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Organic Nitro Compounds as Ligands. A Comparison between the Ligand Behaviour of $MeNO_2$ and $PhNO_2$ towards $AlCl_3$

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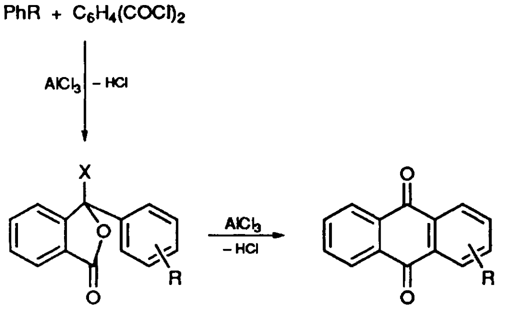
The crystal-structure analyses of the complexes $[AlCl_3(RNO_2)]$ (R = Me or Ph) and NMR data in solution suggest a stronger Al–O co-ordinative interaction in the case of nitrobenzene compared to nitromethane; this could account for the dramatic solvent effects observed during certain electrophilic acylation processes involving $AlCl_3$ as a promoter.

Metal complexes of organic nitro compounds deserve particular attention owing to their important role in several synthetic processes, either as 'co-ordinatively unsaturated' catalyst precursors in electrophilic acylations,[1] or as catalytic species in the transformation of nitroaromatics into urea and carbamates.[2]

As regards the first role, during our studies on regiochemical control in metal-template catalysis (electrophilic substitution),[3] we found a one-pot route to variously substituted anthraquinones **II** *via ortho*-double acylation of the aromatic substrates PhR (R = H, Me or OMe) with phthaloyl chloride,[4] through a phthalidic intermediate **I**.



I II

We discovered that the solvent dramatically affected the complete process. In fact, by performing the reaction at room temperature in $MeNO_2$ we obtained the expected anthraquinone in 75% yield. On the contrary, the intermediate **I** was obtained as the sole product in 60% yield when the reaction was carried out in $PhNO_2$.[4] This effect must be attributed to differences in the solvent–$AlCl_3$ interactions, such that $AlCl_3$ behaves as a *weaker* Lewis acid in $PhNO_2$ than in $MeNO_2$.

Organic nitro compounds are notoriously weak bases, exhibiting very similar (sometimes intriguing) values for the well known donor parameters;[5] in particular, whereas the donor-number value of $PhNO_2$ (4.4) is higher than that of $MeNO_2$ (2.7), the corresponding $-\Delta H(RNO_2{\cdot}BF_3)$ values show an opposite trend ($PhNO_2$, 35.8; $MeNO_2$, 37.6 kJ mol^{-1}). Therefore it was difficult to rationalize the reactivity data on the basis of the general donor scales. As more specific parameters of comparison were needed, we decided to obtain detailed information on the two RNO_2–$AlCl_3$ complexes (R = Me **1** or Ph **2**) involved in the synthetic processes, by solving their crystal structures and by collecting multinuclear NMR data in solution.

Air-sensitive, colourless crystals of the two complexes were obtained by cooling dry dichloromethane solutions containing equimolar amounts of $AlCl_3$ and the nitro compound. Their crystal structures are shown in Fig. 1.† Although three previous structural studies[7] had demonstrated the ligand behaviour of RNO_2 compounds and recent spectroscopic data had evidenced the formation of an aluminium complex of *p*-nitrotoluene,[8] to our knowledge compounds **1** and **2** represent the first structural examples of aluminium complexes containing organic nitro compounds as ligands.‡ Moreover, for the first time it is possible to compare the structural changes induced on a nitroalkane and a nitroaromatic compound by co-ordination to the same metal.

In both complexes the aluminium atom is tetrahedrally co-ordinated by three chlorine atoms and an oxygen atom of the nitro derivative. The structural parameters for the $AlCl_3$ moieties of both compare well with those found in other pseudo-tetrahedral complexes with stronger oxygen-donor ligands,[10] whereas the two Al–O bond distances are significantly longer

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† Crystal data. For **1**: $CH_3AlCl_3NO_2$, $M = 194.38$, orthorhombic, space group *Pnma*, $a = 13.365(4)$, $b = 7.392(3)$, $c = 7.722(3)$ Å, $U = 762.9(5)$ Å^3, $Z = 4$, $D_c = 1.692$ g cm^{-3}, $F(000) = 384$, $\lambda = 0.710\,73$ Å, μ(Mo-Kα) = 12.44 cm^{-1}, crystal dimensions 0.36 × 0.41 × 0.48 mm. For **2**: $C_6H_5AlCl_3NO_2$, $M = 256.45$, monoclinic, space group $P2_1/c$, $a = 8.046(3)$, $b = 17.673(5)$, $c = 7.837(3)$ Å, $\beta = 92.30(2)°$, $U = 1113.5(7)$ Å^3, $Z = 4$, $D_c = 1.530$ g cm^{-3}, $F(000) = 512$, $\lambda = 1.541\,838$ Å, μ(Cu-Kα) = 81.89 cm^{-1}, crystal dimensions 0.25 × 0.32 × 0.51 mm. Data collected on a Siemens AED diffractometer ($\theta/2\theta$ mode); 909 ($3 \leqslant \theta \leqslant 27°$) and 1899 ($3 \leqslant \theta \leqslant 65°$) unique reflections giving 659 and 961 with $I \geqslant 2\sigma(I)$, for **1** and **2** respectively; absorption corrections for **2**. Both structures were solved by heavy-atom methods and refined by least squares to R and R' values of 0.0348 and 0.0499 for **1** and 0.0559 and 0.0751 for **2**. The weighting schemes were $w = 0.6124/[\sigma^2(F_o) + 0.0025F_o^2]$ and $w = 0.5983/[\sigma^2(F_o) + 0.0054F_o^2]$ for **1** and **2** respectively. The programs used in the structure determination were SHELX 76 and SHELX 86.[6] Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

‡ The unit-cell data of some 1:1 addition compounds formed from $AlCl_3$ and organic nitro-derivatives have been obtained previously.[9]

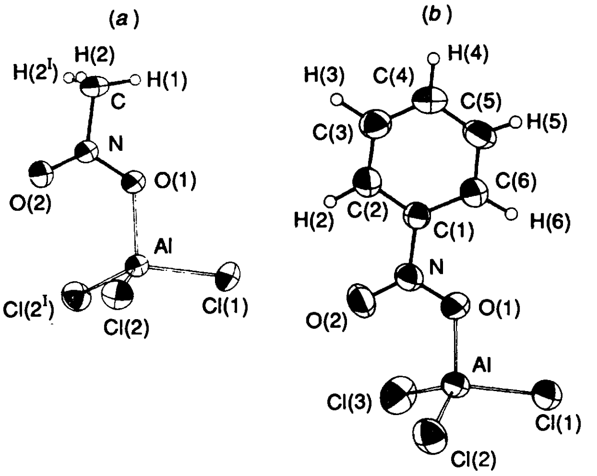

Fig. 1 Perspective views of [$AlCl_3(RNO_2)$] [R = Me **1** (*a*) or Ph **2** (*b*)]. Selected bond distances (Å) for **1**: Al–O(1) 1.867(2), Al–Cl(1) 2.103(2), Al–Cl(2) 2.096(1), N–O(1) 1.268(4), N–O(2) 1.170(4) and N–C 1.470(5) (symmetry operation I: $x, \frac{1}{2} - y, z$); for **2**: Al–O(1) 1.856(5), Al–Cl(1) 2.091(3), Al–Cl(2) 2.081(3), Al–Cl(3) 2.093(3), N–O(1) 1.279(8), N–O(2) 1.198(8) and N–C(1) 1.429(8)

than those observed previously (1.733–1.847 Å). Only in trigonal-bipyramidal $AlCl_3O_2$ environments have longer Al–O bond distances been observed,[11] *e.g.* 1.990(1) Å in [$AlCl_3(thf)_2$] (thf = tetrahydrofuran).[11a]

Although the Al–O distance for the $PhNO_2$ complex **2** is slightly shorter than for **1**, in accordance with the expected trend,* more significant differences occur in the structural parameters of the organic moieties. In both compounds the co-ordination of an oxygen atom leads to a remarkable lengthening of the N–O(Al) bond and to a shortening of the other N–O distance [mean N–O distances in free $PhNO_2$[12] and $MeNO_2$[13] are 1.21(1) and 1.223(3) Å respectively]. On the other hand, the C–N bond distance in the $PhNO_2$ compound is considerably shorter with respect to the free molecule [1.49(2) Å], whereas the corresponding parameter in the $MeNO_2$ complex is slightly longer [1.449(6) Å in free $MeNO_2$]. This is evidence that co-ordination to the metal modifies the electron delocalization in the $PhNO_2$ molecule and suggests an effective participation of the aromatic electron reservoir to the co-ordinative interaction. This mechanism, which obviously does not apply to the $MeNO_2$ complex, should provide increased electron density on the oxygen atom, thus strengthening the Al–O bond.

The comparison between the ligand behaviour of the two nitro derivatives was extended by a study in dichloromethane using ^{17}O and ^{27}Al NMR spectroscopy.† The ^{27}Al NMR spectra of 1 : 1 Al–RNO_2 solutions show in both cases broad peaks ($\Delta\nu_{\frac{1}{2}}$, 10^3 Hz) centred at *ca.* 100 ppm due to the presence of low-symmetry four-co-ordinated aluminium complexes.[14a] The direct metal–oxygen interaction is confirmed by the upfield ^{17}O resonances[14] observed for the same solutions, the $\Delta\delta$ values relative to the free nitro derivatives being −41 and −16 ppm for $PhNO_2$ and $MeNO_2$ respectively. A stronger Al–O interaction in the $PhNO_2$ complex could account for its larger $\Delta\delta$. Finally the greater increase in the ^{17}O linewidth (Fig. 2) up to 1500 Hz for the 1 : 1 Al–$PhNO_2$ complex could be a direct consequence of the electron delocalization arising from co-ordination, which should cause an increase in electron anisotropy on the oxygen atom.

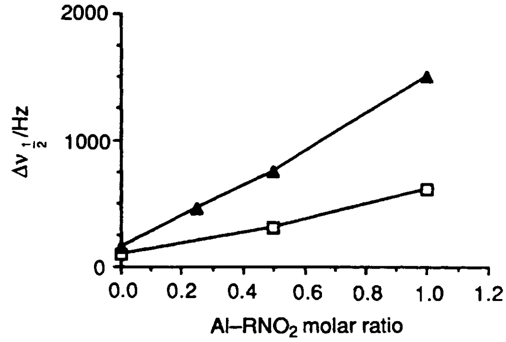

Fig. 2 Variation of ^{17}O linewidth with Al–RNO_2 molar ratio for $AlCl_3$–RNO_2 in dichloromethane; R = Me (□) or Ph (▲)

Acknowledgements

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* Also with $AlCl_3$ adducts of acyl chlorides an α aromatic ring causes a shorter Al–O interaction: 1.828(2) Å in [$AlCl_3(4\text{-}MeC_6H_4COCl)$];[10c] 1.847(6) Å in [$AlCl_3(EtCOCl)$].[10b]

† The ^{27}Al and ^{17}O NMR spectra were recorded on a Bruker CXP 200 instrument operating at 52.12 and 27.11 MHz, respectively; ^{27}Al and ^{17}O shifts are referred to external [$Al(H_2O)_6$]$^{3+}$ and H_2O, respectively. Dichloromethane solutions of the organic nitro derivative (*ca.* 6 mol dm^{-3}) were added, under a nitrogen atmosphere, with increasing amounts of $AlCl_3$ until a 1 : 1 molar ratio was reached.