Transition-metal Derivatives of Arenediazonium Ions. Part VI.[†] Ligand-substitution Reactions of Some Iron(I) Arenediazo- and Nitrosyl Cations

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The benzenediazo-cations $[(PhN_2)Fe(CO)_2L_2]^+$ (L = PPh$_3$, PMePh$_2$, or PMe$_2$Ph), unlike their nitrosyl analogues, are almost inert to substitution of a carbonyl group by excess of ligand L. Only where L = P{(OCH$_2$)$_3$CMe} has formation of a trisubstituted cation been detected. Both the ions $[(p\text{-}MeC_6H_4N_2)Fe(CO)_2(PPh_3)_2]^+$ and $[(NO)Fe(CO)_2(PPh_3)_2]^+$ react smoothly with $(Ph_3P{=}N{=}PPh_3)^+X^-$ (X = Cl or Br) to give new complexes $[(p\text{-}MeC_6H_4N_2)Fe(CO)(PPh_3)_2X]$ and $[(NO)Fe(CO)(PPh_3)_2X]$ respectively. The corresponding azide salt reacts with the p-toluenediazo-cation to yield only $[(p\text{-}MeC_6H_4N_2)Fe(CO)(PPh_3)_2N_3]$. With the nitrosyl analogue, this reaction gives both $[(NO)Fe(CO)(PPh_3)_2N_3]$ and $[(NO)Fe(CO)(PPh_3)_2NCO]$. These results are interpreted in terms of the ArN_2^+ ligand being a poorer π-acceptor than the NO^+ group.

THE reactivity of some recently reported[1-3] arenediazo-cations $[(ArN_2)Fe(CO)_2L_2]^+$ [Ar = Ph : L = PPh$_3$, PMePh$_2$, PMe$_2$Ph, or P{(OCH$_2$)$_3$CMe}; Ar = p-MeC$_6$H$_4$: L = PPh$_3$] has now been investigated. Since isoelectronic and isostructural nitrosyl complexes are known,[4,5] this permits a comparison to be made between the chemical effect of the closely related PhN_2^+ and NO^+ ligands.

RESULTS AND DISCUSSION

Reactions with Neutral Nucleophiles.—Johnson and Segal[5] have described the reactions of the ions $[(NO)Fe(CO)_2L_2]^+$ with excess of ligand L. Small ligands [L = P(OMe)$_3$, PMePh$_2$, or PMe$_2$Ph] displace carbon monoxide as in equation (1). This reaction does not proceed for

$$[(NO)Fe(CO)_2L_2]^+ + L \xrightarrow[25-40\ ^\circ C]{CH_2Cl_2} [(NO)Fe(CO)L_3]^+ + CO \quad (1)$$

more bulky ligands [PPh$_3$, P(OPh)$_3$, *etc.*]. The benzenediazo-cations are much less susceptible to attack. As expected, no reaction took place between the ion $[(PhN_2)Fe(CO)_2(PPh_3)_2]^+$ and excess of PPh$_3$. More surprisingly, the cations $[(PhN_2)Fe(CO)_2(PMePh_2)_2]^+$ and $[(PhN_2)Fe(CO)_2(PMe_2Ph)_2]^+$ were inert to an excess of the appropriate phosphine ligand under the conditions employed by Johnson and Segal.[5] Only in the case where L was the cage phosphite 4-methyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane (mtpb), and using more vigorous conditions [boiling tetrahydrofuran (thf)], could formation of a trisubstituted cation, $[(PhN_2)Fe(CO)(mtpb)_3]^+$, be detected. The product could not be induced to crystallise. Although its i.r. spectrum (Table 1) indicated it to be pure, satisfactory microanalytical data were not obtained. Treatment of the cation $[(PhN_2)Fe(CO)_2(PPh_3)_2]^+$ with excess of Me$_2$S or Me$_2$S$_2$ in boiling thf did not displace CO.

TABLE 1

Analytical (%) [a] and i.r. data (cm^{-1}) [b] for salts of the type $[(Z{\equiv}N)Fe(CO)_nL_{4-n}]X$

Z	L	*n*	X	C	H	N	ν(CO)	ν(NN) or ν(NO)
PhN	PMePh$_2$	2	BF$_4$	57·8 (58·0)	4·2 (4·4)	3·8 (4·0)	2 028, 1 975	1 723
PhN	PMe$_2$Ph	2	PF$_6$	44·6 (45·1)	4·4 (4·2)	4·4 (4·4)	2 021, 1 970	1 710
PhN	mtpb [c]	2	BF$_4$	35·5 (36·0)	3·8 (3·9)	4·7 (4·7)	2 072, 2 018	1 768
PhN	mtpb [c]	2	BF$_4$				2 008	1 734
p-MeC$_6$H$_4$N	PPh$_3$	2	BF$_4$	64·4 (64·1)	4·8 (4·4)	3·0 (3·3)	2 026, 1 972	1 724
PhN	PPh$_3$	2	I	60·6 (60·8)	4·2 (4·1)	3·2 (3·2)	2 028, 1 975	1 723
O	PPh$_3$	2	I	58·0 (57·5)	4·0 (3·8)	1·6 (1·8)	2 051, 1 995	1 792

[a] Calculated values in parentheses. [b] Determined in CH$_2$Cl$_2$ solution. [c] mtpb = 4-Methyl-2,6,7-trioxa-1-phosphabicyclo-[2.2.2]octane.

The reduction in susceptibility to CO displacement on going from the ion $[(NO)Fe(CO)_2L_2]^+$ to $[(PhN_2)Fe(CO)_2L_2]^+$ might reflect the greater steric bulk of the PhN_2^+ ligand. We consider this to be improbable as the greatest bulk of the ligand is concentrated at some distance from the iron nucleus and should not hinder rearward attack by the nucleophile. We prefer to regard the phenomenon as being due to reduced π-acceptor character for the ion PhN_2^+ compared with NO^+. I.r.[2,3]

[†] Part V, M. E. Deane and F. J. Lalor, *J. Organometallic Chem.*, 1974, **67**, C19.

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

[2] W. E. Carroll and F. J. Lalor, *J. Organometallic Chem.*, 1973, **54**, C37.

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

[4] G. R. Crooks and B. F. G. Johnson, *J. Chem. Soc.* (*A*), 1968, 1238.

[5] B. F. G. Johnson and J. A. Segal, *J.C.S. Dalton*, 1972, 1268.

and Mössbauer[6] spectroscopic data for comparable sets of PhN_2^+ and NO^+ complexes have already suggested that the latter ligand is the more powerful π-acceptor of the two. This, in turn, would imply stronger and less labile Fe–CO bonds in the benzenediazo-complex. That the ion $[(PhN_2)Fe(CO)_2(mtpb)_2]^+$ undergoes further substitution by mtpb may thus not reflect the small steric demand of the ligand but be due to labilising of a CO group consequent on increased π-acceptor character of the phosphite compared to the other ligands studied.

Reactions with Anionic Nucleophiles.—Although the cation $[(p\text{-}MeC_6H_4N_2)Fe(CO)_2(PPh_3)_2]^+$ (as its BF_4^- salt) and the complex $[(NO)Fe(CO)_2(PPh_3)_2]PF_6$ reacted rapidly with alkali-metal or tetra-alkylammonium salts of chloride, bromide, or azide ions only intractable products were formed. In contrast, bis(triphenylphosphine)iminium, $Ph_3P{=}\overset{+}{N}{=}PPh_3$, salts of these anions cleanly displaced a CO group from the *p*-toluenediazo-cation to give a new class of neutral five-co-ordinate complexes $[(p\text{-}MeC_6H_4N_2)Fe(CO)(PPh_3)_2X]$ (X = Cl, Br, or N_3). Sodium iodide converted the parent *p*-toluenediazo-complex into the corresponding iodide salt but no further reaction ensued.

TABLE 2

Analytical (%),[a] i.r. (cm^{-1}),[b] and Mössbauer data ($mm\ s^{-1}$)[c] for complexes of the type $[(Z{\equiv}N)Fe(CO)(PPh_3)_2X]$

Z	X	C	H	N	ν (CO)	ν (NO) or ν (NN)	Other bands	δ	$\lvert\Delta E_q\rvert$
$p\text{-}MeC_6H_4N$	Cl[d]	69·1 (69·2)	4·9 (4·9)	3·6 (3·7)	1 903s	1 640m		0·339 ± 0·003	0·746 ± 0·006
$p\text{-}MeC_6H_4N$	Br	65·45 (65·9)	4·6 (4·2)	3·5 (3·0)	1 903s	1 640m			
$p\text{-}MeC_6H_4N$	N_3	69·0 (68·6)	4·9 (4·8)	8·9 (9·1)	1 905s	1 639s[e]	ν_{asym} (N_3) 2 050s	0·325 ± 0·001	0·778 ± 0·002
O	Cl[f]	65·7 (65·9)	4·7 (4·5)	2·1 (2·1)	1 922s	1 690s		0·319 ± 0·003	1·57 ± 0·006
O	Br	61·3 (61·8)	4·2 (4·2)	1·7 (1·95)	1 922s	1 690s			
O	I				1 925s	1 693s			
O	N_3				1 923s	1 680s[g]	ν_{asym} (N_3) 2 050s	0·296 ± 0·005	1·878 ± 0·001
O	NCO				1 923s	1 669s[g]	ν_{asym} (NCO) 2 222s	0·296 ± 0·005	1·433 ± 0·008

[a] Calculated values in parentheses. [b] CH_2Cl_2 Solution; s = strong, m = medium. [c] Determined at liquid N_2 temperature and referred to trisodium pentacyanonitrosylferrate(II) standard at room temperature. [d] Cl 4·9 (4·65%). [e] $\nu(^{14}N^{15}N)$ 1 621 cm^{-1}. [f] Cl 5·0 (5·3%). [g] Assignment to azide or isocyanate complex not certain.

The new *p*-toluenediazo-complexes are red or brown crystalline solids which appear to be indefinitely stable in the air. All showed a single ν(CO) and ν(NN) absorption, the latter being identified by observation of the expected isotopic shift in $[(p\text{-}MeC_6H_4{}^{14}N^{15}N)Fe(CO)(PPh_3)_2N_3]$ (see Table 2). Both absorptions occurred at considerably lower wavelength than in the parent cation. ^{57}Fe Mössbauer isomer shifts of the chloro- and azido-complexes lay at more positive velocities than for $[(p\text{-}MeC_6H_4N_2)Fe(CO)_2(PPh_3)_2]^+$.[1-3,6] Thus replacement of CO by Cl^- or N_3^- ion causes a net decrease in the total *s*-electron density at the iron nucleus. This may be due to radial expansion of the *s* orbitals resulting from the decrease in overall charge on the complex or to decrease in *d* shielding at the nucleus following replacement of CO by the (at most) weakly π-accepting N_3^- or Cl^- ion. Quadrupole splittings for the neutral complexes, while remarkably small, were within the range documented[6] for complexes of known trigonal-bipyramidal geometry. The available spectroscopic information does not allow a choice to be made between trigonal-bipyramidal and square-pyramidal geometries for the new complexes. Pending a full structural determination, the former alternative seems the more probable.

The cation $[(NO)Fe(CO)_2(PPh_3)_2]^+$ reacted with the salts $(Ph_3P{=}\overset{+}{N}{=}PPh_3)\text{-}Cl^-$ and $\text{-}Br^-$ to give new neutral five-co-ordinate complexes $[(NO)Fe(CO)(PPh_3)_2X]$ (X = Cl or Br). The initial products of the reactions are probably the salts $[(NO)Fe(CO)_2(PPh_3)_2]X$ (X = Cl or Br). The latter have been isolated by Crooks and Johnson[4] from the reaction of NOCl or NOBr with the complex $[Fe(CO)_3(PPh_3)_2]$ and described as unstable unpurifiable solids. The nature of the decomposition products, presumably the neutral nitrosyl complexes reported in the present work, was not ascertained. I.r. spectra of the new nitrosyls are similar to those of the related *p*-toluenediazo-complexes and of $[(NO)Fe(CO)(PPh_3)_2X]$ ($X = CF_3CO$,[7] C_2F_5CO,[7] or MeOCO[5]), the only previously known complexes of this type. Reaction of the nitrosyl cation with NaI gave initially the known iodide salt[4] which was very slowly converted to neutral $[(NO)Fe(CO)(PPh_3)_2I]$. The latter could not be isolated in completely pure form.

Reaction of the ion $[(NO)Fe(CO)_2(PPh_3)_2]^+$ with $(Ph_3P{=}\overset{+}{N}{=}PPh_3)N_3^-$ followed a more complicated pattern. Two neutral products were formed which could not be readily separated. Both components were identified on the basis of the i.r. and Mössbauer spectrum of the mixture. The i.r. spectrum showed a single ν(CO) band but two ν(NO) peaks. Absorptions typical of both the co-ordinated azide[8] and isocyanate[8] ligands were also observed. This suggests that azide ion attacks the nitrosyl cation both at the central Fe atom and the carbon atom of a CO group. The latter reaction is

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[6] W. E. Carroll, F. A. Deeney, and F. J. Lalor, unpublished work.

[7] W. Hieber, W. Klingshirn, and W. Beck, *Chem. Ber.*, 1965, **98**, 307.

[8] K. R. Laing and W. R. Roper, *J. Chem. Soc.* (*A*), 1970, 2149.

known[9] to transform co-ordinated CO into co-ordinated NCO. The mixture gave a four-line Mössbauer spectrum in which can be recognised two quadrupole doublets of differing intensity and quadrupole splitting but having identical isomer shifts. Of the two observed doublets one had a splitting greater than that observed for $[(NO)Fe(CO)(PPh_3)_2Cl]$, while the splitting of the second doublet was smaller than that of the latter complex. In the related series of *p*-toluenediazo-complexes, $[(p\text{-}MeC_6H_4N_2)Fe(CO)(PPh_3)_2N_3]$ had a greater quadrupole splitting than $[(p\text{-}MeC_6H_4N_2)Fe(CO)(PPh_3)_2Cl]$. The doublet of greater quadrupole splitting in the N_3^-–NCO mixture thus may be assigned to the complex $[(NO)Fe(CO)(PPh_3)_2N_3]$ and the second doublet to $[(NO)Fe(CO)(PPh_3)_2NCO]$. On the basis of the relative intensities of the two doublets, the isocyanate complex predominated in the mixture by a factor of *ca.* 2·5 : 1·0.

Methoxide ion is reported to attack $[(NO)Fe(CO)_2(PPh_3)_2]^+$ at a carbonyl carbon atom to give a neutral methoxycarbonyl complex $[(NO)Fe(CO)(PPh_3)_2(CO{\cdot}OMe)]$.[5] The analogous reaction with the ion $[(p\text{-}MeC_6H_4N_2)Fe(CO)_2(PPh_3)_2]^+$ did not give $[(p\text{-}MeC_6H_4N_2)Fe(CO)(PPh_3)_2(CO{\cdot}OMe)]$. Instead an orange, unstable, nitrogen-free solid resulted. Although the material could not be fully purified, microanalytical, i.r., and Mössbauer data were consistent with its formulation as the known[10] complex $[Fe(CO)_2(PPh_2)_3]$. When the reaction was carried out under an atmosphere of CO the only isolable product was $[Fe(CO)_3(PPh_3)_2]$. The mechanism of the process is obscure but, by analogy with reactions of the *p*-toluenediazo-cation discussed above, may involve initial attack by MeO^- at the central iron atom followed by decomposition of the intermediate to $[Fe(CO)_2(PPh_3)_2]$. This co-ordinatively unsaturated fragment is known[10] to be a precursor of the complex $[Fe(CO)_2(PPh_3)_3]$ and would be expected to react readily with CO to give $[Fe(CO)_3(PPh_3)_2]$.

The evident tendency of the ion $[(NO)Fe(CO)_2(PPh_3)_2]^+$ to be attacked by suitable nucleophiles at a carbonyl carbon atom while $[(p\text{-}MeC_6H_4N_2)Fe(CO)_2(PPh_3)_2]^+$ is attacked at the iron nucleus * is further evidence in support of the suggestion put forward above that NO^+ is a stronger π-acceptor ligand than ArN_2^+. Greater delocalisation of electron density from the metal atom on to the NO^+ ligand would imply greater relative partial positive charge on the CO carbon atoms in the NO^+ complex than in its ArN_2^+ analogue. Hence the greater tendency of the former complex to undergo preferential attack at a carbonyl carbon atom.†

EXPERIMENTAL

Aromatic amines were available commercially and were converted to diazonium salts by conventional procedures.[11] Phosphine ligands were commercial samples and literature procedures[12] were used to convert these into the corresponding $[L_2Fe(CO)_3]$ complexes. Sodium nitrite ^{15}N (99%) was purchased from Stohler Isotope Chemicals, Berne, Switzerland, and was used for preparation of the salt $(p\text{-}MeC_6H_4{}^{14}N^{15}N)BF_4$. The $Ph_3P{=}\overset{+}{N}{=}PPh_3$ salts were prepared by the procedure of Ruff.[13] Procedures used for synthesis of $[(NO)Fe(CO)_2(PPh_3)_2]^+$ and $[(ArN_2)Fe(CO)_2L_2]^+$ salts have been described previously.[1–5] All preparations were carried out under an atmosphere of dry oxygen-free nitrogen.

I.r. spectra were recorded on a Perkin-Elmer 257 spectrophotometer. Mössbauer spectra were determined at liquid-nitrogen temperatures using a commercial drive unit, transducer, and associated electronics (supplied by Harwell Instruments) in conjunction with a Nuclear Data ND441 Analyser and Harwell Instruments top-loading nitrogen cryostat. Details of the source, preparation of absorbers, and treatment of raw data have been published elsewhere.[14]

*Preparation of (Benzenediazo)carbonyltris{4-methyl-*2,6,7-*trioxa-*1-*phosphabicyclo*[2.2.2]*octane}iron*(I) *Tetrafluoroborate.*—A mixture of the salt $[(PhN_2)Fe(CO)_2(mtpb)_2]BF_4$ (200 mg) and mtpb (70 mg) was heated under reflux in dry thf for 10 min, the mixture cooled, and the solvent removed *in vacuo*. An orange oil resulted which could not be induced to crystallise. The i.r. spectrum (Table 1) showed single ν(CO) and ν(NN) bands only, with no evidence for the presence of unreacted starting material.

Reactions.—*Dicarbonyl*(p-*toluenediazo*)*bis*(*triphenylphosphine*)*iron*(I) *tetrafluoroborate with* $Ph_3P{=}\overset{+}{N}{=}PPh_3$ *salts or* NaI. The complex (1·0 g) was dissolved in acetone (*ca.* 12 cm³) and a slight excess of the appropriate $Ph_3P{=}\overset{+}{N}{=}PPh_3$ salt or NaI was added. Gas evolution was immediate and the solution became brown. The mixture was stirred for 1 h during which a precipitate was deposited. This was removed by filtration, washed with a little acetone, and vacuum dried. The brown crystalline *products* were iso-

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* In the case of the reaction with MeO^- we cannot exclude initial attack at the ArN_2 ligand to give a σ-bonded complex of a diazomethoxide ligand, ArN_2OMe, which subsequently acts as precursor of $[Fe(CO)_2(PPh_3)_2]$. Such a possibility would imply greater relative position charge on co-ordinated ArN_2^+ than on co-ordinated NO^+, in keeping with the ideas expressed above.

† *Note added at proof:* A recent report (G. Dolcetti, L. Busetto, and A. Palazzi, *Inorg. Chem.*, 1974, **13**, 222) describes the reactions of the ion $[(NO)Fe(CO)_2(PPh_3)_2]^+$ with LiX (X = Cl, Br, or I) and NaX (X = N_3, NCO, *etc.*) in aqueous acetone. Several important differences from the present work are evident. No neutral products were isolated from the reactions with halide ions. More significantly, the reaction with NaN_3 was reported to lead exclusively to the complex $[(NO)Fe(CO)(PPh_3)_2N_3]$. Attempts to reproduce these results in our laboratories (L. Brookes, W. E. Carroll, and F. J. Lalor, unpublished work) were hindered by the ambiguous nature of the experimental details, differently described in the text and Experimental section, and by various other inaccuracies. We found that any possible interpretation of the experimental details of Dolcetti *et al.* always led to a product containing significant quantities of $[(NO)Fe(CO)(PPh_3)_2NCO]$, although the amount formed was indeed rather less than under our conditions. Several attempts to reproduce Dolcetti's reaction with NaNCO produced only decomposition products. The complex $[(NO)Fe(CO)(PPh_3)_2NCO]$ was successfully synthesised from $(Ph_3P{=}\overset{+}{N}{=}PPh_3)NCO^-$ using our procedure and was confirmed by i.r. spectroscopy to be identical with the second product of the reaction with azide ion described in the present paper and with the product described by Dolcetti. Differences between the i.r. spectra reported in the two papers are due to medium effects.

[9] Z. Dori and R. F. Ziolo, *Chem. Rev.*, 1973, **73**, 247.

[10] W. Hieber and J. Muschi, *Chem. Ber.*, 1965, **98**, 3931.

[11] A. Roe, *Org. Reactions*, 1949, **5**, 193.

[12] T. A. Manuel, *Inorg. Chem.*, 1963, **2**, 854.

[13] J. K. Ruff, personal communication.

[14] W. E. Carroll, F. A. Deeney, J. A. Delaney, and F. J. Lalor, *J.C.S. Dalton*, 1973, 718.

lated in *ca.* 80% yield. In the case of the reaction with $(Ph_3P=\overset{+}{N}=PPh_3)N_3^-$ the filtrate from the crude reaction mixture was shown to contain neutral azide complex only, with no evidence for formation of the corresponding isocyanate complex. The isotopically labelled azide complex was prepared by a similar procedure from $[(p\text{-}MeC_6H_4{}^{14}N^{15}N)Fe(CO)_2(PPh_3)_2]BF_4$.

Dicarbonyl(nitrosyl)bis(triphenylphosphine)iron(I) *hexafluorophosphate with* $Ph_3P=\overset{+}{N}=PPh_3$ *salts or* NaI. The procedure followed was essentially that described above. In the case of reaction with NaI the initial product was the iodide salt (see Table 1). If this was not isolated and stirring was continued for a further 2 h the characteristic spectrum of the salt began to disappear and new bands corresponding to formation of the neutral iodo-complex were observed (Table 2). The latter could not be obtained in a pure state.

Dicarbonyl(p-*toluenediazo*)*bis*(*triphenylphosphine*)*iron*(I) *tetrafluoroborate with methoxide ion.* (a) The complex (810 mg) in absolute methanol (60 cm^3) was treated with a solution of sodium (360 mg) in absolute methanol (60 cm^3). The solution was stirred for 1 h and the resulting orange precipitate (380 mg) collected by filtration, washed with methanol, and dried *in vacuo*. The ^1H n.m.r. spectrum ($[^2H_6]Me_2CO$) showed no methyl resonances. The i.r. spectrum (Nujol mull) had ν(CO) at 1 888 and 1 824 cm^{-1} {Hieber [10] reports 1 894 and 1 841 cm^{-1} for the complex $[Fe(CO)_2(PPh_3)_3]$ in thf solution}. The Mössbauer spectrum at liquid N_2 temperature showed a single quadrupole doublet centred on δ 0·313 mm s^{-1} with $|\Delta E_q|$ 2·455 mm s^{-1} [Found: (crude sample) C, 72·9; H, 5·25; N, 0·00. Calc. for $C_{56}H_{45}FeO_2P_3$: C, 78·4; H, 5·05; N, 0·00%]. The complex decomposed on attempted recrystallisation.

(b) The procedure above was repeated with CO bubbling through the reaction mixture. After 1·5 h the yellow precipitate of $[Fe(CO)_3(PPh_3)_2]$ (300 mg, 45%) was removed by filtration and dried *in vacuo*. The i.r. spectrum of the solid was identical to that of an authentic sample of $[Fe(CO)_3(PPh_3)_2]$. An analytical sample was obtained from dichloromethane–hexane (Found: C, 70·0; H, 4·4. Calc. for $C_{39}H_{30}FeO_3P_2$: C, 70·5; H, 4·5%).

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