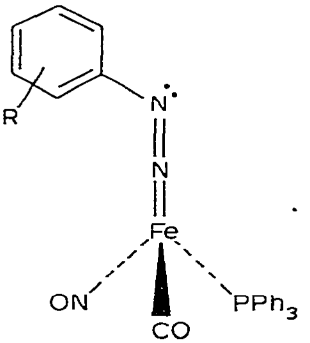
$$\mathrm{Fe(N_2C_6H_4R)(NO)(CO)_2} \xrightarrow[-70^\circ\mathrm{C}]{\mathrm{PPh_3}} \underset{(\mathrm{I})}{\mathrm{Fe(N_2C_6H_4R)(NO)(CO)(PPh_3)}}$$

(Ia, R = *p*-CH_3; Ib, R = *p*-CH_3CONH; Ic, R = H; Id, R = *p*-F; Ie, R = *p*-CF_3; If, R = *p*-CH_3CO; Ig, R = *p*-NO_2; Ih, R = *m*-F).

Addition of solid $[RC_6H_4N_2][BF_4]$ to yellow solutions of $[(Ph_3P)_2N]$-$[Fe(NO)(CO)_3]$ [5] in acetone at —70°C causes vigorous evolution of gas and the development of a deep red colour. The subsequent chemical behaviour of these red solutions leaves little doubt that they contain new arenediazo complexes of the type $Fe(N_2Ar)(NO)(CO)_2$, isoelectronic with the known [6] dinitrosyl $Fe(NO)_2(CO)_2$. Careful attempts to isolate the former species at —70°C were not successful and allowing the solutions to warm to room temperature resulted in total decomposition. If, however, one equivalent of triphenylphosphine is added to the solutions of $Fe(N_2Ar)(NO)(CO)_2$ at —70°C there is further evolution of gas and relatively stable arenediazo complexes of formula $Fe(N_2Ar)(NO)(CO)(PPh_3)$ (Ia—Ih) can be isolated in ca. 25—70% yield following warming to room temperature. Under similar conditions reaction of $Fe(N_2Ar)(NO)(CO)_2$ with $PhSCH_3$, CH_3SSCH_3 or $[(Ph_3P)_2N]X$ (X = Cl, CN) does not lead to any isolable organometallic complexes.

Complexes Ia—Ig are reddish-brown or purple microcrystalline solids which are moderately stable in the solid state although less so than the two previously-known groups of arenediazoiron complexes. Their solutions in nitrogen-saturated acetone or ether are also reasonably stable but the complexes are much less stable in chlorinated solvents, even in the absence of air. The IR spectra of the new complexes in cyclohexane (Table 1) show three strong bands at average positions of 1975, 1728 and 1657 cm^{-1}. The band at ca. 1657 cm^{-1} was identified as $\nu(NN)$ by the ^{15}N isotopic labelling technique [7]. By analogy with the IR spectrum of the isoelectronic complex $Fe(NO)_2(CO)(PPh_3)$ [8] the bands at ca. 1728 and ca. 1975 cm^{-1} were assigned to $\nu(NO)$ and $\nu(CO)$, respectively.

The ^1H NMR spectrum of complex Ia (Ar = $C_6H_4CH_3$-*p*) in acetone-d_6 (see Experimental) is in agreement with the proposed formulation and indicates that the complexes are diamagnetic. The ^{19}F NMR spectra of complexes Id and Ih [7] (Ar = C_6H_4F-*p* and C H_4F-*m*, respectively) demonstrate, as anticipated, that there is a greater degree of delocalisation of π-electron density from iron



(I)

to the arenediazo ligand in the iron(—II) complexes of type I than in the cationic iron(0) complexes $[Fe(N_2Ar)(CO)_2(PPh_3)_2]^+$. The relative positions of ν(NN) in the two groups of complexes (although, in general, not a reliable indicator of π-bonding effects) follow the trend indicated by the ^{19}F NMR studies [7].

Complexes Ia—Ih are most reasonably formulated as tetrahedrally-coordinated derivatives of iron(—II) in which the nitrosyl is linear and the arenediazo group is singly-bent (formal $[NO]^+$ and $[ArN_2]^+$, respectively) (see I). Structures with angular nitrosyl groups and/or a doubly-bent arenediazo ligand (formal $[NO]^-$ and $[ArN_2]^-$) would imply a coordinatively unsaturated iron atom, an improbable situation in view of the relative stability of the compounds concerned. Attempts to grow crystals of one of the new complexes which would be suitable for an X-ray crystallographic determination of the structure have not been successful so far although our efforts in this area are continuing.

Treatment of complexes Ia or Ic with an excess of PPh_3 in boiling 60—80° petroleum ether does not lead to further substitution. Formation of $Fe(N_2Ar)(NO)(PPh_3)_2$ is not observed and both reactants are recovered unchanged. Since $Fe(NO)_2(CO)(PPh_3)$ is readily converted into $Fe(NO)_2(PPh_3)_2$ under similar conditions [9] we conclude that the reduced π-acceptor capacity of $[ArN_2]^+$ vis-à-vis $[NO]^+$ (see below) is responsible for the relatively greater stabilisation of the carbonyl co-ligand in the arenediazo complexes.

Inspection of the IR data in Table 1 shows that the electronic effect of the substituent R in the coordinated $[p\text{-}RC_6H_4N_2]^+$ ligands is transmitted to the CO and $[NO]^+$ ligands via the $[p\text{-}RC_6H_4N_2Fe]$ structural unit. As R becomes progressively more electron-withdrawing, the energy of the C—O and N—O stretching vibrations is increased (reduced Fe → CO and Fe → $[NO]^+$ π-bonding) while that of the N—N stretching vibration is decreased (increased Fe → $[ArN_2]^+$ π-bonding). A plot of ν(CO) as a function of the substituent constant σ_p^- for R [10] reveals a good linear correlation with a correlation coefficient of 0.98 (Fig. 1). The correlation between σ_p^- and either ν(NO) or ν(NN) is markedly poorer (r = 0.89 and 0.79, respectively). This is hardly surprising since it is

TABLE 1

INFRARED [a] AND MÖSSBAUER [b] SPECTROSCOPIC DATA FOR THE COMPOUNDS $Fe(N_2C_6H_4R\text{-}p)(NO)(CO)(PPh_3)$

Compound	R	ν(CO) (cm^{-1})	ν(NO) (cm^{-1})	ν(NN) (cm^{-1})	S (mm s^{-1})	ΔE_q (mm s^{-1})
Ia	p-CH_3	1968	1724	1662	0.285 ± 0.001	1.273 ± 0.002
Ib	p-CH_3CONH	1969	1720	1658	0.279 ± 0.002	1.257 ± 0.004
Ic	p-H	1971	1727	1661	0.282 ± 0.001	1.188 ± 0.002
Id	p-F	1974	1728	1659	0.273 ± 0.001	1.262 ± 0.002
Ie	p-CF_3	1979	1731	1658	0.289 ± 0.004	1.191 ± 0.008
If	p-CH_3CO	1980	1731	1658	0.274 ± 0.001	1.178 ± 0.002
Ig	p-NO_2	1985	1737	1643	0.270 ± 0.002	1.001 ± 0.004
					0.268 ± 0.004	1.342 ± 0.008

[a] Cyclohexane solution. All absorptions are strong. [b] Measured at liquid nitrogen temperature and referred to the spectrum of sodium nitroprusside as standard.

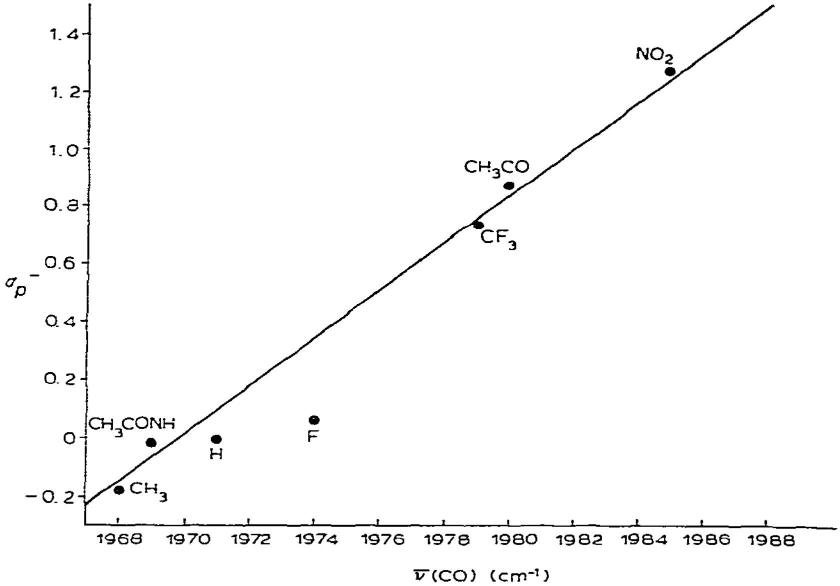


Fig. 1. Correlation between ν(CO) and σ_p^- for R in $Fe(N_2C_6H_5R\text{-}p)(NO)(CO)(PPh_3)$.

known that these parameters are relatively poor indicators of π-bonding effects.

The ^{57}Fe Mössbauer spectra of complexes Ia—Ig were recorded at liquid nitrogen temperature and the results are summarised in Table 1. With the exception of the *p*-nitro derivative, Ig, all the compounds studied give a simple doublet spectrum with an average quadrupole splitting parameter, ΔE_q, of ca. 1.225 mm s^{-1}. The spectrum of complex Ig is anomalous. Two doublets are

TABLE 2

MICROANALYTICAL DATA FOR COMPOUNDS Ia—Ih

Compound	Formula	Analysis (Found (calcd.) (%))		
		C	H	N
Ia	$C_{26}H_{22}FeN_3O_2P$	63.30 (63.05)	4.70 (4.45)	8.51 (8.49)
Ib	$C_{27}H_{23}FeN_4O_3P$	59.85 (60.24)	4.08 (4.28)	10.19 (10.41)
Ic	$C_{25}H_{21}FeN_3O_2P$	62.04 (62.40)	4.14 (4.16)	8.35 (8.73)
Id	$C_{25}H_{20}FFeN_3O_2P$	60.08 (60.14)	3.74 (3.81)	8.21 (8.42)
Ie	$C_{26}H_{19}F_3FeN_3O_2P$	56.37 (56.85)	3.21 (3.46)	7.27 (7.65)
If	$C_{27}H_{22}FeN_3O_3P$	61.71 (61.98)	4.05 (4.21)	7.90 (8.03)
Ig	$C_{25}H_{20}FeN_4O_4P$	57.00 (57.06)	3.95 (3.61)	10.16 (10.65)
Ih	$C_{25}H_{20}FFeN_3O_2P$	59.71 (60.14)	3.63 (3.81)	8.07 (8.42)

observed with similar isomer shifts (S = 0.270 ± 0.002 and 0.268 ± 0.004 mm s^{-1}) but with markedly different quadrupole splittings (ΔE_q = 1.001 ± 0.004 and 1.342 ± 0.008 mm s^{-1} respectively). The doublet with the smaller ΔE_q value is ca. three times more intense than that with the larger ΔE_q. The sample of Ig used was of analytical purity and there was no evidence for decomposition during the Mössbauer experiment itself. The presence of a pair of structural isomers with inequivalent iron atoms seem improbable and is not supported by the IR data quoted earlier. No obvious explanation for the phenomenon offers itself and consequently the data for complex Ig is excluded from the discussion which follows.

The values of the isomer shift parameter, S, for complexes Ia—If cover a range of 0.016 mm s^{-1} and are between 0.009 (Ie) and 0.025 mm s^{-1} (Id) smaller than the value of 0.298 mm s^{-1} reported [9] for the isoelectronic and, presumably, isostructural dinitrosyl complex $Fe(NO)_2(CO)(PPh_3)$. (Data from ref. 9 have been converted to refer to sodium nitroprusside standard). Hence, in the group of arenediazo complexes as a whole, the s-electron density at the iron nucleus, $\rho^{(0)}$, is greater than in the dinitrosyl to which they are formally related via replacement of an arenediazonium by a nitrosonium ligand. Just this effect would result if $[ArN_2]^+$ were a stronger σ-donor than $[NO]^+$. Alternatively, if $[ArN_2]^+$ were more efficient at removing d-electron density from the iron atom by a d_π—p_π process, the reduced d-orbital screening of the s-electrons would have a similar consequence. Elsewhere [7] we have produced evidence from the ^{19}F NMR spectra of m- and p-fluorobenzenediazo complexes which argues that $[ArN_2]^+$ is, in fact, a poorer π-acceptor than $[NO]^+$ and this conclusion now appears to have been generally accepted. (Further corroborative evidence on this point emerges from the discussion of the quadrupole splitting values of the present complexes, see below). We may conclude, therefore, that the isomer shift for complexes Ia—If demonstrates that $[ArN_2]^+$ is a stronger σ-donor than $[NO]^+$.

The quadrupole splitting parameters, ΔE_q, of complexes Ia—If are ca. 2.1—3.3 times larger than the value of 0.553 mm s^{-1} recorded by Mazak and Collins [9] for $Fe(NO)_2(CO)(PPh_3)$. Some of this increase in ΔE_q may be a result of structural distortion consequent upon the greater steric demand of $[ArN_2]^+$ compared to $[NO]^+$. However, the aryl ring, which accounts for most of the increased steric bulk of the $[ArN_2]^+$ ligand, is relatively remote from the iron atom and we are not inclined to believe that structural effects make a major contribution to the observed difference in ΔE_q. In support of this contention, we note that replacement of CO in $Fe(NO)_2(CO)(PPh_3)$ by the much more bulky PPh_3 ligand to give $Fe(NO)_2(PPh_3)_2$ increases ΔE_q by only a factor of 1.2 and some of this increase can be ascribed to the reduced π-acceptor capacity of PPh_3 vis-à-vis CO (see below) [9].

Cullen and his co-workers [11] have convincingly argued that for iron(—II) complexes the quadrupole splitting parameter, ΔE_q, decreases with increasing π-acceptor capacity of the attached ligands. The larger ΔE_q values observed for complexes Ia—If compared to their dinitrosyl analogue are thus in keeping with the relative π-acceptor strengths of $[NO]^+$ and $[ArN_2]^+$. In the —II oxidation state Fe has a formal d^{10} configuration. Since the spherically symmetrical d^{10} electron shell will make no intrinsic contribution to the electric field gradient at the nucleus, quadrupole splittings will arise only from the disposition and electronic character of the ligands surrounding the metal center. The σ-bonding skeleton of the complexes is constructed from iron 4*s* and 4*p* orbitals in approximately sp^3 hybridisation. Since iron 3*d* orbitals are not involved in the σ-skeleton σ-bonding effects will not directly effect the electric field gradient at the nucleus or quadrupole splitting. (Indirect effects may arise due to the synergistic relationship between metal—ligand σ- and π-bonding, see below). Thus the quadrupole splittings observed for iron(—II) complexes should be capable of being related in a fairly straightforward fashion to the π-acceptor capacity of the attached ligands. These factors, together with the IR data discussed earlier, led us to anticipate that there should be a relatively simple relationship between the σ_p^- substituent constant of R in $Fe(N_2C_6H_4R\text{-}p)(NO(CO)(PPh_3)$ (Id—If), the degree of π-bonding from the iron atom to the $[p\text{-}RC_6H_4N_2]^+$ ligand and the ^{57}Fe Mössbauer quadrupole splitting values.

Figure 2 presents a plot of ΔE_q for the complexes Ia—If as a function of σ_p^- for R. If all the data is included the correlation is poor (R = 0.75). However, if the unsubstituted complex (Ic, R = H) is excluded, the remaining points define an excellent straight line with a correlation coefficient of 0.99. This result, while unexpected, is not without precedent. In 1971 Dewar and his co-workers carried out an extensive statistical study of the relationship between ^{19}F substituent chemical shifts for a wide range of substituted fluoroarenes and the Hammett σ-constants of the substituents [12]. In almost all of the systems studied they noted that the data for the hydrogen substituent deviated significantly from the least-squares line defined by the data for other substituents. They attributed the phenomenon to "substituent-induced structural distortion", concluding that "the insertion of any substituent into a fluorinated aromatic produces a chemical shift merely by its presence, independent of any electronic effect". It appears that we are observing a similar,

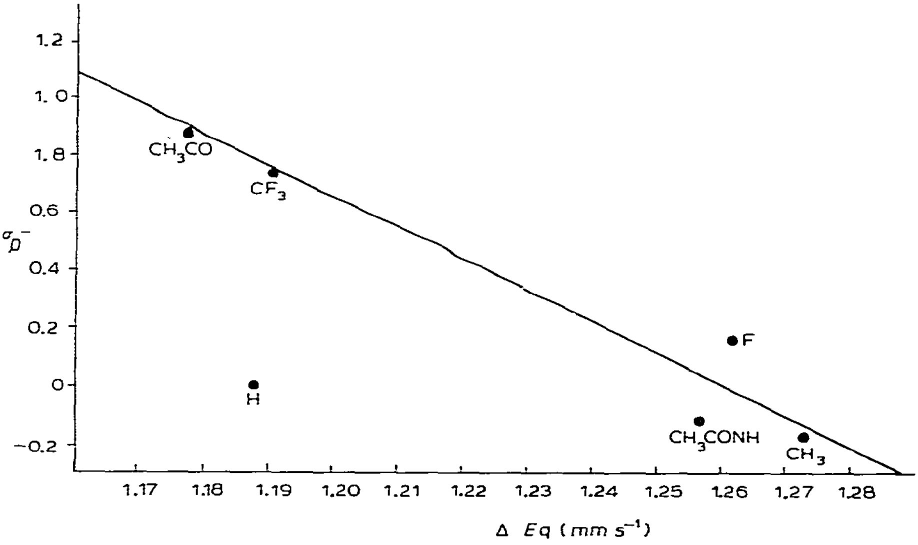


Fig. 2. Correlation between ΔE_q and σ_p^- for R in $Fe(N_2C_6H_4R\text{-}p)(NO)(CO)(PPh_3)$.

though not necessarily identical, effect in our quadrupole splitting data. Replacement of the arenediazo *p*-hydrogen atom by any substituent appears to produce a substituent-independent perturbation in the system which is transmitted to the iron atom together with the specific electronic effect characteristic of the individual substituent itself. Given the long-range nature of the effect it seems likely that the basic perturbation effect in our compounds is itself electronic in nature rather than the purely structural phenomenon envisaged by Dewar [12]. The linearity of the $\sigma_p^-/\Delta E_q$ correlation for substituents other than hydrogen implies that the magnitude of the perturbation effect is virtually independent of the nature of the substituent. Failure to observe a similar phenomenon in the $\sigma_p^-/\nu(CO)$ correlation discussed earlier is not surprising in view of the fact that the Mössbauer technique is much more sensitive to subtle electronic effects than is infrared spectroscopy.

In complexes of the type $Fe(N_2C_6H_4R\text{-}p)(NO)(CO)(PPh_3)$ an increase in the electron-withdrawing character of R should increase the π-acceptor capacity of the arenediazo ligand and, as the data in Table 1 and Fig. 2 demonstrate, this produces the expected decrease in ΔE_q. As mentioned earlier, the σ-donor and π-acceptor capacities of $[p\text{-}RC_6H_4N_2]^+$ are likely to be synergistically related rather than purely independent properties of the ligands. An increase in σ-donor strength should shorten and strengthen the $ArN_2 \rightarrow Fe$ σ-bond and this in turn should enhance $[Fe \rightarrow N_2Ar]$ $d_\pi \rightarrow p_\pi$ interaction and reinforce back-bonding to the ligand. A decrease in σ-donor strength will have the opposite effect. However, so far as the effect of an individual substituent R in $[p\text{-}RC_6H_4N_2]^+$ is concerned, the conjugative (π) and inductive (σ) effects of the substituent will have opposing effects on the net π-acceptor strength of the ligand. An electron-withdrawing substituent R will reduce σ-donation by an inductive mechanism, hence weakening π-bonding and increasing ΔE_q. However the effect of conjugative electron-withdrawal by R will be to reinforce π-bonding and decrease ΔE_q. Since ΔE_q is experimentally observed to decrease under these conditions we may conclude that the direct conjugative effect of the substituent on π-bonding to the arenediazo ligand substantially outweighs any indirect synergistic effect propagated via the σ-framework of the molecule. Finally we may note that the linear relationship between *S* and ΔE_q which we [13,14] and other workers [15] have observed for neutral [13,15] and cationic [14] five-coordinate derivatives of iron(0) does not hold for the four-coordinate iron(—II) complexes described here.

$$[Co(CO)_4]^- \xrightarrow[\text{(ii) } PPh_3,\ -50^\circ C]{\text{(i) } [C_6H_5N_2]^+,\ -70^\circ C} Co(N_2C_6H_5)(CO)_2(PPh_3)$$

Sequential treatment of $[(Ph_3P)_2N][Co(CO)_4]$ [16] with $[C_6H_5N_2][BF_4]$ and PPh_3 in acetone at —70°C followed by work-up at room temperature yields an unstable red oil. Although this material decomposes fairly rapidly it is sufficiently stable for its IR spectrum to be recorded in nitrogen-saturated cyclohexane solution. Two strong bands are observed in the carbonyl-stretching region (2010 and 1960 cm^{-1}) with a third strong band at 1689 cm^{-1}, Repetition of the experiment using $[C_6H_5{}^{14}N{}^{15}N]^+$ yields a product with unchanged carbonyl bands but causes a shift to 1661 cm^{-1} in the third band which is thus identified as $\nu(NN)$. Although meaningful microanalytical data could not be obtained for the product of this reaction the IR data strongly indicates that it is $Co(N_2C_6H_5)(CO)_2(PPh_3)$ (II) isoelectronic and isostructural with the iron complexes of type I. Attempts to enhance the stability of II By further substitution with triphenylphosphine or methyldiphenylphosphine were not successful.

Experimental

Microanalyses were performed by the staff of the Microanalytical Laboratory, Department of Chemistry, University College, Cork. Infrared spectra (calibrated with respect to a polystyrene film) were obtained on a Perkin—Elmer 257 spectrometer and ^1H NMR spectra on a Perkin—Elmer/Hitachi R20-A instrument. Details of the technique used for the ^{15}N labelling experiments have been published elsewhere [7]. Mössbauer spectra were determined using a drive unit, transducer and electronics supplied by Harwell Instruments in conjunction with a Nuclear Data ND4410 data analyser. The source was ^{58}Co in Pd and was of 50 mCi nominal strength. Absorbers of 0.05 g cm^{-1} thickness were made up in aluminium foil and were mounted in a Harwell Instruments top-loading cryostat. All spectra were run at liquid nitrogen temperature. The data output was in the form of punched paper tape from an ASR 33 teletype. After conversion to cards, the data was processed on an IBM 1130 computer using a non-linear least-squares curve-fitting programme. All data are referred to the spectrum of sodium nitroprusside as standard.

Preparation of the complexes $Fe(N_2Ar)(NO)(CO)(PPh_3)$ *(Ia—Ih)*

Since all the complexes were prepared in the same manner a single example only will be described. Solid $[C_6H_5N_2][BF_4]$ (0.38 g, 1.98 mmol) was added portionswise to a stirred solution of $[(Ph_3P)_2N][Fe(NO)(CO)_3]$ [5] (1.42 g, 2.00 mmol) in degassed acetone at —70°C under nitrogen. The solution was allowed to stir for 10 min and then triphenylphosphine (0.52 g, 1.98 mmol) was added and the mixture was allowed to warm slowly to room temperature. The solvent was removed in vacuo, the residue was extracted with nitrogen-saturated ether (ca. 50 ml) and the extracts were filtered under nitrogen. Nitrogen-saturated pentane (150 ml) was added to the filtrate and the solution (still under a nitrogen atmosphere) was cooled to —78°C for 1 h. Most of the solvent was then decanted and the remaining cold solution was rapidly filtered. Brownish-red crystalline $Fe(N_2C_6H_5)(NO)(CO)(PPh_3)$ (Ia) was obtained in 59% yield (0.56 g).

Microanalytical data for complexes Ia—Ih are in Table 2. The ^1H NMR spectrum of complex Ia, $Fe(N_2C_6H_4CH_3\text{-}p)(NO)(CO)(PPh_3)$, in acetone-$d_6$ (internal tetramethylsilane reference) showed a complex multiplet at ca. τ 2.58 (19 protons, PPh_3 ligand and aromatic protons of the p-toluenediazo ligand) and a singlet at τ 7.65 (3 protons, methyl group of p-toluenediazo ligand).

Preparation of $Co(N_2C_6H_5)(CO)_2(PPh_3)$ *(II)*

Solid $[C_6H_5N_2][BF_4]$ (0.096 g, 0.49 mmol) was added portionswise to a solution of $[(Ph_3P)_2N][Co(CO)_4]$ [16] in degassed acetone (15 ml) under nitrogen at —70°C. When gas evolution had ceased the solution was allowed to warm to —50°C and 0.13 g of triphenylphosphine (0.49 mmol) was added, following which the solution was allowed to warm slowly to room temperature and worked-up as for the iron complexes Ia—Ih to yield a red oil which could not be induced to crystallise. The infrared spectrum of the product (see text) was determined by solution in nitrogen-saturated cyclohexane and transfer by means of a syringe to a nitrogen-flushed infrared cell.

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References

1 W.E. Carroll and F.J. Lalor, J. Chem. Soc. Dalton, (1973) 1754.
2 D.R. Fisher and D. Sutton, Canad. J. Chem., 51 (1973) 1697.
3 W.E. Carroll, F.A. Deeney and F.J. Lalor, J. Chem. Soc. Dalton, (1974) 1430.
4 W.E. Carroll,and F.J. Lalor, J. Organometal. Chem., 54 (1973) C37.
5 N.G. Connelly and C. Gardener, J. Chem. Soc. Dalton, (1976) 1525.
6 J.S. Anderson and W. Hieber, Z. Anorg. Allgem. Chem., 208 (1932) 238.
7 W.E. Carroll, M.E. Deane and F.J. Lalor, J. Chem. Soc. Dalton, (1974) 1837.
8 W. Beck and K. Lottes, Ber., 98 (1965) 2657.
9 R.A. Mazak and R.L. Collins, J. Chem. Phys., 51 (1969) 3220.
10 K.B. Wiberg, Physical Organic Chemistry, John Wiley and Sons, New York, 1964, 410—411 and ref. therein.
11 J.P. Crow, W.R. Cullen, F.G. Herring, J.R. Sams and R.L. Tapping, Inorg. Chem., 10 (1971) 1616.
12 M.J.S. Dewar, R. Golden and J.M. Harris, J. Amer. Chem. Soc., 93 (1971) 4187.
13 W.E. Carroll, F.A. Deeney, J.A. Delaney and F.J. Lalor, J. Chem. Soc. Dalton, (1973) 718.
14 W.E. Carroll, F.A. Deeney and F.J. Lalor, unpublished work.
15 M. Herberhold, K. Leonhard, U. Wagner, F.E. Wagner and J. Danon, J. Chem. Soc. Dalton, (1978) 654 and ref. therein.
16 J.K. Ruff and W.J. Schlientz, Inorg. Synth., 15 (1974) 84.
17 D. Condon, G. Ferguson, F.J. Lalor and M. Khan, Inorg. Chem., submitted.