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Preliminary communication

Transition metal derivatives of aryl diazonium ions
III. Arylazo complexes of iron and cobalt

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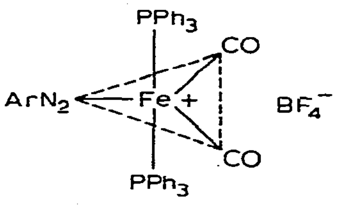
SUMMARY

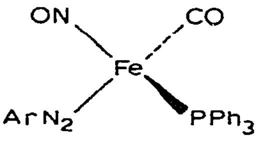
The synthesis of the first arylazo derivatives of iron and cobalt is described.

Since their initial discovery[1] a large number of arylazo complexes of the transition metals have been characterised. However the presently known range of complexes surprisingly excludes derivatives of the first-row transition metals. We now report the first successful syntheses of arylazo derivatives of iron and cobalt.

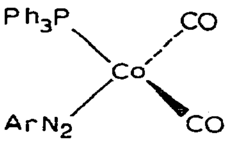
In a manner analogous to the recently reported synthesis of $[NOFe(CO)_2(PPh_3)_2]^+PF_6^-$ from $Fe(CO)_3(PPh_3)_2$ and $NOPF_6$ [2], phenyldiazonium tetrafluoroborate reacts with the phosphine complex to yield very stable orange $[C_6H_5N_2Fe(CO)_2(PPh_3)_2]^+BF_4^-$ (I). The IR spectrum of (I) is qualitatively similar to that of the related nitrosyl with three strong bands at 2030, 1978 and 1723 cm^{-1}. A labelling experiment with $[C_6H_5-N\equiv^{15}N]^+BF_4^-$ identified the 1723 cm^{-1} band as $\nu(NN)$. The two carbonyl bands in (I) occur at lower wavenumber than in the related nitrosyl indicating a reduced π-acceptor capacity for the $(C_6H_5N_2)$ ligand vis-à-vis (NO). A preliminary crystal structure determination[3] confirms the expected[2,4] trigonal bipyramidal (tbp) geometry with the phosphines occupying apical positions. The $C_6H_5N_2Fe$ unit is non-linear



(I)



(II)



(III)

overall with angle Fe—N—N ≈ 180° and angle C_6H_5—N—N ≈ 120°. The ^{19}F NMR parameters* of the *m*-F and *p*-F phenylazo analogs of (I), by indicating significant conjugative transfer of electron density from the aromatic ring towards the iron atom, confirm that Fe → N_2Ar backbonding cannot be extensive. The Mössbauer quadrupole splitting parameter of complex (I) at 0.97 ± 0.07 mm·sec^{-1} is the smallest yet recorded for a complex of unambiguously tbp geometry.

The anions $[Fe(CO)_3NO]^-$ and $[Co(CO)_4]^-$ as salts of the bis(triphenylphosphine)imminium cation, $[Ph_3P{=}N{=}PPh_3]^+$, react with $[C_6H_5N_2]^+BF_4^-$ at −70°C to yield red solutions which undoubtedly contain arylazo complexes but these do not survive warming to room temperature. However addition of triphenylphosphine at −70° followed by work-up at room temperature allows the isolation of the brown or red crystalline phosphine-stabilised complexes (II) and (III) respectively. Both complexes exhibit three strong absorbtion bands between 2010 and 1663 cm^{-1}, (1975, 1729 and 1663 cm^{-1} for (II) and 2010, 1960 and 1689 cm^{-1} for (III)). Isotopic labelling identified the absorption of lowest wavenumber as ν(NN) in both cases. The remaining absorptions ν(NO), (II) and ν(CO), (II) and (III) are displaced by ca. 22—36 cm^{-1} to lower wavenumber vis-à-vis the closely related nitrosyls[5] $Fe(NO)_2(CO)(PPh_3)$ and $Co(NO)(CO)_2(PPh_3)$, again reflecting the lower π-acceptor character of the arylazo ligand. Complex (II) is indefinitely stable as a solid or in acetone solution but decomposes rapidly in halogenated solvents. Complex (III) is much less stable and decomposes on attempted recrystallisation. It was identified on the basis of its IR spectrum alone. Attempts to enhance the stability of (III) by further substitution with triphenylphosphine were not successful. A full crystal structure determination is currently in progress on complex (II).

Diazonium salts react with $[V(CO)_6]^-$, $[Mn(CO)_5]^-$, $[CpFe(CO)_2]^-$, $[Ph_3SnFe(CO)_4]^-$ and $[CpNi(CO)]^-$ at −70° to give highly coloured solutions which may contain arylazo derivatives but even after phosphine addition no stable complexes could be isolated.

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* *m*-F, −3.28 ppm; *p*-F, −8.22 ppm measured at 56.54 MHz in CH_2Cl_2 solution and referenced to external fluorobenzene.