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Preliminary communication

Transition metal derivatives of aryldiazonium ions
IV. Oxidative addition of nitrosyl chloride to arylazo-molybdenum and -tungsten complexes

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SUMMARY

Oxidative addition of nitrosyl chloride to several arylazo complexes of molybdenum or tungsten yields novel remarkably stable arylazonitrosyl complexes.

Despite considerable current interest in arylazo derivatives of the transition metals there have been few reports of the subsequent derivative chemistry of this new class of complexes. We now describe the synthesis of novel mixed arylazonitrosyl complexes via the oxidative addition of nitrosyl chloride to arylazo derivatives of molybdenum and tungsten.

$$\underset{\text{(I)}}{LM(CO)_2N_2Ph} \xrightarrow[-25^\circ C]{NOCl} \underset{\text{(II)}}{LM(NO)(N_2Ph)Cl}$$

(a, $L = HBPz_3$, $M = Mo$; b, $L = HBPz_3$, $M = W$; c, $L = C_5H_5$, $M = Mo$).

Tris-1-pyrazolylborate, $(HBPz_3)$[1] or cyclopentadienyl[2] arylazo dicarbonyl derivatives of molybdenum or tris-1-pyrazolylborate derivatives of tungsten[1] (Ia–Ic), react cleanly with one equivalent of nitrosyl chloride in CH_2Cl_2 at −25°C to give the arylazonitrosyl complexes (IIa–IIc) in excellent yield. Formation of compounds (IIa–IIc) parallels the preparation of $(HBPz_3)Mo(NO)_2Cl$ by oxidative addition of NOCl to $(HBPz_3)Mo(CO)_2NO$[1] and is the first authenticated example of oxidative addition to an arylazo complex. The orange crystalline complexes are indefinitely stable both in the air and in solution. All complexes give well-resolved NMR spectra, indicative of diamagnetism.

In the NMR spectrum of complex (IIa) the H(3) atoms of the tris-1-pyrazolylborate ligand appear as three distinct well-separated triplets[3] of relative area 1/1/1. This indicates a rigid octahedral coordination sphere around Mo with no rotation of the $HBPz_3$ ligand. The IR spectrum of (IIa) shows ν(BH) at 2500 cm^{-1} and two intense absorptions at 1710 and 1642 cm^{-1}. Repetition of the synthetic procedure with complex (Ia) in which the Mo-bound N-atom of the PhN_2 group had been labelled with ^{15}N caused a shift of ca. 15 cm^{-1} to lower wavenumber in the 1642 cm^{-1} band which is thus identified as ν(NN). The ν(NO) band at 1710 undergoes a slight shift to lower wavenumber (<ca. 5 cm^{-1}) under these conditions suggesting slight coupling of the two absorptions.

An extensive substitution chemistry of complexes (IIa–IIc) was expected on the basis of the known lability of the closely related $C_5H_5Cr(NO)_2Cl$ (*cf.* ref. 1 and references therein). Disappointingly this expectation was not realised. Both complexes (IIa) and (IIc) were unaffected by C_5H_5Tl in refluxing acetone while (IIa) was similarly unreactive towards PPh_3 or KCN under similar conditions. Complex (IIa) was also recovered quantitatively after treatment with MeMgI in boiling Et_2O or, under more drastic conditions, from $MeCN/AlCl_3$ in boiling benzene. The lack of reactivity of the complexes (IIa–IIc) is surprising. For the tris-1-pyrazolylborate derivative (IIa) an explanation may lie in a shielding of the metal atom by the bulky[4] pyrazolylborate ligand. No such explanation is applicable to complex (IIc) however. The properties of these novel complexes are currently receiving further study.

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