$Cr(NAr)(O)(NPr^i_2)(Ar)$: a strongly-bent monoimido complex resulting from nitrosyl ligand cleavage

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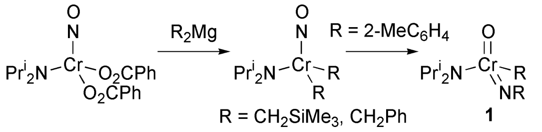
The molecular structure of $Cr(NAr)(O)(NPr^i_2)(Ar)$ (Ar = 2-MeC_6H_4) is analysed by X-ray crystallographic and density functional theoretical techniques.

Tetrahedral imido complexes of the Group 6 metals are in the vanguard of applied organometallic chemistry.[1–4] In d^0 $M(NR)(E)X_2$ complexes (E = O, NR, CHR; X = OR, NR_2, CH_2R), the competition among the π-donor ligands for available metal orbitals is a critical component of their overall reactivity.[5] Here, we report the molecular structure of $Cr(NAr)(O)(Ar)(NPr^i_2)$ (Ar = 2-MeC_6H_4), which contains a strongly-bent imido ligand.[6] Density functional theory (DFT) calculations have been employed to help analyse the π-bonding conflicts that underpin the experimentally observed geometry.

We recently reported that the alkylation of $Cr(NO)(NPr^i_2)(O_2CPh)_2$ with $R_2Mg{\bullet}x$(dioxane) reagents yields unsaturated diamagnetic Cr(II) alkyl complexes (Scheme 1).[7] The structures of $Cr(NO)(NPr^i_2)(CH_2SiMe_3)_2$ and $Cr(NO)(NPr^i_2)(CH_2Ph)_2$ were confirmed by X-ray crystallography, and fluxional processes involving the amido and benzyl ligands were established by variable-temperature ^1H NMR spectroscopy.[7] However, the product resulting from treatment of $Cr(NO)(NPr^i_2)(O_2CPh)_2$ with $Ar_2Mg{\bullet}x$(dioxane) has an anomalously sharp ^1H NMR spectrum with no indication of amido rotation. When the structure of this product was determined by X-ray crystallography, it was established that the original assignment as $Cr(NO)(NPr^i_2)Ar_2$ was incorrect; the complex is in fact $Cr(NAr)(O)(NPr^i_2)(Ar)$ **1** (Fig. 1, Table 1).

The most remarkable feature of the structure of **1**[8] is the strikingly non-linear Cr1–N1–C1 angle of 146.2(3)°. The NAr ligand lies in the O–Cr–N(imido) plane, with the aryl substituent bent toward the oxo group. The Cr–N(amido) bond length, and the amido group planarity (sum of angles at N2 = 359.8°) and alignment are indicative of a Cr–N(amido) π-bonding interaction.[5] Similarly, the Cr–O bond length is consistent with maximum oxo-to-chromium π-donation. The O–Cr–N angles between the oxo and both the amido and imido groups are larger than the typical tetrahedral angle. The structure of complex **1** exhibits disorder in the Cr-bound aryl ligand. This ligand occupies two distinct orientations, in equal proportions, related by a roughly 180° rotation about the Cr–C8 bond. Each disordered fragment was modelled using rigid phenyl groups with isotropic thermal parameters.



Scheme 1 Alkylation of $Cr(NO)(NPr^i_2)(O_2CPh)_2$.

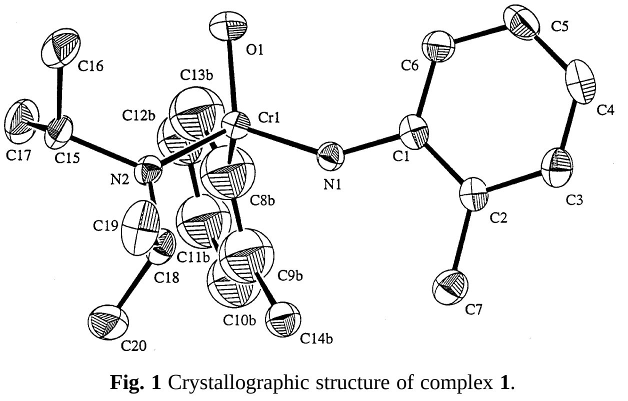


Fig. 1 Crystallographic structure of complex **1**.

Table 1 Comparison of experimental (**1**)[a] and calculated (**2**) bond lengths (Å) and angles (°) of $Cr(NR)(O)(NR'_2)(R)$[b]

Parameter	1	2
Cr–N1	1.670(2)	1.626
Cr–N2	1.801(3)	1.797
Cr–O	1.589(3)	1.592
Cr–C8a	2.103(6)	2.011
Cr–C8b	2.025(5)	
Cr–N1–C1	146.2(3)	149.0
O–Cr–N1	115.3(2)	115.2
O–Cr–N2	115.5(1)	115.4
O–Cr–C8a	112.6(2)	103.0
O–Cr–C8b	99.9(2)	
N1–Cr–N2	109.9(1)	110.8
N1–Cr–C8a	99.3(2)	101.8
N1–Cr–C8b	107.9(2)	
N2–Cr–C8a	102.3(2)	109.1
N2–Cr–C8b	107.9(2)	

[a] Parameters to C8 in **1** represent the two distinct orientations of the disordered aryl group. [b] **1**: R = 2-MeC_6H_4, R′ = Pr^i; **2**: R = R′ = Me.

DFT calculations[9] were performed on $Cr(NMe)(O)(NMe_2)(Me)$ **2** to investigate the origin and relative importance of the imido angle in this unusual structure.[10] While the simplified model compound lacks the steric bulk present in **1**, the DFT-optimised geometry faithfully reproduces the pertinent structural features determined by X-ray crystallography (Fig. 2, Table 1). The Cr–N(imido)–C angle is calculated to be 149.0°, confirming that this distortion is electronic rather than steric in origin. Remarkably good agreement is attained for the Cr–O and Cr–N(amido) bond lengths and the O–Cr–N bond angles, which match the structural determination within experimental error. The parameters involving the Cr–C bond show poorer agreement, surely due to the disorder exhibited by the aryl group. Interestingly, the DFT-optimised structure has Cr–N(imido)

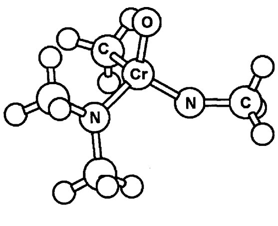


Fig. 2 Calculated structure of complex **2**.

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and N(imido)–C distances that are markedly shorter and longer, respectively, than the corresponding experimental bond lengths. This discrepancy may be due to the delocalisation of electron density from the N atom to the aromatic substituent, an electronic redistribution that is unavailable to the NMe ligand of the computational model.

Complex **1** is the most strongly-bent chromium imido complex observed to date, as confirmed by a search of the Cambridge Structural Database (October 1999 release), and is the *only* example of a chromium *mono*imido compound with a Cr–N–C angle $< 165°$.[11] While $Cr(NR)_2X_2$ compounds exhibit a wide range of Cr–N–C angles (typically 155 to 175°), none approaches the degree of bending observed in **1** unless the two imido groups are joined in a strained chelate ring.[3b] The evident π-donation of the NPr^i_2 group is not responsible for the Cr–N–Ar bending, in that amido π-bonding in the related $Cr(NR)_2(NHR)Cl$ complexes fails to disrupt the Cr–imido interaction.[12,13] The geometry of **1** is therefore attributed to the competition between the oxo and imido groups for available d_π orbitals.[14]

A series of single-point calculations were performed to see what variation of the overall energy of **2** would result from variation of the imido Cr–N–C angle. As shown in Fig. 3, this is a remarkably soft deformation mode, requiring $< 18\ \mathrm{kJ\ mol^{-1}}$ to make the imido ligand perfectly linear. The relative ease of imido bending/straightening has been established theoretically,[15] spectroscopically[16] and structurally.[17]

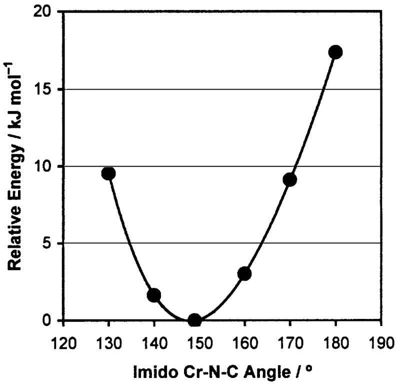

Fig. 3 Energy change with imido ligand angle in **2**.

As indicated in Scheme 1, $Cr(NO)(NPr^i_2)Ar_2$ is presumably an intermediate in the formation of complex **1**, though our attempts to trap or observe the diaryl precursor have thus far been unsuccessful. The relative instability of the putative diaryl compound with respect to nitrosyl bond cleavage may be related to the propensity of aryl (in contrast to alkyl) groups to undergo migration reactions to M=E linkages.[20] The cleavage of nitrosyl ligands is still relatively rare, but several examples of this reactivity are now known for unsaturated Group 6 complexes.[21] The transformation of R–Cr–NO to RN=Cr=O provides access to rare chromium d^0 monoimido species,[22] a potentially useful synthetic alternative to the chromyl chloride-derived $Cr(NR)_2X_2$ compounds that dominate Cr(VI) imido research.[12]

As established by DFT calculation, the strongly-bent imido angle of **1** clearly has an electronic origin, which we attribute to oxo–imido π-conflict, and which stands in contrast to the range of angles found in related bisimido structures. The calculations further reveal the soft nature of the distortion, in accord with experimentally determined examples of facile imido bending in Group 6 $M(NR)(E)X_2$ complexes. Given the influence of imido geometry on the reactivity of such complexes,[23] we feel the effect of these π-conflicts on imido-bending energy surfaces has been underappreciated. Further synthetic and theoretical studies to explore this phenomenon will undoubtedly aid in the rational design of catalysts for ROMP,[1] RCM[2] and olefin polymerisation[3] chemistries.

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