Simple Halogenonitrosyl Anions of Iron

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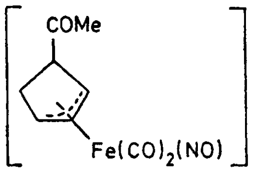
The complex $[N(PPh_3)_2][Fe(CO)_3(NO)]$ reacts with alkyl halides to afford $[N(PPh_3)_2]$ $[FeX_2(NO)_2]$ (X = Cl, Br, or I) and with halogens to afford $[N(PPh_3)_2][FeX_3(NO)]$ (X = Cl or Br) and $[N(PPh_3)_2][FeI_2(NO)_2]$. The relations between the two sets of paramagnetic anions, their reactivity, and their magnetic and e.s.r. spectral properties are discussed.

It is somewhat surprising that no simple halogenonitrosyl anions of iron have been fully characterised, particularly in view of the existence of the ruthenium and osmium species $[MX_5(NO)]^{2-}$ (M = Ru [1] and Os; [2] X = Cl, Br, or I). The e.s.r. spectra of mixtures of iron(II) salts, NO, and halide ions in aqueous ethanol have been interpreted [3] in terms of the existence of $[FeX_2(NO)_2]^-$ and $[FeX(NO)_2(OH_2)]$, and $[FeCl_2(NO)_2]^-$ was suggested as the product of reductive nitrosylation of $FeCl_2$ by NO.[4] In neither case, however, was a stable complex prepared. In addition, although the reaction of iron(II) salts, NO, and *o*-phenylenebis(dimethylarsine) (pdma) gave $[Fe(pdma)_2X(NO)][FeX_2(NO)_2]$ (X = Br or I), the identity of the anion was not unequivocally established.[5] We now report the isolation and complete characterisation of two series of halogenonitrosyliron anions, $[FeX_2(NO)_2]^-$ (X = I, Br, or Cl) and $[FeX_3(NO)]^-$ (X = Br or Cl), stabilised by the bis(triphenylphosphine)iminium cation.

RESULTS AND DISCUSSION

It has been shown previously [6] that $Na[Fe(CO)_3(NO)]$ reacts with cyclopentadiene or cyclohexadiene in the presence of methyl iodide to afford acetyl-substituted allyl complexes such as (I). We now find that reaction of $[N(PPh_3)_2][Fe(CO)_3(NO)]$ with MeI and cyclo-octatetraene (cot) in CH_2Cl_2 does not afford the analogous cyclo-octatrienyl complex but, instead, yields black crystalline $[N(PPh_3)_2][FeI_2(NO)_2]$ (Table 1) and small amounts of $[Fe(\eta\text{-}C_8H_8)(CO)_3]$. In the absence of cot the di-iodo-complex was still isolated, but apparently in a slightly decreased yield. The corresponding dibromo- and dichloro-complexes were also prepared, as dark red-brown crystalline solids, by allowing EtBr or Pr^nCl to react with $[N(PPh_3)_2][Fe(CO)_3(NO)]$ in refluxing CH_2Cl_2. The i.r. spectrum of each of the new complexes exhibited two bands in the nitrosyl-stretching region. The positions of the absorptions for the dichloride are virtually identical with those reported by Caulton,[4] thus confirming the formulation, $[NEt_3H][FeCl_2(NO)_2]$, proposed for the product of the reaction between $FeCl_2$ and NO in the presence of NEt_3. That $[FeX_2(NO)_2]^-$ has not previously been recognised in the reaction of $[Fe(CO)_3(NO)]^-$ with alkyl halides, RX, and that we have found no evidence for the usually formed acyl $[Fe(COR)(CO)_3(NO)]$, results from the use of the $[N(PPh_3)_2]^+$ cation, which stabilises the dinitrosyl anion, and of CH_2Cl_2 in which the acyl is unstable.



(I)

TABLE 1

I.r., analytical, m.p., and conductance data for $[N(PPh_3)_2][FeX_2(NO)_2]$, (I), and $[N(PPh_3)_2][FeX_3(NO)]$, (II)

Complex	X	M.p. (θ_c/°C)	Yield (%)	Analyses (%) [a] C	H	N	$\bar{\nu}$(NO) [b] / cm^{-1}	Λ [c] / S cm^2 mol^{-1}
(I)	I	160—161	97	47.8 (47.6)	3.7 (3.3)	4.4 (4.6)	1 778, 1 719	171
	Br	176—178	23	53.8 (53.1)	4.0 (3.7)	5.1 (5.2)	1 780, 1 710	176
	Cl	212—213	50	59.5 (59.6)	4.2 (4.2)	5.6 (5.8)	1 781, 1 708	168
(II)	Br	221—222	65	50.0 (50.0)	3.5 (3.5)	3.5 (3.2)	1 802	194
	Cl	237—239	66	58.9 (59.2)	4.1 (4.1)	3.4 (3.8)	1 802	192

[a] Calculated values are given in parentheses. [b] In CH_2Cl_2. [c] 10^{-4} mol dm^3 solutions in pure acetone.

In order to optimise the yields of the dinitrosyl anions, the reactions of the tricarbonyl with halogens and with nitrosyl halides were examined. Addition of I_2 to $[N(PPh_3)_2][Fe(CO)_3(NO)]$ in CH_2Cl_2 very rapidly gave a deep brown-black solution from which the di-iodo-complex was isolated in excellent yield. The dichloride is, however, best prepared by dropwise addition of NOCl in CH_2Cl_2 to $[N(PPh_3)_2][Fe(CO)_3(NO)]$ in the same solvent. It is interesting to note that the initial formation of $[Fe(CO)_2(NO)_2]$ in this reaction may be detected by i.r. spectroscopy. The isolation of $[Fe(CO)_2(NO)_2]$

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from $[Fe(CO)_4]^{2-}$ and NOCl has recently been reported;[7] there is no doubt, therefore, that $[Fe(CO)_3(NO)]^-$ is formed as an intermediate.

In contrast to the reaction of I_2 with $[N(PPh_3)_2][Fe(CO)_3(NO)]$, addition of Br_2 or Cl_2 in CH_2Cl_2 to the carbonyl anion afforded deep green solutions from which dark green crystals of $[N(PPh_3)_2][FeX_3(NO)]$ (X = Br or Cl) (Table 1) were isolated. The solid complexes are stable for at least several weeks, but their solutions in air are fairly rapidly decomposed to give $[N(PPh_3)_2][FeX_4]$ {as confirmed by the isolation of small amounts of $[N(PPh_3)_2][FeBr_4]$}. Although the anionic trihalogenonitrosyls have never been characterised before it is possible that they have been generated. We were, however, unable to isolate them from the deep green solutions prepared from NO and $FeCl_2$ in methanol [ν(NO) at 1 802 cm^{-1}],[4] $FeCl_3$ in ethanol [ν(NO) 1 775 cm^{-1}],[8] and $FeBr_2$ in tetrahydrofuran (thf) [ν(NO) 1 800 cm^{-1}].[5]

Although $[FeX_3(NO)]^-$ are the only nitrosyl complexes isolable from the reactions between $[Fe(CO)_3(NO)]^-$ and Br_2 or Cl_2, it is possible that they are formed *via* the dinitrosyls $[FeX_2(NO)_2]^-$. Solutions of the latter slowly afford the trihalides on standing, and do so more rapidly in the presence of the appropriate halide ion, X^-. The non-isolation of the tri-iodo-complex from $[N(PPh_3)_2][Fe(CO)_3(NO)]$ and I_2 is probably a result of steric factors. In the presence of I^- only $[N(PPh_3)_2][I_3]$ could be isolated from $[N(PPh_3)_2][FeI_2(NO)_2]$. With Br^-, however, the di-iodo-complex slowly gave a mononitrosyl, identified only by i.r. spectroscopy, which was possibly $[N(PPh_3)_2][FeBrI_2(NO)]$.

As precursors to iron nitrosyl complexes the two series of anions are somewhat disappointing. For example the reactions of $[FeI_2(NO)_2]^-$ with PPh_3, and of $[N(PPh_3)_2][FeBr_3(NO)]$ with 1,2-bis(diphenylphosphino)ethane (dppe) gave only low yields of $[Fe(NO)_2(PPh_3)_2]$ and $[Fe(NO)_2(dppe)]$ respectively. In addition, although the nitrosyl group of the dihalogeno-anion is apparently labile, it has not been possible to transfer it to an organic substrate. The complex $[Co(CO)_2I(NO)]^-$ reacts with benzyl halides to afford benzaldoximes,[9] but a similar reaction with $[FeI_2(NO)_2]^-$ did not give any organonitrogen compounds.

Magnetic and E.S.R. Studies.—Both $[N(PPh_3)_2][FeX_2(NO)_2]$ and $[N(PPh_3)_2][FeX_3(NO)]$ are paramagnetic. Measurement of the magnetic susceptibilities of these species, by a variation of Evans' n.m.r. method,[10] shows that the dihalides have one unpaired electron while the trihalides have three (Table 2). That $\mu_{eff.}$ for the dibromo- and dichloro-complexes are slightly higher than the calculated spin-only value of 1.73 B.M. is probably due to the presence of small amounts of trihalide impurity.* Although analytically pure samples were used for all the susceptibility measurements, slow formation of $[FeX_3(NO)]^-$ from $[FeX_2(NO)_2]^-$ (X = Br or Cl) occurred in solution even under nitrogen. As $[FeI_2(NO)_2]^-$ does not transform to $[FeI_3(NO)]^-$ (see above), the measured value of $\mu_{eff.}$ is close to the calculated value for one unpaired electron. In the case of the trihalides the measured susceptibility of $[N(PPh_3)_2][FeBr_3(NO)]$ is in good agreement with the spin-only value for three unpaired electrons. For the trichloro-complex, however, two measurements of $\mu_{eff.}$ gave values of 4.77 and 4.84 B.M. which are considerably higher than the expected value. It seems likely that such high values arise from the formation in solution of $[N(PPh_3)_2][FeCl_4]$ which, with five unpaired electrons, would cause the measured $\mu_{eff.}$ to be raised.

TABLE 2

Magnetic moments and e.s.r.[a] spectral values for $[FeX_2(NO)_2]^-$, (I), and $[FeX_3(NO)]^-$, (II)

Complex	X	$\mu_{eff.}$/B.M.	$\langle A \rangle$/G	$\langle g \rangle$
(I)	I	1.72	19.2	2.072
	Br	1.75	18.9	2.049
	Cl	1.81		2.033
(II)	Br	3.82		
	Cl	4.77, 4.84[b]		

[a] In CH_2Cl_2 at room temperature. [b] See text.

While nitrosyl-stretching frequencies are a poor aid to the assignment of either bent (formally NO^-) or linear (formally NO^+) structures to metal nitrosyl complexes, in both sets of anions reported here the frequencies are, for negatively charged nitrosyls, relatively high. The metal nitrosyl groups are, therefore, probably linear and best regarded as containing the NO^+ ligand. The assignment of the nitrosyl ligand as NO^+ leads to the assignment of oxidation states −I and +I to the iron atoms in $[FeX_2(NO)_2]^-$ and $[FeX_3(NO)]^-$ respectively. The measured magnetic susceptibilities are then in good agreement with the iron atoms having basically tetrahedral geometry with d^9 and d^7 configurations respectively.

In CH_2Cl_2 at room temperature and at −196 °C, the trihalides showed no detectable e.s.r. signals. The dihalides, however, showed well resolved spectra at room temperature. Burlamacchi *et al.*[3] previously reported the e.s.r. spectra of aqueous alcoholic solutions of iron(II) salts and halide ions saturated with nitrogen mono-oxide. In each case spectra were observed which were dependent on the concentration of X^- and which were interpreted as indicating the presence of mixtures of $[FeX(NO)_2(OH_2)]$ and $[FeX_2(NO)_2]^-$. In the case of X = I the spectrum of the anion, free of the neutral species, was seen at high iodide concentration. For X = Cl or Br, however, only spectra of the mixtures were observed. The di-iodo- and dibromo-complexes reported here each showed an e.s.r. spectrum with hyperfine coupling to two halogen atoms, but, as found previously, not to nitrogen. In each case the $\langle g \rangle$ and $\langle A \rangle$ values (Table 2) are close to those assigned by Burlamacchi for the anionic dihalogeno-species in the mixtures studied. Thus, the di-iodide showed an 11-

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* 1 B.M. ≈ 9.27×10^{-24} A m^2.

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line spectrum due to coupling with two equivalent iodine atoms [I (^{127}I) = $\frac{5}{2}$], and the dibromide a septet due to coupling with two equivalent bromine nuclei [$I(^{79}\mathrm{Br}) = I(^{81}\mathrm{Br}) = \frac{3}{2}$]. In the case of $[N(PPh_3)_2][FeCl_2(NO)_2]$ we only observed a single line with no hyperfine coupling to either ^{35}Cl or ^{37}Cl ($I = \frac{3}{2}$). The $\langle g \rangle$ value is, however, in good agreement with that previously measured. It is probable that the non-observation of coupling is due to poor resolution in CH_2Cl_2; the insolubility of the complex prevented the use of aqueous ethanol as the solvent for e.s.r. studies.

EXPERIMENTAL

The preparation and purification of the complexes described were carried out under an atmosphere of dry nitrogen. All solvents were dried and distilled before use.

Infrared spectra were recorded on Perkin-Elmer PE257 or PE457 spectrophotometers and were calibrated against the 1 601 cm^{-1} absorption of polystyrene. X-Band e.s.r. spectra were recorded on a Varian Associates 4502/15 instrument and were calibrated against a solid sample of the diphenylpicrylhydrazyl radical. Magnetic-susceptibility measurements were carried out, using a modification of Evans' n.m.r. method,[10] on a Varian Associates HA100 instrument. Bulk susceptibilities were calculated from the difference between the chemical shift of pure CH_2Cl_2 and that of the CH_2Cl_2 proton resonance of *ca.* 0.05 mol dm^{-3} solutions of the paramagnetic complexes. Both shifts were measured relative to an internal cyclohexane reference. Microanalyses were by the Microanalytical Service of the School of Chemistry, University of Bristol. Melting points are uncorrected.

Bis(triphenylphosphine)iminium Tricarbonylnitrosyliron, $[N(PPh_3)_2][Fe(CO)_3(NO)]$.—To sodium (4 g) in methanol (270 cm^3) were added $Na[NO_2]$ (5.2 g) and $[Fe(CO)_5]$ (10 cm^3). After refluxing for 90 min, $[N(PPh_3)_2]Cl\cdot CH_2Cl_2$, (49.0 g) in CH_2Cl_2 (150 cm^3) was added. After partial evaporation the crude product was filtered from the reaction mixture and recrystallised from acetone–hexane to afford bright yellow crystals of $[N(PPh_3)_2][Fe(CO)_3(NO)]$ (31.5 g) {yield 60% based on $[Fe(CO)_5]$}. The *complex* is soluble in polar solvents such as acetone and CH_2Cl_2 to give deep yellow solutions which only slowly decompose in air. The solid complex is stable in air for at least several months.

Bis(triphenylphosphine)iminium Dichlorodinitrosyliron, $[N(PPh_3)_2][FeCl_2(NO)_2]$.—To $[N(PPh_3)_2][Fe(CO)_3(NO)]$ (1.0 g) in CH_2Cl_2 (100 cm^3) was added dropwise a dilute solution of NOCl in CH_2Cl_2. The reaction was judged to be complete when the carbonyl absorptions of $[Fe(CO)_3(NO)]^-$ and of the intermediate $[Fe(CO)_2(NO)_2]$ were absent from the i.r. spectrum. The brown solution was then evaporated to dryness and the residue recrystallised from dichloromethane–ethanol to give red-brown crystals of $[N(PPh_3)_2][FeCl_2(NO)_2]$ (0.51 g) {yield 50% based on $[N(PPh_3)_2][Fe(CO)_3(NO)]$}. The *complex* is soluble in polar solvents such as acetone and CH_2Cl_2 to give red-brown solutions which decompose slowly in air. The solid complex is stable in air for a period of weeks.

Bis(triphenylphosphine)iminium Dibromodinitrosyliron, $[N(PPh_3)_2][FeBr_2(NO)_2]$.—The complex $[N(PPh_3)_2][Fe(CO)_3(NO)]$ (2.0 g), cyclo-octatetraene (1 cm^3), and EtBr (5 cm^3) were heated under reflux in CH_2Cl_2 (75 cm^3) for 26 h. The brown solution was then evaporated to dryness and the residue recrystallised from dichloromethane–ethanol to give dark red-brown crystals of $[N(PPh_3)_2][FeBr_2(NO)_2]$ (0.52 g) {yield 45% based on the nitrosyl group of $[N(PPh_3)_2][Fe(CO)_3(NO)]$}. The solid *complex* is reasonably stable in air; brown solutions in polar solvents such as acetone and CH_2Cl_2 slowly decompose.

Bis(triphenylphosphine)iminium Di-iododinitrosyliron, $[N(PPh_3)_2][FeI_2(NO)_2]$.—To $[N(PPh_3)_2][Fe(CO)_3(NO)]$ (5.0 g) in CH_2Cl_2 (50 cm^3) was added I_2 (1.79 g). After stirring until the carbonyl absorptions of $[Fe(CO)_3(NO)]^-$ had disappeared from the i.r. spectrum of the reaction mixture (*ca.* 30 min) the brown solution was evaporated to dryness. Recrystallisation from dichloromethane–ethanol gave black crystals of $[N(PPh_3)_2][FeI_2(NO)_2]$ {yield 98% based on the nitrosyl group of $[N(PPh_3)_2][Fe(CO)_3(NO)]$}. The solid complex is stable for some weeks in air, slowly decomposing with loss of iodine. Dark brown solutions of the complex in polar solvents such as acetone and CH_2Cl_2 slowly decompose in air.

Bis(triphenylphosphine)iminium Trichloronitrosyliron, $[N(PPh_3)_2][FeCl_3(NO)]$.—To $[N(PPh_3)_2][Fe(CO)_3(NO)]$ (1.0 g) in CH_2Cl_2 (50 cm^3) was added dropwise a solution of chlorine in CH_2Cl_2, until the carbonyl absorptions of $[Fe(CO)_3(NO)]^-$ were absent from the i.r. spectrum. On addition of ethanol and evaporation at the water pump, dark green crystals of $[N(PPh_3)_2][FeCl_3(NO)]$ (0.68 g) were deposited (yield 66% based on $[N(PPh_3)_2][Fe(CO)_3(NO)]$). The *complex* dissolves in polar solvents such as CH_2Cl_2 and acetone to give green solutions which decompose fairly rapidly in air. The solid complex is stable in air for several weeks. The *complex* $[N(PPh_3)_2][FeBr_3(NO)]$ may be similarly prepared as dark green crystals (yield 65% after recrystallisation from dichloromethane–ethanol).

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