Transition Metal Derivatives of Aryl Diazonium Ions. Part II.[1] Arylazo Derivatives of Substituted Iron Carbonyls

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Diazonium salts react with phosphine-substituted iron carbonyls, $L_2Fe(CO)_3$, to give stable orange arylazo derivatives of formula $\{ArN_2Fe(CO)_2L_2\}^+BF_4^-$. I.r., electronic, n.m.r. (^1H, ^{19}F, and ^{31}P), and Mössbauer spectroscopic data have been recorded for selected complexes. The π-acceptor character of the ArN_2 ligand is discussed in the context of preliminary results of a structural determination.

ALTHOUGH the reaction of diazonium salts with transition metal carbonyls was first studied ten years ago,[2] it is only recently that stable arylazo derivatives of the transition metals have been isolated, but no derivative of a first-row transition metal has yet been described. Recent work in these laboratories has resulted in the development of useful synthetic routes to neutral arylazo complexes of cobalt and both neutral and ionic arylazo derivatives of iron. The present paper reports the synthesis and properties of one such class of compounds.

$[(NO)Fe(CO)_2(PPh_3)_2]^+X^-$ (Ia) $X = Cl$
(Ib) $X = PF_6^-$
$[RC_6H_4{\cdot}N_2{\cdot}Fe(CO)_2L_2]^+X^-$ (II)

Disubstituted derivatives of pentacarbonyliron such as bis(triphenylphosphine)tricarbonyliron react with nitrosyl chloride[3] or nitrosonium hexafluorophosphate[4] to give salts of a nitrosyl-cation (Ia) and (Ib). Since the nitrosonium and diazonium cations are isoelectronic we felt that arylazo complexes of iron might be accessible *via* the reactions of $L_2Fe(CO)_3$ with diazonium tetrafluoroborates. This reaction does proceed smoothly and the major products are orange crystalline solids for which microanalytical data suggest the empirical formulae (IIa—f).

In the case of complex (IIe) where L is 4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane, (etpb), we had difficulty in obtaining the pure precursor $L_2Fe(CO)_3$ by

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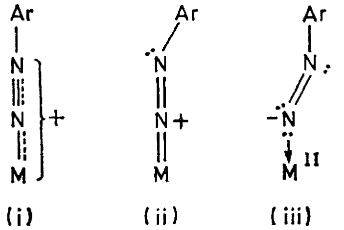
standard procedures.[5] Crooks and Johnson[3] had found that the nitrosyl complex (Ib) could also be prepared in reasonable yield from $(Ph_3P)Fe(CO)_4$ and we successfully synthesised complex (IIe) starting with $(etpb)Fe(CO)_4$ or a crude mixture of the mono- and bis-etpb iron carbonyls. Similarly the only product isolated from the reaction of $(Ph_3P)Fe(CO)_4$ and benzenediazonium salts was the bis-phosphine substituted arylazo complex (IIa). However the related tetracarbonyl $(o\text{-}CH_3C_6H_4)_3PFe(CO)_4$ failed to react. We have shown elsewhere[6] that this latter complex has a sterically crowded iron atom and it seems likely that steric reasons are responsible for the failure to react with diazonium ion. Trofimenko[7] has shown that the nitrosonium ion is less sensitive to steric effects than the diazonium cation, and in agreement with this $(o\text{-}CH_3C_6H_4)_3PFe(CO)_4$ does react[8] with $NOPF_6$ to yield $\{(o\text{-}CH_3C_6H_4)_3PFe(CO)_3NO\}^+PF_6^-$.

All the new compounds are stable, both in solution in polar solvents and as solids. Complex (IIa) has been exposed to normal laboratory atmospheres for periods in excess of one year without appreciable deterioration. The analogous nitrosyl-cations decompose after *ca.* three weeks.[3] Conductance values in acetone solution are in the region expected[9] for 1 : 1 electrolytes and the complexes are diamagnetic (n.m.r. method[10]).

A yellow air-stable cationic nitrogen-free iron complex (III) inevitably accompanies the formation of complexes (IIa—f) in these reactions. Interestingly a similar (and probably isostructural) nitrogen-free complex (IV) is the sole product from the reaction of diazonium salts and $Ru(CO)_3(PPh_3)_2$. Johnson and Segal[4] have reported that whereas $L_2Fe(CO)_3$ reacts with $NOPF_6$ to give the nitrosyl complex (Ib), $L_2Ru(CO)_3$ gives instead $\{L_2Ru(CO)_3H\}^+$. On the basis of their stability in air and the absence of any n.m.r. evidence for a hydridic hydrogen it appears that neither complex (III) or (IV) is a hydrido-cation. These compounds are receiving further study.



(i) (ii) (iii)

Following the work of Ibers and others[11] on nitrosyl complexes, two limiting structures (i) and (iii) may be considered for the co-ordinated arylazo ligand. Structure (i) involves a formal $ArNN^+$ ligand (analogous to $\overset{+}{NO}$) behaving as σ-donor to the metal, with some degree of reverse π-bonding from metal to ligand π* orbitals. Both N atoms of the azo-structure are *sp* hybridised and the ArNN ligand is linear. Structure (iii) is related to (ii) by a formal transfer of two electrons from metal to ligand so that the ligand now behaves as $ArNN^-$ (analogous to NO^-). The ligand–metal interaction is purely σ in nature, both N atoms are sp^2 hybridised and the metal–arylazo structure has a bent azobenzene-like geometry. A third possibility (ii) may be recognised for the ArN_2 ligand and, unlike structures (i) and (iii), structure (ii) has no geometric equivalent in nitrosyl chemistry. Here $M \longrightarrow L$ electron transfer may be considered to have taken place to such an extent as to involve a full formal M–L double bond, but falling short of the complete transfer envisaged for (iii). The NN linkage is now a double bond with *sp* hybridisation at the metal-bonded nitrogen atom and sp^2 hybridisation at the nitrogen bonded to the aryl group. This implies linear MNN and angular ArNN structures. Of course structures (i)—(iii) are limiting only and a broad continuum of geometries between (i) and (iii) may be expected with deviation from linearity becoming more pronounced as $M \longrightarrow L$ electron-transfer increases.

Preliminary structural data[12] for complex (IIa) indicates that the overall geometry is trigonal-bipyramidal with apical phosphines, the equatorial positions being occupied by the carbonyl groups and the arylazo ligand. A similar geometry has recently been confirmed[13] for the related complex $\{(NO)Os(CO)_2(Ph_3P)_2\}^+ClO_4^-$ and has been inferred on the basis of i.r. spectroscopic data for the iron analogue (Ib). While the data for complex (IIa) is in an early state of refinement it is clear that the FeNN unit is linear with an N–N bond length of *ca.* 1·19 Å. The PhNN unit on the other hand is distinctly bent with a C–N–N angle *ca.* 124°. The structure thus approximates to bonding condition (ii) above.

The new complexes have been characterised by their ^1H, n.m.r., i.r., and u.v.–visible spectra. In addition the ^{19}F and ^{31}P n.m.r. spectra and ^{57}Fe Mössbauer spectra have been recorded for selected compounds. These results are summarised in the Table.

The ^1H n.m.r. spectra for complexes (IIa—d) and (IIf) are uninformative as the proton resonances of the phosphine or arsine ligands overlap with those of the aryl ring of the ligand. In complex (IIe) the protons of the cyclic phosphite ligand and the arylazo ligand may be distinguished. As expected the $-OCH_2-$ protons of the phosphite show the triplet pattern characteristic of virtual coupling.[14] The value of $J(POCH_2)$ is almost unchanged from that observed[5] for the related complex $Fe(CO)_3\{P(OCH_2)_3CCH_3\}_2$. The ^{31}P spectrum of complex (IIa) displays a single resonance as expected for a structure with two equivalent phosphorus atoms.

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Complexes (IIa—f) owe their orange colour to strong end-absorption from the u.v. region. No maximum was observed in the region 412—600 nm assigned by previous workers to the $n \longrightarrow \pi^*$ transition of the co-ordinated azo group.[1,15-19] At higher energies a weak inflection occurs in the region 349—398 nm which we tentatively assign to $\lambda_{n-\pi^*}$. Following the conclusions of previous workers[18] a shift to high energy of $\lambda_{n-\pi^*}$ implies that delocalisation of electron density from the iron atom along the arylazo chain is not extensive.

Some degree of confirmation for this suggestion is provided by the i.r. spectra of complexes (IIa—f) (see Table) and the ^{19}F n.m.r. spectra of complexes (IIb and c). Of the three strong bands in the 2100—1700 cm^{-1} region the two of highest wavenumber are assigned to ν(CO). The third band is confirmed by an isotopic labelling experiment to be due to ν(NN). Assignment of ν(NN) in arylazo complexes to absorptions in the range 1440—1620 cm^{-1} (neutral compounds)[1,15-17,19-22] and 1622—1700 cm^{-1} (cationic complexes)[18,23,24] has been made by previous workers. Confirmation of assignment by isotopic substitution is only available[17] for the narrower range of 1440—1505 cm^{-1}. Our work considerably extends the verified range of ν(NN). The value of ν(NN) in compounds (IIa—f) is the highest yet recorded and suggests, with the u.v. evidence, a lower degree of metal–arylazo back bonding than previously observed for complexes of this type. The two ν(CO) absorptions in compounds (IIa—f) lie at lower wavenumber than those in the analogous nitrosyl (I)[4] suggesting that the arylazo group is moreover a weaker π-acceptor than is NO.

Because the *p*-fluorine atom of complex (IIb) is deshielded relative to the *m*-fluorine atom of complex (IIc) by −4·8 to −4·9 p.p.m. (internal and external C_6H_5F standard respectively), there is significant conjugative withdrawal of electrons from the aromatic ring by the attached $-\{N_2\overset{+}{Fe}(CO)_2L_2\}$ structure, hence transfer of electron density from metal to ligand by back-bonding cannot be extensive.

In view of the probable relationship between M $\longrightarrow$ L electron transfer and the geometry of the ArNN ligand it is interesting to compare the foregoing results with those reported[19] for $[Mo(CO)_2\{HB(C_3H_3N_2)\}(PhNN)]$ in which the geometry of the ArNN ligand is structurally similar[25] to that in complexes (IIa—f). For complexes of this type the ^{19}F n.m.r. results * indicate a very much smaller deshielding of the *p*-F atom (*ca.* −0·04 p.p.m.) and therefore significantly more back-bonding from the metal to the arylazo ligand. The close similarity of structures is unexpected. It appears that the geometry of the ArNN ligand is more sensitive to the effects of population of the ligand π* orbitals than might have been predicted; even the small degree of back-bonding evident in (IIa—f) being sufficient to significantly distort the structure from linearity.

Finally we have determined the ^{57}Fe Mössbauer spectra of arylazo complexes (IIa and d) and the nitrosyl analogue (Ib). Replacing the NO ligand by the ArNN structure produces a marked increase in the isomer shift (δ) of the iron nucleus and decreases the quadrupole splitting ($|\Delta E_q|$). Thus the effective *s*-electron density at the ^{57}Fe nucleus is greater in the nitrosyl than in the arylazo complex. This information is certainly consistent with our tentative conclusion from i.r. data that ArN_2 is the poorer π-acceptor of the two. However a similar effect would be produced if ArN_2 were a weaker σ-donor than NO. More information will be necessary to separate the two effects. Complex (Ia) may be described as formally d^8-Fe^0 or d^7-Fe^I. In either case the non-spherically symmetric *d* shell renders it difficult to interpret changes in $|\Delta E_q|$ values in terms of changes in metal to ligand π-bonding. While there are some grounds for suggesting that in complexes of this type increasing π-bonding produces a decrease in $|\Delta E_q|$, the evidence is not conclusive.[6] Here too more work is needed. It may be pointed out, however, that complex (IIa) has the smallest value of $|\Delta E_q|$ yet recorded for complexes of unambiguously trigonal-bipyramidal geometry. In future greater care will be necessary before the geometry of a co-ordinate sphere can be assigned simply on the basis of $|\Delta E_q|$ value. We are presently carrying out an extensive study of the transmission of electronic effects along the PhNNFe chain using Mössbauer and other spectroscopic techniques as well as investigating the chemistry of these new and very stable iron complexes.

EXPERIMENTAL

Substituted anilines were available commercially and were converted to diazonium tetrafluoroborates or hexafluorophosphates by standard procedures.[26] Sodium [^{15}N]-nitrite (99%) was purchased from the Isomet Corporation, 103 Bauer Drive, Oakland, New Jersey, and was used to synthesise ^{15}N-labelled benzenediazonium tetrafluoroborate. Triphenylphosphine, triphenylarsine, and 4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2.2.2]octane were commercially available and were used as received. The $L_2Fe(CO)_3$

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* Data from ref. 19 measured with respect to external C_6H_5F standard. For this complex ^{19}F n.m.r. spectra are complicated by specific solute–standard interactions when the standard is internal. Our measurements on (IIb—c) were not similarly affected.

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compounds were synthesised by literature methods.[5,27] Microanalytical and molecular weight data were carried out in the Analytical Laboratory of this department and by the Pascher Microanalytical Laboratory, Buchstrasse 54, Bonn, W. Germany.

I.r. spectra were recorded on a Perkin-Elmer 257 grating spectrophotometer. Electronic spectra were measured using a Perkin-Elmer 402 u.v.–visible instrument. ^{1}H and ^{19}F n.m.r. spectra were obtained on a Perkin-Elmer–Hitachi R 20A spectrometer at 60·0 and 56·456 MHz respectively. Field-sweep mode was used in both cases. The ^{31}P spectrum of complex (IIa) was measured on a Bruker HFX spectrometer with complete proton decoupling. We are indebted to Dr. W. R. Jackson of Queen's University, Belfast, and Dr. B. E. Mann of the University of Leeds for this data. Conductivity measurements were made with a Radiometer CDM2e direct-reading conductivity meter using a CDClO4 electrode. Mössbauer spectra were run at room temperature using a commercial drive unit and transducer, TMC model 305/306 with a TMC Gammascope II multichannel analyser. The source was ^{57}Co in Pd and was of nominal strength 5 mCi. Absorbers were made up in Al foil and were *ca.* 50 mg cm^{-1} in thickness. A non-linear curve-fitting programme was used and the data processed on an 1130 IBM computer. We are grateful to Dr. F. A. Deeney of the Experimental Physics Department of this College for the Mössbauer data.

Analytical, spectroscopic, and other data

				Analytical data (%) [a]				Infrared [b]							Mössbauer spectra [e]	
Complex	R	L	X	C	H	N	M.p./°C	ν(CO)		ν(NN)	Electronic spectra [c]			Δ_M [d]	δ/mm s^{-1}	$\|\Delta E q\|$/ mm s^{-1}
(IIa)	H	PPh_3	BF_4	64·0(63·8)	4·6(4·3)	3·5(3·4) [f]	204—205	2030	1978	1723 [g]	349(4·23)	293(45·0)	232(61·5)	143 ± 3	0·092 ± 0·01	0·97 ± 0·01
(IIb)	*p*-F	PPh_3	BF_4	62·6(62·4)	4·2(4·0)	3·6(3·3)	210—211	2027	1976	1720	346(5·55)	296(43·1)	232(45·0)	140 ± 2		
(IIc)	*m*-F	PPh_3	BF_4	62·8(62·4)	4·2(4·0)	3·4(3·3)	187	2030	1981	1714	349(3·75)	295(44·6)	231(51·2)			
(IId)	*p*-NO_2	PPh_3	BF_4	60·4(60·5)	4·0(3·9)	4·7(4·8)	166—168	2036	1984	1703	398(2·74)	308(37·4)	231(49·8)	132 ± 2	0·092 ± 0·01	1·08 ± 0·01
(IIe)	*p*-F	etpb	PF_6	33·9(34·1)	3·7(3·7)	4·2(4·0)	170	2070	2014	1763	350(1·60)	276(33·0)	212(22·5)			
(IIf)	H	$AsPh_2$	BF_4	57·7(57·6)	3·9(3·8)	3·3(3·0)	173—174	2028	1978	1720	370(3·15)	299(47·3)	217(59·0)			
(Ib)								2051 [h]	1995 [h]	1792 [h,i]					0·075 ± 0·01	2·05 ± 0·01

[a] Calculated values in parentheses. [b] In cm^{-1}, CH_2CH_2 solution, 2100—1700 cm^{-1} region. [c] Methanol solution, in nm, extinction coefficients ×10^{-3} in parentheses. [d] Acetone solution, concentration $1{\cdot}0 \times 10^{-3}$—$2{\cdot}0 \times 10^{-4}$ mol^{-1} l^{-1}, in Ω^{-1} cm^{2} mol^{-1}. [e] Measured with respect to natural iron. [f] Iron analysis, 6·8(6·7)%. [g] $\nu(^{14}N^{15}N)$ occurs at 1690 cm^{-1}. [h] Data from ref. 4. [i] ν(NO).

Preparation of the Complexes $[ArN_2Fe(CO)_2L_2]^+X^-$ (IIa—f).—A stirred solution or suspension of $L_2Fe(CO)_3$ [or $LFe(CO)_4$ where L is etpb] in acetone or methylene chloride was treated under nitrogen with a slight excess of solid diazonium salt. Vigorous effervescence occurred and the yellow solution developed a transient green tinge, changing rapidly to deep red. After 30 min stirring at room temperature [40 °C in the case of $(etpb)Fe(CO)_4$] the solution was filtered. Addition of ether precipitated the crude product. Orange micro-crystals of analytical purity were obtained by recrystallisation from acetone–ether or methylene chloride–ether. The yield of pure material averaged 50% of theory. Further work-up of the original reaction mixture yielded a second cationic product which is currently being investigated (see text). Microanalytical, m.p., and i.r. spectroscopic data for the new complexes are collected in the Table.

Nuclear Magnetic Resonance Data.—^{1}H Spectrum of complex (IIe) determined in [$^{2}H_6$]acetone (internal Me_4Si): τ *ca.* 2·4(m) (aromatic protons), 5·35(t) ($-OCH_2$-protons), *ca.* 8·65(m) (exocyclic methylene group), and 9·15(m) (methyl group). *J*($POCH_2$) (taken as the separation of the outer parts of the endocyclic methylene triplet) was 5 Hz.

^{31}P Spectra. After full proton decoupling, complex (IIa) (in solution in methylene chloride) showed a single ^{31}P resonance at −59·6 p.p.m. relative to 85% H_3PO_4.

^{19}F Chemical shifts were determined in methylene chloride solution (fluorobenzene standard). A shift to higher frequency is taken as being positive in sign. Complex (IIb); *p*-fluorine; −8·34 p.p.m. (internal standard) −8·22 p.p.m. (external standard). BF_4^- ion; +38·72 p.p.m. (internal standard) and +39·02 p.p.m. (external standard). Complex (IIc): *m*-fluorine; −3·51 p.p.m. (internal standard) and −3·28 p.p.m. (external standard). BF_4^- ion; +39·16 p.p.m. (internal standard) and +39·16 p.p.m. (external standard). $\delta_{p-F} - \delta_{m-F} = -4{\cdot}83$ p.p.m. (internal standard) and −4·94 p.p.m. (external standard).

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