

Synthesis of some zero-valent complexes of iron *via* aryldiazeno cationic complexes

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Abstract. Bis (triphenylphosphine) dicarbonylaryldiazeno-iron, $[\text{Fe}^0(\text{ArN}_2)(\text{CO})_2(\text{PPh}_3)_2]^+(\text{I})$, reacts in a solution of LiOEt under nitrogen atmosphere, with a variety of group V donor ligands, substituting the aryldiazeno ligand, ArN_2^+ . The effect of substitution on the stretching frequency of CO is discussed.

Keywords. Aryldiazeno cationic complex; substitution reactions; zero-valent complexes; iron.

1. Introduction

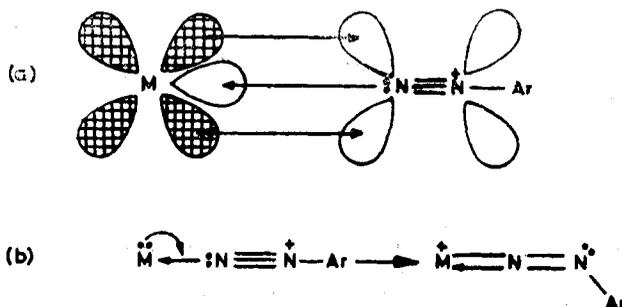
Disubstituted derivatives of iron pentacarbonyl such as $\text{L}_2\text{Fe}(\text{CO})_3$ ($\text{L} = \text{Phosphine}$) react with nitrosyl chloride (Crooks and Johnson 1968) or nitrosonium hexafluorophosphate (Johnson and Segal 1972) to give salts of a nitrosyl cation of the type, $[\text{NO Fe}(\text{CO})_2(\text{PPh}_3)_2]^+\text{X}^-$ ($\text{X} = \text{Cl}^-$ or PF_6^-). Since the nitrosonium and diazonium cations are isoelectronic, arylazo complexes of iron might be accessible *via* the reactions of $\text{L}_2\text{Fe}(\text{CO})_3$ with diazonium tetrafluoroborates. The first arylazo complex of iron, $(\text{R} \cdot \text{C}_6\text{H}_4\text{N}_2) \text{Fe}(\text{CO})_2 \text{L}_2]^+ \text{BF}_4^- (\text{I})$ was reported by Fisher and Sutton (1973). Aryldiazeno ligand has a strong resemblance to dinitrogen. Besides, applications in biological fixation and activation of dinitrogen (Fisher and Sutton 1973; Einstein and Sutton 1972, 1973), aryldiazeno complexes offer novel route for the synthesis of mixed ligand complexes of zero-valent iron.

Stirring a solution of I in lithium ethoxide (prepared by reacting stoichiometric quantities of lithium and ethanol) with a variety of ligands L , resulted in the new complexes listed in table 1.

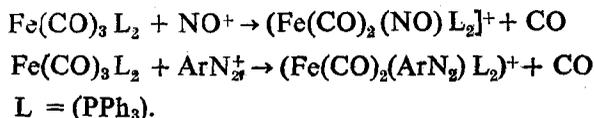
2. Discussion

Aryldiazeno ligand is analogous to nitrosyl ligand. This can be viewed as a three electron donor or as the cation ArN_2^+ coordinated through the σ -lone pair on the terminal nitrogen together with strong back donation of electrons from the metal. In NO ligand, according to valence bond model, a hybridisation

change at oxygen from sp to sp^2 occurs. But the mere population of π^* orbitals of ArN_2^+ leaves the angle at N^2 (nitrogen away from the metal M in figure 1) close to 180° (a) whereas the valence bond prediction is 120° (b).



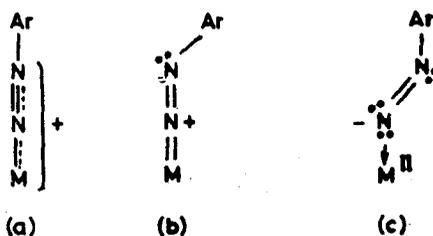
The substitution of CO in $Fe(CO)_3(PPh_3)_2$ by ArN_2^+ merits special consideration (Johnson and Segal 1972; Carrol and Lalor 1973).



In view of the positive charge it is doubtful whether they could act as Lewis bases towards the electron-rich metal centre. However it is sensible to consider an electrophilic attack at the electron-rich low-valent metal atom and the displacement of CO which occurs as a result of the competition between the electrophilic ArN_2^+ or NO^+ and the incumbent ligand CO for the metal d -electrons.

When a metal complex reacts with an aryldiazonium salt, the product is formed by the displacement of another ligand. Such replacement by ArN_2^+ maintains the 18 electron configuration. ArN_2^+ being an electrophile, attack at an electron rich CO is favoured. Thus $Fe(CO)_3(PPh_3)_2$ undergoes replacement of one CO group by ArN_2^+ to form $(Fe(ArN_2)(CO)_2(PPh_3)_2)^+$, the formal oxidation state of iron being zero (Fisher and Sutton 1973).

For a coordinated diazenato ligand two limiting structures are possible (figure 2; Mingos and Ibers 1971). Structures (a) and (c) are analogous to NO^+ and NO^- . (c) is related to (b) by a formal transfer of two electrons from metal to ligand so that the ligand behaves as ArN_2^- . Structure (c) has no geometric equivalent in nitrosyl chemistry.



The complex I has TBP geometry (Lalor and Pauson 1970) similar to that of $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$. Very high values of νN_2 (1720 cm^{-1}) suggest a low degree of back-bonding to the ArN_2^+ ligand. The diazonium cation could be considered formally to be either $3e$ donor towards Fe^+ or $2e$ donor to Fe^0 . Consistency in νN_2 values for various X -substituted aryl group favours the latter view.

Infra-red spectra of the complexes (1) through (6) exhibit two peaks in the carbonyl region expected for *cis* dicarbonyl groups (table 1; figure 3). For the phosphite complex which is more π -acidic than phosphine, one can expect an increase in the CO bond order and νCO value which is in agreement with observed values of νCO . On the contrary complex (6) with a *p*-tolyl group, electron donating CH_3 adds to the electron population of $\text{CO}\pi^*$ orbital and naturally ν_{CO} is shifted to lower region. Ditertiary phosphine and arsine substitute two phosphine groups from I which is expected for a bidentate ligand.

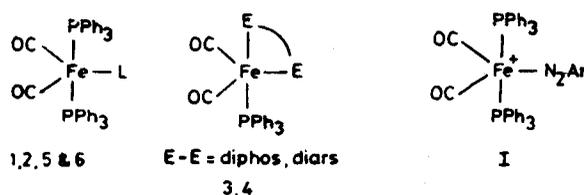


Table 1. Analytical and important infra-red spectral data of complexes.

Complex	Found (calcd) %		CO (cm^{-1})*
	C	H	
$\text{Fe}(\text{CO})_2(\text{PPh}_3)_2(\text{ASPh}_3)$	70.9 (71.35)	4.72 (4.78)	1978 (S), 1916 (V·S)
$\text{Fe}(\text{CO})_2(\text{PPh}_3)_2(\text{SbPh}_3)$	68.05 (67.97)	4.57 (4.55)	1975 (S), 1955 (V·S)
$\text{Fe}(\text{CO})_2(\text{PPh}_3)$ (diphos)	71.56 (71.52)	5.02 (5.05)	1980 (S), 1920 (V·S)
$\text{Fe}(\text{CO})_2(\text{PPh}_3)$ (Diars)	64.5 (64.2)	4.52 (4.54)	1982 (S), 1922 (V·S)
$\text{Fe}(\text{CO})_2(\text{PPh}_3)_2\{(\text{PhO})_3\text{P}\}$	70.8 (71.0)	4.72 (4.75)	1995 (S), 1934 (V·S)
$\text{Fe}(\text{CO})_2(\text{PPh}_3)_2\{(p\text{-tolyl})\text{Ph}_2\text{P}\}$	75.2 (75.01)	5.12 (5.15)	1968 (S), 1903 (V·S)

* Chloroform solutions were used unless otherwise mentioned.

All peaks were calibrated using polystyrene as reference (1601.8 cm^{-1}).

Reactions of $\text{Fe}(\text{CO})_2(\text{PPh}_3)_3$ in solution has already been studied (Vancheesan 1982). It is established that this complex dissociates to a coordinately unsaturated, 16e complex, $\text{Fe}(\text{CO})_2(\text{PPh}_3)_2$, which readily reacts with L to form $\text{Fe}(\text{CO})_2(\text{PPh}_3)_2L$. It is the axial phosphine which is replaced by L . Such substitution reaction is possible in the case of arsine and stibine complexes also, provided L is sterically favoured. When compared to $\text{Fe}(\text{CO})_2(\text{PPh}_3)_3$, complexes 1, 2 and 6 are expected to exchange L more readily, because the axial ligands arsine, stibine and diphenyl *p*-tolyl phosphine are sterically less favourable than phosphine to be accommodated in the axial position. It is difficult to predict the behaviour of diphos and diars complexes, 3 and 4. Further studies on the reactions of the complexes are in progress.

References

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