

# Cyclopentadienyl nitrosyl compounds of chromium: aqueous solution chemistry, $\pi$ bonding and nitric oxide loss †

Peter Legzdins,<sup>\*,a</sup> Steven J. Rettig,<sup>a</sup> Kevin M. Smith,<sup>a</sup> Vicki Tong<sup>a</sup> and Victor G. Young, Jr.<sup>b</sup>

<sup>a</sup> Department of Chemistry, The University of British Columbia, Vancouver, British Columbia, Canada V6T 1Z1

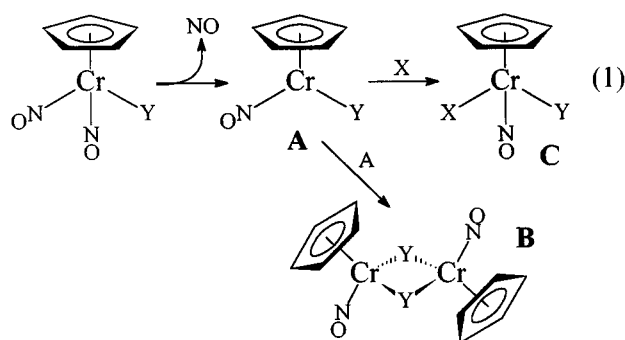
<sup>b</sup> Department of Chemistry, The University of Minnesota, 207 Pleasant St. SE, Minneapolis, Minnesota 55455, USA

The complex  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})_2(\text{CF}_3\text{SO}_3)]$  **1** was synthesised in order to explore the relationship between  $\pi$ -donor ligands and nitrosyl lability and to investigate the aqueous chemistry of the  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})_2]^+$  fragment. Treatment of **1** with  $\sigma$ -donor ligands gave  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})_2(\text{L})][\text{CF}_3\text{SO}_3]$  salts. Potentiometric titrations and  $^1\text{H}$  NMR spectroscopic studies of **1** provided evidence for the existence of  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})_2(\text{H}_2\text{O})]^+$  and  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})_2(\text{OH})]$  in aqueous solution. When generated *in situ*,  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})_2(\text{OH})]$  reacted with acetylacetone, pyridinecarboxylic acid, or salicylaldehyde to form paramagnetic, mononitrosyl complexes, which were independently synthesised from the mononitrosyl precursor  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})(\mu\text{-I})_2]$ . The solid-state molecular structures of  $[\text{Cr}(\eta\text{-C}_5\text{Me}_5)(\text{NO})_2(\text{CF}_3\text{SO}_3)]$  **2**,  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})_2(\text{N}_2\text{C}_5\text{H}_7)]$  **9** and  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})(\text{O}_2\text{C}_5\text{H}_7)]$  **10** were determined by X-ray crystallography. Crystals of **2** are monoclinic,  $a = 8.575(1)$ ,  $b = 8.642(1)$ ,  $c = 21.8626(9)$  Å,  $\beta = 91.760(7)^\circ$ ,  $Z = 4$ , space group  $P2_1/n$ ; crystals of **9** are monoclinic,  $a = 18.3382(4)$ ,  $b = 11.1774(3)$ ,  $c = 12.9102(1)$  Å,  $\beta = 121.386(1)^\circ$ ,  $Z = 8$ , space group  $C2/c$ ; and those of **10** are orthorhombic,  $a = 17.373(2)$ ,  $b = 8.833(1)$ ,  $c = 6.926(2)$  Å,  $Z = 4$ , space group  $Pnma$ .

In 1956 Piper and Wilkinson<sup>2</sup> reported the synthesis of  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})_2\text{Cl}]$ , one of the first well characterized organometallic complexes of chromium.<sup>3</sup> The compound is slightly water soluble, and upon treatment with aqueous  $\text{AgNO}_3$  forms solutions of  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})_2(\text{H}_2\text{O})]^+$ <sup>4</sup> {originally formulated as  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})_2]^+$ }.<sup>2</sup> The remarkable water stability of the  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})_2]^+$  fragment is demonstrated by the isolation of  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})_2\text{X}]$  ( $\text{X} = \text{halide or pseudo-halide}$ ) complexes upon addition of  $\text{KX}$  salts to *in situ* generated  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})_2(\text{H}_2\text{O})]^+$  followed by  $\text{CHCl}_3$  extraction.<sup>2</sup>

Subsequent metathesis studies of  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})_2\text{Cl}]$  have been performed in anhydrous organic solvents.<sup>5–8</sup> Under these conditions, several alkyl complexes of the type  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})_2\text{R}]$  (*e.g.*,  $\text{R} = \text{Me}$ ,<sup>5a</sup>  $\text{Et}$ ,<sup>5a</sup>  $\text{CH}_2\text{Ph}$ ,<sup>5b</sup>  $\text{Bu}^i$ ,<sup>5c</sup>  $\text{CH}_2\text{SiMe}_3$ ,<sup>5d</sup> and  $\text{CH}_2\text{X}$ <sup>5e</sup>) have been synthesised. The electron-donating ability of the alkyl groups is apparent in the shift of  $\nu(\text{NO})$  from 1815 and 1710  $\text{cm}^{-1}$  for  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})_2\text{Cl}]$  to  $\approx 1780$  and 1670  $\text{cm}^{-1}$  for  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})_2\text{R}]$  as measured by solution IR spectroscopy ( $\text{CH}_2\text{Cl}_2$ ).<sup>5</sup> The results of the alkylation reactions contrasts with metathesis reactions of  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})_2\text{Cl}]$  with  $\text{Y}^-$  sources ( $\text{Y} = \text{SR}$ ,  $\text{NR}_2$  or  $\text{OR}$ ) which depend on the electronic nature of the  $\text{Y}^-$  group. All known compounds of the composition  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})_2\text{Y}]$  contain strongly electron-withdrawing substituents (*e.g.*,  $\text{Y} = \text{SCN}$ ,<sup>2</sup>  $\text{SO}_2\text{CH}_3$ ,<sup>5b</sup>  $\text{SCF}_3$ ,<sup>6a</sup>  $\text{OSO}_2\text{C}_6\text{H}_4\text{Me}$ ,<sup>6c</sup>  $\text{NCO}$ ,<sup>6b</sup> and  $\text{NO}_2$ ,<sup>2,6d</sup>). However, if  $\text{Y}$  contains electron-donating substituents (*e.g.*,  $\text{Y} = \text{SPh}$ ,<sup>7b</sup>  $\text{OMe}$ ,<sup>7e</sup>  $\text{OEt}$ ,<sup>7e</sup>  $\text{OPr}^i$ ,<sup>8b</sup>  $\text{NMe}_2$ ,<sup>7d</sup> or  $\text{NPh}_2$ ,<sup>8a</sup>) the products isolated have lost one nitric oxide ligand, as illustrated in equation (1). These reactions likely proceed via the intermediate  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})_2\text{Y}]$  **A**, which then either dimerises to  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})(\mu\text{-Y})_2]$  **B**,<sup>7</sup> or forms chromium(II) species  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})(\text{X})\text{Y}]$  **C**,<sup>8</sup> via a subsequent one-electron oxidation process.

The reaction depicted in equation (1) initially seems counter-intuitive due to the unexpected ejection of a strong  $\pi$ -acceptor nitrosyl ligand being triggered by increased electron donation



from the  $\text{Y}^-$  ligand. Furthermore,  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})_2\text{X}]$  complexes containing strong  $\sigma$ -donor alkyl ligands display no propensity to lose NO.<sup>5</sup> The observed reactivity is limited to  $\pi$ -donor  $\text{Y}^-$  ligands because  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})_2]^+$  is a  $\pi$ -loaded fragment. The cyclopentadienyl and nitrosyl ligands each form one  $\sigma$  and two  $\pi$  interactions, leaving no empty orbital available on the  $\text{M}(1\sigma, 2\pi)_3$  fragment to accept  $\pi$  donation from the  $\text{Y}^-$  ligand.<sup>9</sup> This unfavourable filled/filled  $\pi$ -interaction is relieved by loss of nitric oxide. Related ligand-loss reactions have also been attributed to the repulsion between filled p orbitals on  $\pi$ -donor ligands and filled metal orbitals.<sup>10</sup> These reactions typically involve the dissociation of two-electron donor ligands such as  $\text{CO}$ <sup>11a</sup> or  $\text{PPh}_3$ ,<sup>11b,c</sup> and thus do not result in a change in electron count at the metal centre, unlike the one-electron oxidation which formally accompanies the loss of NO radical.

Taken together, these observations are of potential significance for the rational design of metallonitrosyl complexes capable of releasing NO *in vivo*.<sup>12</sup> Several features make  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})_2\text{X}]$  complexes particularly suitable as model compounds for the study of NO release from transition metals. These  $\text{Cr}^0$ ,  $d^6$  complexes† are diamagnetic with two equivalents

† Dedicated to the memory of Professor Sir Geoffrey Wilkinson.  
 $\pi$  Bonding and reactivity in transition-metal nitrosyl complexes. Part 4.<sup>1</sup>

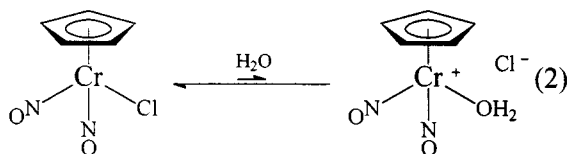
‡ Linear dinitrosyl compounds of  $\text{Cr}^0$  are more accurately described as having a  $\{\text{Cr}(\text{NO})_2\}^6$  electronic configuration using Enemark–Feltham notation.<sup>13</sup>

of NO per Cr atom, and the paramagnetic Cr<sup>I</sup>, d<sup>5</sup> mononitrosyl compounds that would be the products expected upon loss of NO radical have been shown to be unusually inert.<sup>14</sup> We have recently investigated the oxidatively-triggered NO release from [Cr(η-C<sub>5</sub>H<sub>5</sub>)(NO)Cl<sub>2</sub>]<sup>-</sup> in organic solvents.<sup>15</sup> Given the stability of the [Cr(η-C<sub>5</sub>H<sub>5</sub>)(NO)<sub>2</sub>]<sup>+</sup> fragment in aqueous solution,<sup>2</sup> we hypothesised that treatment of aqueous [Cr(η-C<sub>5</sub>H<sub>5</sub>)(NO)<sub>2</sub>·(H<sub>2</sub>O)]<sup>+</sup> with base should form [Cr(η-C<sub>5</sub>H<sub>5</sub>)(NO)<sub>2</sub>(OH)]. The strong π-donor hydroxide ligand might then induce loss of one of the nitrosyl ligands under mild, physiologically-relevant conditions. Our investigations of these concepts of π loading and NO loss are presented here.

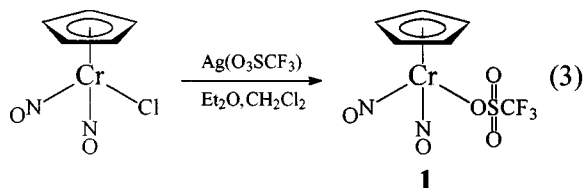
## Results and Discussion

### Synthesis of [Cr(η-C<sub>5</sub>R<sub>5</sub>)(NO)<sub>2</sub>(CF<sub>3</sub>SO<sub>3</sub>)]

The slight water solubility of [Cr(η-C<sub>5</sub>H<sub>5</sub>)(NO)<sub>2</sub>Cl] initially reported by Piper and Wilkinson<sup>2</sup> is presumably due to hydrolysis of the Cr–Cl bond as illustrated in equation (2).



Similar reactions have been studied in detail for [M(η-C<sub>5</sub>-H<sub>5</sub>)<sub>2</sub>Cl<sub>2</sub>] complexes (M = Ti, Zr, V or Mo).<sup>16</sup> More recent investigations of aqueous organometallic chemistry<sup>17</sup> have relied on the trifluoromethanesulfonate (CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>) ligand which dissociates more readily from the metal centre.<sup>18</sup> As shown in equation (3), [Cr(η-C<sub>5</sub>H<sub>5</sub>)(NO)<sub>2</sub>(CF<sub>3</sub>SO<sub>3</sub>)] **1** can be



synthesised by treatment of [Cr(η-C<sub>5</sub>H<sub>5</sub>)(NO)<sub>2</sub>Cl] with Ag(CF<sub>3</sub>SO<sub>3</sub>), in a manner analogous to previous chloride abstraction reactions with AgPF<sub>6</sub><sup>19</sup> and AgBF<sub>4</sub>.<sup>20</sup> The preparation of **1** is usually best performed in diethyl ether, but larger scale reactions (>1 mmol) give optimum results when conducted in a 1:1 mixture of diethyl ether and CH<sub>2</sub>Cl<sub>2</sub>.

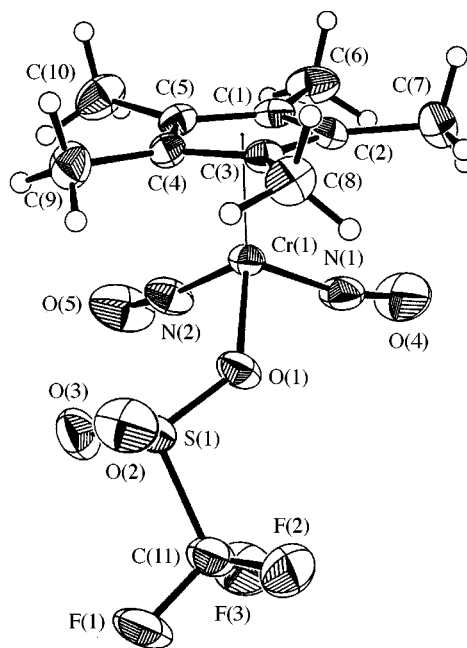
Complex **1** is soluble in CH<sub>2</sub>Cl<sub>2</sub>, CH<sub>3</sub>CN, alcohols, water, ethers and aromatic solvents, and is isolated as large, air-stable, black crystals. The single resonance in the <sup>1</sup>H NMR spectrum of **1** corresponds to the cyclopentadienyl ligand, and the higher-energy value of the IR ν(NO) bands of **1** at 1836 and 1730 cm<sup>-1</sup> (CH<sub>2</sub>Cl<sub>2</sub>) as compared to the Cl precursor reflects the greater electron-withdrawing properties of the CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> ligand.<sup>15</sup> The Nujol mull IR spectrum also contains six bands between 1000 and 1350 cm<sup>-1</sup>, consistent with the presence of a covalently bound CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> ligand.<sup>21</sup>

Attempts to obtain single crystals of **1** from numerous solvent mixtures resulted only in twinned crystals. In order to confirm the presence of a Cr–O<sub>3</sub>SCF<sub>3</sub> bond in **1**, the related [Cr(η-C<sub>5</sub>Me<sub>5</sub>)(NO)<sub>2</sub>(CF<sub>3</sub>SO<sub>3</sub>)] **2** was synthesised. As expected, the pentamethylcyclopentadienyl ligand imparted increased solubility and crystallinity to the complex,<sup>22</sup> and a sample suitable for X-ray crystallographic analysis was obtained from diethyl ether. The solid-state molecular structure of **2** is illustrated in Fig. 1, and its intramolecular parameters are listed in Table 1. The CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> group is indeed covalently bound to the metal centre in **2**; the Cr–O distance of 2.030(2) Å is consistent with a Cr–O single bond.

**Table 1** Bond lengths (Å) and angles (°) for [Cr(η-C<sub>5</sub>Me<sub>5</sub>)(NO)<sub>2</sub>(CF<sub>3</sub>SO<sub>3</sub>)] **2**\*

|                 |          |                 |          |
|-----------------|----------|-----------------|----------|
| Cr(1)–O(1)      | 2.030(2) | Cr(1)–N(1)      | 1.713(3) |
| Cr(1)–N(2)      | 1.712(3) | Cr(1)–C(1)      | 2.176(3) |
| Cr(1)–C(2)      | 2.226(3) | Cr(1)–C(3)      | 2.253(3) |
| Cr(1)–C(4)      | 2.211(3) | Cr(1)–C(5)      | 2.211(3) |
| Cr(1)–CP        | 1.85     | S(1)–O(1)       | 1.475(2) |
| S(1)–O(2)       | 1.419(3) | S(1)–O(3)       | 1.428(3) |
| S(1)–C(11)      | 1.810(4) | F(1)–C(11)      | 1.330(4) |
| F(2)–C(11)      | 1.317(4) | F(3)–C(11)      | 1.306(4) |
| O(4)–N(1)       | 1.169(3) | O(5)–N(2)       | 1.167(3) |
| C(1)–C(2)       | 1.438(4) | C(1)–C(5)       | 1.413(4) |
| C(1)–C(6)       | 1.504(4) | C(2)–C(3)       | 1.409(4) |
| C(2)–C(7)       | 1.498(4) | C(3)–C(4)       | 1.429(4) |
| C(3)–C(8)       | 1.485(4) | C(4)–C(5)       | 1.428(4) |
| C(4)–C(9)       | 1.493(4) | C(5)–C(10)      | 1.492(4) |
| O(1)–Cr(1)–N(1) | 100.8(1) | O(1)–Cr(1)–N(2) | 101.3(1) |
| O(1)–Cr(1)–CP   | 117.3    | N(1)–Cr(1)–N(2) | 95.3(2)  |
| N(1)–Cr(1)–CP   | 118.0    | N(2)–Cr(1)–CP   | 120.2    |
| O(1)–S(1)–O(2)  | 112.8(2) | O(1)–S(1)–O(3)  | 114.1(1) |
| O(1)–S(1)–C(11) | 101.0(2) | O(2)–S(1)–O(3)  | 117.7(2) |
| O(2)–S(1)–C(11) | 104.2(2) | O(3)–S(1)–C(11) | 104.7(2) |
| Cr(1)–O(1)–S(1) | 131.7(1) | Cr(1)–N(1)–O(4) | 165.7(3) |
| Cr(1)–N(2)–O(5) | 169.9(3) | C(2)–C(1)–C(5)  | 108.2(3) |
| C(2)–C(1)–C(6)  | 125.1(3) | C(5)–C(1)–C(6)  | 126.5(3) |
| C(1)–C(2)–C(3)  | 107.8(3) | C(1)–C(2)–C(7)  | 125.4(3) |
| C(3)–C(2)–C(7)  | 126.7(3) | C(2)–C(3)–C(4)  | 108.2(3) |
| C(2)–C(3)–C(8)  | 126.4(3) | C(4)–C(3)–C(8)  | 125.3(3) |
| C(3)–C(4)–C(5)  | 107.9(3) | C(3)–C(4)–C(9)  | 126.1(3) |
| C(5)–C(4)–C(9)  | 125.8(3) | C(1)–C(5)–C(4)  | 107.8(3) |
| C(1)–C(5)–C(10) | 127.0(3) | C(4)–C(5)–C(10) | 125.1(3) |
| S(1)–C(11)–F(1) | 109.5(3) | S(1)–C(11)–F(2) | 111.3(3) |
| S(1)–C(11)–F(3) | 111.7(3) | F(1)–C(11)–F(2) | 107.6(3) |
| F(1)–C(11)–F(3) | 108.5(3) | F(2)–C(11)–F(3) | 108.1(3) |

\* CP refers to the unweighted centroid of the C(1–5) ring.

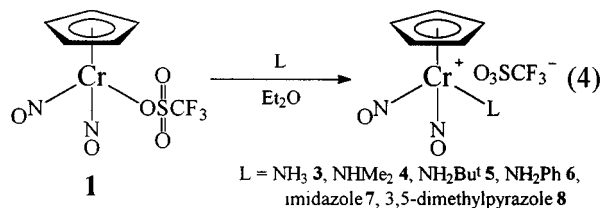


**Fig. 1** The solid-state molecular structure of [Cr(η-C<sub>5</sub>Me<sub>5</sub>)(NO)<sub>2</sub>(CF<sub>3</sub>SO<sub>3</sub>)] **2**, 50% probability ellipsoids

### Reaction of **1** with σ-donor ligands

To test the ability of the CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> ligand to act as a leaving group, **1** was treated with potential σ-donor ligands. As expected, the reaction of **1** with amines and N-containing heterocycles generated the salts [Cr(η-C<sub>5</sub>H<sub>5</sub>)(NO)<sub>2</sub>(L)][CF<sub>3</sub>SO<sub>3</sub>]<sup>-</sup> (L = NH<sub>3</sub> **3**, NHMe<sub>2</sub> **4**, NH<sub>2</sub>Bu<sup>t</sup> **5**, NH<sub>2</sub>Ph **6**, imidazole **7**, 3,5-dimethylpyrazole **8**) in good to moderate yields as analytically pure, air-stable green powders. This reaction is most conveni-

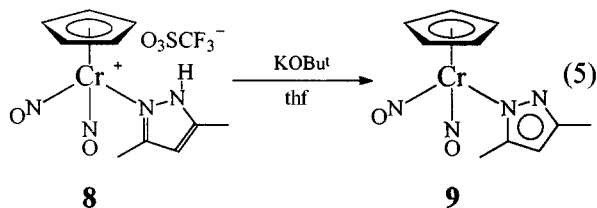
ently conducted in diethyl ether, as the resulting cationic products are ether insoluble and are readily isolated by filtration. As shown in equation (4), isolated  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})_2(\text{CF}_3\text{SO}_3)]$



may be used for these reactions, or **1** may be generated *in situ* from  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})_2\text{Cl}]$  and  $\text{Ag}(\text{CF}_3\text{SO}_3)$  in diethyl ether.

Compound **6** was treated with  $\text{LiBu}^n$  or  $\text{KOBU}^t$  in (tetrahydrofuran) thf in an attempt to generate the neutral dinitrosyl amide complex  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})_2(\text{NHPh})]$  at low temperatures by deprotonation. Monitoring this reaction by solution IR spectroscopy did not reveal any  $\nu(\text{NO})$  bands consistent with  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})_2(\text{NHPh})]$ . Instead, the  $\nu(\text{NO})$  bands of **6** were replaced upon slow warming with many weak bands in the region expected for mononitrosyl products; the precise nature of these products was not investigated further.

In contrast, the heterocycle-containing species **7** and **8** reacted cleanly as monitored by IR spectroscopy. The product of **7** and  $\text{LiBu}^n$  or  $\text{KOBU}^t$  displayed new  $\nu(\text{NO})$  bands at 1817 and 1712  $\text{cm}^{-1}$  ( $\text{CH}_2\text{Cl}_2$ ), but the presumed  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})_2(\text{N}_2\text{C}_3\text{H}_3)]$  product cannot be separated from the  $\text{CF}_3\text{SO}_3^-$  containing by-product. In contrast, the neutral 3,5-dimethylpyrazolyl product  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})_2(\text{N}_2\text{C}_5\text{H}_7)]$  **9** can be isolated in a pure state due to its greater solubility [equation (5)].

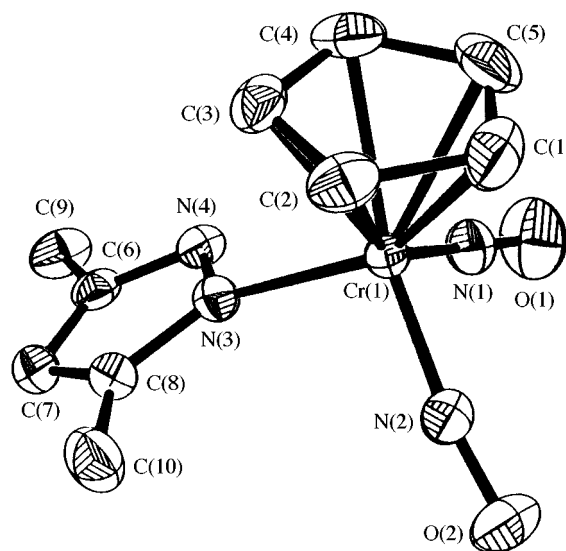


Complex **9** is relatively air-stable in the solid state, and is soluble in thf,  $\text{CH}_2\text{Cl}_2$ ,  $\text{C}_6\text{H}_6$  and  $\text{Et}_2\text{O}$ . The shift in  $\nu(\text{NO})$  from 1839 and 1722  $\text{cm}^{-1}$  (Nujol) for cationic **8** to 1800 and 1686  $\text{cm}^{-1}$  (Nujol) for neutral **9** reflects the increase in electron density at the Cr centre that accompanies the deprotonation reaction. The solid-state molecular structure of **9** is illustrated in Fig. 2, and its intramolecular parameters are collected in Table 2. The Cr–N (pyrazolyl) bond length is a relatively long 2.011(2) Å, and the planar pyrazolyl group seems to be oriented so as to avoid unfavourable steric interactions with the  $\text{C}_5\text{H}_5$  ligand. This contrasts with the short Cr–N bonds and electronically-enforced ON–Cr–NR<sub>2</sub> coplanarity recently observed for  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})(\text{NR}_2)]$ -containing species which possess a Cr–N  $\pi$  bond,<sup>1</sup> thereby suggesting that such an interaction is absent in **9**.

The different reactivity observed for **6**, **7** and **8** with strong bases could be due to the different sites of deprotonation. Imidazole and 3,5-dimethylpyrazole contain acidic N–H bonds on the nitrogen atom distal to the Cr centre, which are more sterically accessible than the N–H bonds of the amine complexes. However, we believe that the stability of the  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})_2(\text{N}_2\text{C}_3\text{HR}_2)]$  complexes (R = H or Me) is due to the aromatic nature of the heterocyclic ring. Disruption of the Cr–NO  $\pi$  bonds is avoided by delocalising the filled N p orbital electron density over the  $\text{N}_2\text{C}_3$  moiety. The strong  $\pi$ -donor NHPH ligand presumably formed upon reaction of **6** with base lacks this option to relieve this filled/filled interaction, thereby rendering the complex prone to loss of NO and subsequent

**Table 2** Bond lengths (Å) and angles (°) for  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})_2(\text{N}_2\text{C}_5\text{H}_7)]$  **9**

|                 |            |                 |            |
|-----------------|------------|-----------------|------------|
| Cr(1)–N(1)      | 1.707(2)   | Cr(1)–N(2)      | 1.716(2)   |
| Cr(1)–N(3)      | 2.011(2)   | Cr(1)–C(5)      | 2.192(2)   |
| Cr(1)–C(1)      | 2.198(3)   | Cr(1)–C(4)      | 2.212(2)   |
| Cr(1)–C(2)      | 2.240(2)   | Cr(1)–C(3)      | 2.245(2)   |
| N(1)–O(1)       | 1.168(3)   | N(2)–O(2)       | 1.173(2)   |
| C(1)–C(5)       | 1.392(4)   | C(1)–C(2)       | 1.423(4)   |
| C(2)–C(3)       | 1.402(3)   | C(3)–C(4)       | 1.399(4)   |
| C(4)–C(5)       | 1.401(3)   | N(3)–C(6)       | 1.350(3)   |
| N(3)–N(4)       | 1.383(3)   | N(4)–C(6)       | 1.340(3)   |
| C(6)–C(7)       | 1.393(3)   | C(6)–C(9)       | 1.503(3)   |
| C(7)–C(8)       | 1.380(3)   | C(8)–C(10)      | 1.498(3)   |
| N(1)–Cr(1)–N(2) | 91.86(9)   | N(1)–Cr(1)–N(3) | 95.57(9)   |
| N(2)–Cr(1)–N(3) | 100.29(8)  | N(1)–Cr(1)–C(5) | 90.28(11)  |
| N(2)–Cr(1)–C(5) | 124.14(11) | N(3)–Cr(1)–C(5) | 134.99(10) |
| N(1)–Cr(1)–C(1) | 115.61(11) | N(2)–Cr(1)–C(1) | 94.81(10)  |
| N(3)–Cr(1)–C(1) | 144.83(9)  | C(5)–Cr(1)–C(1) | 36.98(12)  |
| N(1)–Cr(1)–C(4) | 100.71(10) | N(2)–Cr(1)–C(4) | 156.47(10) |
| N(3)–Cr(1)–C(4) | 98.21(9)   | C(5)–Cr(1)–C(4) | 37.11(11)  |
| C(1)–Cr(1)–C(4) | 61.84(11)  | N(1)–Cr(1)–C(2) | 151.45(10) |
| N(2)–Cr(1)–C(2) | 98.61(9)   | N(3)–Cr(1)–C(2) | 108.44(9)  |
| C(5)–Cr(1)–C(2) | 61.87(11)  | C(1)–Cr(1)–C(2) | 37.38(10)  |
| C(4)–Cr(1)–C(2) | 61.52(10)  | N(1)–Cr(1)–C(3) | 136.13(10) |
| N(2)–Cr(1)–C(3) | 131.31(9)  | N(3)–Cr(1)–C(3) | 85.10(8)   |
| C(5)–Cr(1)–C(3) | 61.33(10)  | C(1)–Cr(1)–C(3) | 61.42(9)   |
| C(4)–Cr(1)–C(3) | 36.59(9)   | C(2)–Cr(1)–C(3) | 36.43(9)   |
| O(1)–N(1)–Cr(1) | 172.7(2)   | O(2)–N(2)–Cr(1) | 171.8(2)   |
| C(5)–C(1)–C(2)  | 108.1(2)   | C(5)–C(1)–Cr(1) | 71.3(2)    |
| C(2)–C(1)–Cr(1) | 72.92(14)  | C(3)–C(2)–C(1)  | 106.9(2)   |
| C(3)–C(2)–Cr(1) | 71.98(13)  | C(1)–C(2)–Cr(1) | 69.70(14)  |
| C(4)–C(3)–C(2)  | 108.7(2)   | C(4)–C(3)–Cr(1) | 70.40(13)  |
| C(2)–C(3)–Cr(1) | 71.60(13)  | C(3)–C(4)–C(5)  | 107.8(2)   |
| C(3)–C(4)–Cr(1) | 73.01(14)  | C(5)–C(4)–Cr(1) | 70.7(2)    |
| C(1)–C(5)–C(4)  | 108.4(2)   | C(1)–C(5)–Cr(1) | 71.8(2)    |
| C(4)–C(5)–Cr(1) | 72.2(2)    | C(8)–N(3)–N(4)  | 109.9(2)   |
| C(8)–N(3)–Cr(1) | 132.2(2)   | N(4)–N(3)–Cr(1) | 117.87(13) |
| C(6)–N(4)–N(3)  | 105.7(2)   | N(4)–C(6)–C(7)  | 110.8(2)   |
| N(4)–C(6)–C(9)  | 119.8(2)   | C(7)–C(6)–C(9)  | 129.4(2)   |
| C(8)–C(7)–C(6)  | 105.4(2)   | N(3)–C(8)–C(7)  | 108.1(2)   |
| N(3)–C(8)–C(10) | 122.3(2)   |                 |            |



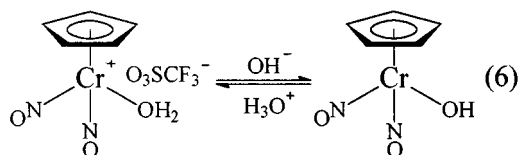
**Fig. 2** The solid-state molecular structure of  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})_2(\text{N}_2\text{C}_5\text{H}_7)]$  **9**, 50% probability ellipsoids

decomposition even when the neutral amide complex is generated under relatively mild conditions.

#### Aqueous chemistry of $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})_2]^+$

With samples of **1** in hand, we could now investigate the aqueous chemistry of the  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})_2]^+$  fragment, to determine if a pH-dependent release of NO would be observed.

As expected, **1** is much more water soluble than  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})_2\text{Cl}]$  due to the readily displaced  $\text{CF}_3\text{SO}_3^-$  ligand.<sup>18</sup> When dissolved in  $\text{D}_2\text{O}$ , **1** shows a single peak in its  $^1\text{H}$  NMR spectrum at  $\delta$  5.90 that is attributable to the  $(\eta\text{-C}_5\text{H}_5)$  ligand of  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})_2(\text{D}_2\text{O})][\text{CF}_3\text{SO}_3]$ . However, in basic  $\text{D}_2\text{O}$ -NaOD solutions, a new cyclopentadienyl peak at  $\delta$  5.75 is the only signal observed; most likely corresponding to the neutral hydroxide complex,  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})_2(\text{DH})]$ . Potentiometric titration of **1** in  $\text{H}_2\text{O}$  using dilute NaOH and  $\text{HO}_3\text{SCF}_3$  solutions determined a  $\text{p}K_{\text{a}}$  value of 6.8 for  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})_2(\text{H}_2\text{O})][\text{CF}_3\text{SO}_3]$ . Consistent with this value, both the  $\delta$  5.75 and 5.90 cyclopentadienyl peaks are present in relatively equal proportions in the  $^1\text{H}$  NMR spectrum when the pH is 6.6. These observations indicate the presence of a pH-dependent equilibrium between  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})_2(\text{H}_2\text{O})][\text{CF}_3\text{SO}_3]$  and  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})_2(\text{OH})]$ , as shown in equation (6).



Thus, aqueous solutions of **1** are unexpectedly stable over a range of pH values, with the  $^1\text{H}$  NMR spectra remaining unchanged for weeks at room temperature under  $\text{N}_2$ . No evidence of hydrolysis of the cyclopentadienyl ligand is observed even at low pH.<sup>16</sup> Even more surprisingly, no evidence for NO loss from  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})_2(\text{OH})]$  at high pH is obtained.

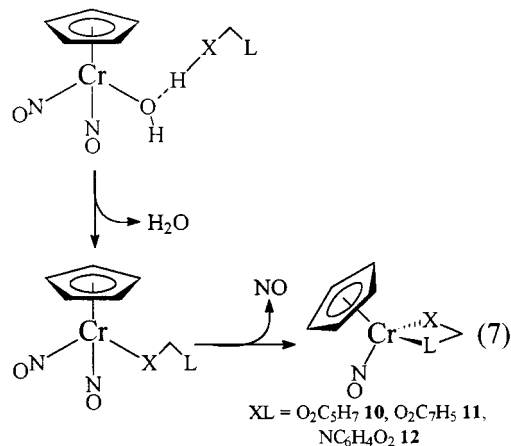
We attribute the unanticipated stability of basic aqueous solutions of **1** to the interaction of the hydrogen atoms of the solvent water molecules with the oxygen atom of the hydroxide ligand of  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})_2(\text{OH})]$ . The Lewis basicity of the hydroxide oxygen atom in  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})_2(\text{OH})]$  has been previously established by the isolation of  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})_2(\text{HO}\cdots\text{A})]$  adducts with Lewis acids  $\{\text{A} = \text{BPH}_3$  or  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})_2]^+\}$ <sup>23</sup> from the basic, aqueous work up of  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})_2(\text{BF}_4)]$ . Also worthy of note is the IR monitoring of the reaction of  $\text{EtO}^-$  and  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})_2\text{Cl}]$  in ethanol which indicates that the species  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})_2(\text{OEt})]$  is stable until the protic solvent is removed *in vacuo*.<sup>7e</sup> Attempts to induce NO loss by generating  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})_2(\text{OH})]$  in aprotic solvents such as thf by reaction of  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})_2(\text{CF}_3\text{SO}_3)]$  with CsOH instead led to the formation of  $\{[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})_2]_2(\mu\text{-OH})\}^+[\text{CF}_3\text{SO}_3]^-$ , identified in solution by IR spectroscopy by comparison with the known  $\text{BF}_4^-$  and  $\text{BPH}_4^-$  analogues.<sup>23</sup> In the absence of a hydrogen-bonding solvent, the initially generated  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})_2(\text{OH})]$  species displaces the  $\text{CF}_3\text{SO}_3^-$  ligand in another molecule of **1** instead of inducing nitrosyl ligand dissociation.

Much research has been conducted recently on alcohol molecules engaged in hydrogen bonding to the oxygen atoms of late-transition-metal alkoxide species, several of which have been characterised in the solid state by X-ray crystallography.<sup>24</sup> These complexes provide an interesting comparison to the Cr nitrosyl complexes reported here, in that in both cases no empty metal orbitals are available to accept  $\pi$  donation, and so strong H-bonding interactions are formed to relieve the resulting filled/filled repulsions.<sup>10</sup> Of particular interest are the studies of Simpson and Bergman<sup>25</sup> who invoke this type of hydrogen bonded species as intermediates in the exchange reactions of alkoxides by protonolysis.

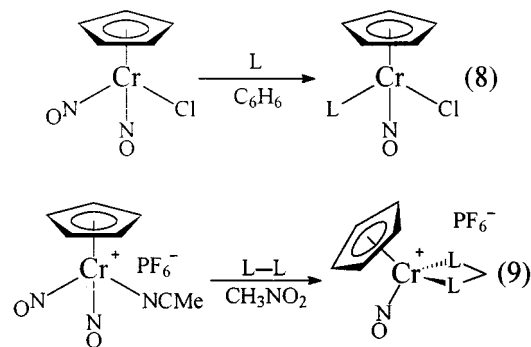
### Synthesis of $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})(\text{LX})]$

While hydrogen bonding prevents one potential route to nitric oxide loss by attenuating the electron density at the hydroxide oxygen of  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})_2(\text{OH})]$ , it presents a second possible route through protonolysis with potentially chelating ligands. Thus, when treated with acids such as acetylacetone,

salicylaldehyde or picolinic acid (pyridinecarboxylic acid) (HXL), *in situ* generated solutions of  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})_2(\text{OH})]$  react slowly to give the *mononitrosyl* products  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})(\text{LX})]$  ( $\text{LX} = \text{O}_2\text{C}_5\text{H}_7$  **10**,  $\text{O}_2\text{C}_7\text{H}_5$  **11**,  $\text{NC}_6\text{H}_4\text{O}_2$  **12**). These compounds slowly precipitate from aqueous solutions as analytically pure powders. These reactions are thought to proceed as illustrated in equation (7). Initial protonolysis of the

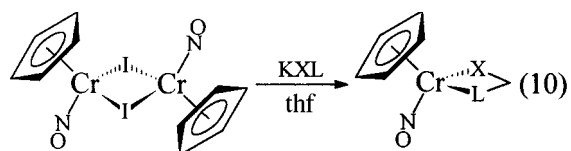


hydroxide ligand occurs *via* a H-bonded intermediate, resulting in a dinitrosyl species with a new Cr–O bond and a dangling Lewis basic heteroatom. The subsequent chelate-assisted intramolecular NO displacement reaction forms a water insoluble paramagnetic product with a six- (**10** or **11**) or five-membered (**12**) metallacyclic ring. Equations (8)<sup>26</sup> and (9)<sup>19</sup> dis-



play previous examples of substitution of nitric oxide from  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})_2]$ -containing species by  $\sigma$ -donor ligands, although these reactions were performed under thermolytic conditions in organic solvents. These harsh conditions contrast sharply with the room-temperature, aqueous solution reactions reported here.

To confirm the identity of the paramagnetic chelate complexes, **10–12** were independently synthesised from  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})(\mu\text{-I})_2]$ <sup>27</sup> and KXL salts in thf [equation (10)]. Compounds

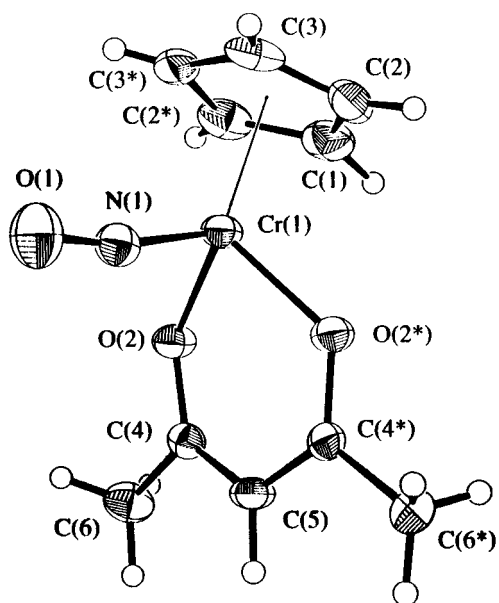


**10–12** are air stable as solids and their  $\nu(\text{NO})$  (1647, 1659 and  $1666\text{ cm}^{-1}$ , respectively), solubility and other physical properties are similar to related, stable 17-valence-electron  $\text{Cr}^{\text{I}}$  mononitrosyl complexes.<sup>14,15</sup> The solid-state molecular structure of **10** was confirmed by X-ray crystallography, as shown in Fig. 3. The intramolecular parameters of **10** are shown in Table 3. The molecule has a mirror plane that passes through the

**Table 3** Bond lengths (Å) and angles (°) for  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})(\text{O}_2\text{C}_5\text{H}_7)]$  **10**\*

|                  |          |                 |          |
|------------------|----------|-----------------|----------|
| Cr(1)–O(2)       | 1.959(2) | Cr(1)–N(1)      | 1.683(5) |
| Cr(1)–C(1)       | 2.255(6) | Cr(1)–C(2)      | 2.231(4) |
| Cr(1)–C(3)       | 2.199(4) | Cr(1)–CP        | 1.89     |
| O(1)–N(1)        | 1.201(5) | O(2)–C(4)       | 1.275(3) |
| C(1)–C(2)        | 1.384(5) | C(2)–C(3)       | 1.381(6) |
| C(3)–C(3')       | 1.393(8) | C(4)–C(5)       | 1.391(3) |
| C(4)–C(6)        | 1.490(5) |                 |          |
| O(2)–Cr(1)–O(2') | 91.0(1)  | O(2)–Cr(1)–N(1) | 98.6(1)  |
| O(2)–Cr(1)–CP    | 119.7    | N(1)–Cr(1)–CP   | 122.6    |
| Cr(1)–O(2)–C(4)  | 124.8(2) | Cr(1)–N(1)–O(1) | 169.5(4) |
| C(2)–C(1)–C(2)   | 107.4(6) | C(1)–C(2)–C(3)  | 108.7(4) |
| C(2)–C(3)–C(3')  | 107.7(3) | O(2)–C(4)–C(5)  | 124.5(3) |
| O(2)–C(4)–C(6)   | 115.5(3) | C(5)–C(4)–C(6)  | 119.9(3) |
| C(4)–C(5)–C(4')  | 125.2(4) |                 |          |

\* CP refers to the unweighted centroid of the C(1–5) ring. Prime refers to symmetry operation:  $x, \frac{1}{2}-y, z$ .

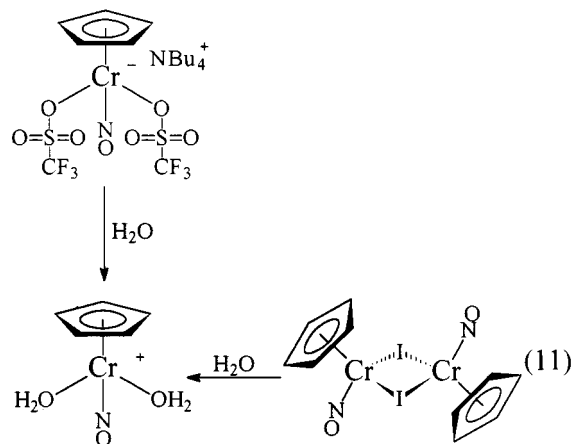


**Fig. 3** The solid-state molecular structure of  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})(\text{O}_2\text{C}_5\text{H}_7)]$  **10**, 50% probability ellipsoids

nitrosyl ligand, the Cr atom, one C atom in the  $\text{C}_5\text{H}_5$  ring and the methine C atom of the acetylacetonate ligand.

#### Aqueous chemistry of $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})(\text{H}_2\text{O})_2]^+$

Since paramagnetic compounds of formula  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})\text{L}_2]^+$  have recently been demonstrated to be remarkably inert,<sup>14</sup> we sought to expand this class of complexes to the bis(aqua) mononitrosyl cation  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})(\text{H}_2\text{O})_2]^+$  which may be synthesised in two ways, as shown in equation (11). Suspensions of  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})(\mu\text{-I})_2]$  in hot water slowly react to give green solutions of  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})(\text{H}_2\text{O})_2]^+$ , while  $[\text{NBu}_4]^+[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})(\text{CF}_3\text{SO}_3)_2]$  dissolves in water at room temperature over 5 min to provide the same complex. Addition of aqueous  $\text{NaBPh}_4$  to concentrated solutions of  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})(\text{H}_2\text{O})_2]^+$  causes the precipitation of  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})(\text{H}_2\text{O})_2][\text{BPh}_4]$  **13** as analytically pure microcrystals. Unfortunately, the  $\text{p}K_a$  of  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})(\text{H}_2\text{O})_2]^+$  could not be determined due to the instability of its conjugate base. At  $\text{pH} > 7$  solutions of  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})(\text{H}_2\text{O})_2]^+$  precipitate  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})(\mu\text{-OH})_2]$  **14** in low yields. Apparently, any hydrogen-bonding interactions that may exist between the expected  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})(\text{OH})(\text{H}_2\text{O})]$  product and the aqueous solvent are insufficient to prevent loss of  $\text{H}_2\text{O}$  and subsequent aggregation reactions. This reactivity contrasts with



the stability of  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})_2(\text{OH})]$ , as expected upon formal replacement of a nitrosyl ligand with an aqua ligand, which should be a much better leaving group. Solutions of  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})(\text{H}_2\text{O})_2]^+$  also react with acetylacetone, salicylaldehyde or picolinic acid to form compounds **10**, **11** and **12**, respectively. These reactions proceed at a qualitatively faster rate than the dinitrosyl reactions described above, again presumably due to the enhanced lability of the aqua ligand compared to the nitrosyl group.

#### Conclusion

The remarkable water stability of the  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})_2]^+$  fragment has been known since the original synthesis of this class of compounds by Piper and Wilkinson<sup>2</sup> in 1956. Subsequent studies directed at the metathesis of the  $\text{Cl}^-$  ligand of  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})_2\text{Cl}]$  with  $\pi$ -donor ligands report only *mono*-nitrosyl products.<sup>7,8</sup> Prompted by these two observations, we postulated that  $\pi$  donation from the hydroxide ligand of  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})_2(\text{OH})]$  might trigger nitric oxide release under physiologically relevant conditions. This mode of NO loss was not observed, as  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})_2(\text{OH})]$  remains unchanged for weeks in basic aqueous solution. The build-up of electron density at the hydroxide oxygen is presumably relieved through hydrogen-bonding interactions with the aqueous solvent.

While hydrogen bonding may prevent the spontaneous release of nitric oxide, it likely *helps* the loss of NO upon treatment of  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})_2(\text{OH})]$  with acetylacetone and related acids. In reactions which likely consist of sequential hydrogen bonding, protonolysis and chelate-assisted nitrosyl-displacement steps, NO is liberated at room temperature in aqueous solution. The identity of the paramagnetic, water insoluble mononitrosyl products was confirmed by their independent synthesis from  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})(\mu\text{-I})_2]$  in aqueous solution and organic solvents.

Our future work in this area will continue along three lines:  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})_2\text{X}]$  derivatives with pendant  $\sigma$ -donor ligands capable of nitrosyl displacement will be synthesised; alternative routes to  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})_2(\text{H}_2\text{O})]^+$  and  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})_2(\text{OH})]$  in organic solvents will be investigated; sterically-stabilized, 17-electron species of formula  $[\text{Cr}(\eta\text{-C}_5\text{R}_5)(\text{NO})(\text{NR}_2)]$  will be generated from  $[\text{Cr}(\eta\text{-C}_5\text{Me}_5)(\text{NO})(\mu\text{-Cl})_2]$ <sup>15</sup> and  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})(\text{NPr}^i_2)\text{X}]$  precursors.<sup>28</sup>

#### Experimental

All reactions and subsequent manipulations were performed under anaerobic conditions using an atmosphere of dinitrogen. General procedures routinely employed in these laboratories have been described in detail previously.<sup>29</sup> The complexes  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})_2\text{Cl}]$ ,<sup>2,30</sup>  $[\text{Cr}(\eta\text{-C}_5\text{Me}_5)(\text{NO})_2\text{Cl}]$ ,<sup>29</sup>  $[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})\text{I}]_2$ <sup>27</sup> and  $[\text{NBu}_4]^+[\text{Cr}(\eta\text{-C}_5\text{H}_5)(\text{NO})(\text{CF}_3\text{SO}_3)_2]$ <sup>15</sup> were prepared by the published procedures. All other reagents were used

as received from commercial suppliers. Filtrations were performed through Celite (1 × 2 cm) supported on a medium porosity glass frit unless otherwise specified. Potentiometric titrations were made with a Corning model 340 pH meter with an Aldrich calomel combination electrode.

### Preparation of complexes

**[Cr(η-C<sub>5</sub>H<sub>5</sub>)(NO)<sub>2</sub>(CF<sub>3</sub>SO<sub>3</sub>)] 1.** To [Cr(η-C<sub>5</sub>H<sub>5</sub>)(NO)<sub>2</sub>Cl] (0.655 g, 3.08 mmol) and Ag(CF<sub>3</sub>SO<sub>3</sub>) (0.793 g, 3.09 mmol) was added CH<sub>2</sub>Cl<sub>2</sub> (15 cm<sup>3</sup>) followed by diethyl ether (15 cm<sup>3</sup>). The solution was stirred for 15 min, and then filtered to remove AgCl. The Celite pad was washed with diethyl ether (4 × 5 cm<sup>3</sup>). The volume of the solution was reduced slightly *in vacuo*, then hexanes (15 cm<sup>3</sup>) added. The volume of the solution was again reduced slightly *in vacuo*, and cooled to -30 °C overnight, to provide black crystals of [Cr(η-C<sub>5</sub>H<sub>5</sub>)(NO)<sub>2</sub>(CF<sub>3</sub>SO<sub>3</sub>)] **1** (0.874 g, 87%) (Found: C, 22.3; H, 1.57; N, 8.49%; *M*<sup>+</sup> 326. C<sub>6</sub>H<sub>5</sub>CrF<sub>3</sub>N<sub>2</sub>O<sub>5</sub>S requires C, 22.1; H, 1.55; N, 8.59%; *M* 326); *v*<sub>max</sub>/cm<sup>-1</sup> (Nujol) 1834 and 1729 (NO); (CH<sub>2</sub>Cl<sub>2</sub>) 1836 and 1730; δ<sub>H</sub>(CDCl<sub>3</sub>) 5.82 (5 H, s, C<sub>5</sub>H<sub>5</sub>); *m/z* 326 (*M*<sup>+</sup>), 296 (*M*<sup>+</sup> - NO), 266 (*M*<sup>+</sup> - 2NO).

**[Cr(η-C<sub>5</sub>Me<sub>5</sub>)(NO)<sub>2</sub>(CF<sub>3</sub>SO<sub>3</sub>)] 2.** To [Cr(η-C<sub>5</sub>Me<sub>5</sub>)(NO)<sub>2</sub>Cl] (0.110 g, 0.38 mmol) and Ag(CF<sub>3</sub>SO<sub>3</sub>) (0.100 g, 0.39 mmol) was added diethyl ether (30 cm<sup>3</sup>). The solution was stirred for 15 min, and then filtered to remove AgCl. The Celite pad was washed with diethyl ether (3 × 10 cm<sup>3</sup>). The volume of the solution was reduced *in vacuo* to ≈ 5 cm<sup>3</sup> and cooled to -30 °C overnight to provide dark brown crystals of [Cr(η-C<sub>5</sub>Me<sub>5</sub>)(NO)<sub>2</sub>(CF<sub>3</sub>SO<sub>3</sub>)] **2** (0.125 g, 82%) (Found: C, 33.3; H, 3.87; N, 6.88%; *M*<sup>+</sup> 396. C<sub>11</sub>H<sub>15</sub>CrF<sub>3</sub>N<sub>2</sub>O<sub>5</sub>S requires C, 33.3; H, 3.81; N, 7.07%; *M* 396); *v*<sub>max</sub>/cm<sup>-1</sup> (Nujol) 1794 and 1708 (NO); (CH<sub>2</sub>Cl<sub>2</sub>) 1801 and 1702; δ<sub>H</sub>(CDCl<sub>3</sub>) 1.86 (15 H, s, C<sub>5</sub>Me<sub>5</sub>); *m/z* 396 (*M*<sup>+</sup>), 366 (*M*<sup>+</sup> - NO), 336 (*M*<sup>+</sup> - 2NO).

**[Cr(η-C<sub>5</sub>H<sub>5</sub>)(NO)<sub>2</sub>(NH<sub>3</sub>)] [CF<sub>3</sub>SO<sub>3</sub>] 3.** To a stirred solution of [Cr(η-C<sub>5</sub>H<sub>5</sub>)(NO)<sub>2</sub>(CF<sub>3</sub>SO<sub>3</sub>)] (0.334 g, 1.02 mmol) in diethyl ether (35 cm<sup>3</sup>) was added an excess of CH<sub>2</sub>Cl<sub>2</sub> saturated with NH<sub>3</sub> (≈ 5 cm<sup>3</sup>). A green powder immediately precipitated from solution. The pale yellow supernatant solution was removed by cannulation, and the solid was washed with pentane (2 × 10 cm<sup>3</sup>). Drying *in vacuo* provided the green powder [Cr(η-C<sub>5</sub>H<sub>5</sub>)(NO)<sub>2</sub>(NH<sub>3</sub>)] [CF<sub>3</sub>SO<sub>3</sub>] **3** (0.206 g, 60%) (Found: C, 21.2; H, 2.23; N, 12.2. C<sub>6</sub>H<sub>8</sub>CrF<sub>3</sub>N<sub>3</sub>O<sub>5</sub>S requires C, 21.0; H, 2.35; N, 12.2%); *v*<sub>max</sub>/cm<sup>-1</sup> (Nujol) 1824 and 1735 (NO); (CH<sub>2</sub>Cl<sub>2</sub>) 1830 and 1727; δ<sub>H</sub>[(CD<sub>3</sub>)<sub>2</sub>CO] 3.72 (3 H, br s, NH<sub>3</sub>) and 6.14 (5 H, s, C<sub>5</sub>H<sub>5</sub>); δ<sub>C</sub>[(CD<sub>3</sub>)<sub>2</sub>CO] 104.3 (C<sub>5</sub>H<sub>5</sub>); *m/z* 194 (*M*<sup>+</sup>); 149 (*M*<sup>+</sup>).

**[Cr(η-C<sub>5</sub>H<sub>5</sub>)(NO)<sub>2</sub>(NHMe<sub>2</sub>)] [CF<sub>3</sub>SO<sub>3</sub>] 4.** To a stirred solution of [Cr(η-C<sub>5</sub>H<sub>5</sub>)(NO)<sub>2</sub>(CF<sub>3</sub>SO<sub>3</sub>)] (0.331 g, 1.01 mmol) in diethyl ether (35 cm<sup>3</sup>) was added an excess of CH<sub>2</sub>Cl<sub>2</sub> saturated with NHMe<sub>2</sub> (≈ 4 cm<sup>3</sup>). A green powder immediately precipitated from solution, which was allowed to stir for 5 min. The pale yellow supernatant solution was removed by cannulation, and the solid was washed with pentane (3 × 10 cm<sup>3</sup>). Drying *in vacuo* provided the green powder [Cr(η-C<sub>5</sub>H<sub>5</sub>)(NO)<sub>2</sub>(NHMe<sub>2</sub>)] [CF<sub>3</sub>SO<sub>3</sub>] **4** (0.159 g, 42%) (Found: C, 25.8; H, 3.12; N, 11.2. C<sub>8</sub>H<sub>12</sub>CrF<sub>3</sub>N<sub>3</sub>O<sub>5</sub>S requires C, 25.9; H, 3.26; N, 11.3%); *v*<sub>max</sub>/cm<sup>-1</sup> (Nujol) 1826 and 1709 (NO); (CH<sub>2</sub>Cl<sub>2</sub>) 1825 and 1723; δ<sub>H</sub>(CDCl<sub>3</sub>) 2.77 [6 H, d, NH(CH<sub>3</sub>)<sub>2</sub>], 5.52 [1 H, br s, NH(CH<sub>3</sub>)<sub>2</sub>] and 5.96 (5 H, s, C<sub>5</sub>H<sub>5</sub>); *m/z* 222 (*M*<sup>+</sup>), 192 (*M*<sup>+</sup> - NO); 149 (*M*<sup>+</sup>).

**[Cr(η-C<sub>5</sub>H<sub>5</sub>)(NO)<sub>2</sub>(NH<sub>2</sub>Bu<sup>t</sup>)] [CF<sub>3</sub>SO<sub>3</sub>] 5.** To a stirred solution of [Cr(η-C<sub>5</sub>H<sub>5</sub>)(NO)<sub>2</sub>(CF<sub>3</sub>SO<sub>3</sub>)] (0.163 g, 0.50 mmol) in diethyl ether (30 cm<sup>3</sup>) was added an excess of NH<sub>2</sub>Bu<sup>t</sup> (0.25 cm<sup>3</sup>, 2.3 mmol). A green powder immediately precipitated from solution, which was allowed to stir for 5 min. The pale yellow supernatant solution was removed by cannulation, and the

solid was washed with pentane (2 × 5 cm<sup>3</sup>). Drying *in vacuo* provided the green powder [Cr(η-C<sub>5</sub>H<sub>5</sub>)(NO)<sub>2</sub>(NH<sub>2</sub>Bu<sup>t</sup>)] [CF<sub>3</sub>SO<sub>3</sub>] **5** (0.104 g, 52%) (Found: C, 30.4; H, 4.30; N, 10.3. C<sub>10</sub>H<sub>16</sub>CrF<sub>3</sub>N<sub>3</sub>O<sub>5</sub>S requires C, 30.1; H, 4.04; N, 10.5%); *v*<sub>max</sub>/cm<sup>-1</sup> (Nujol) 1818 and 1700 (NO); (CH<sub>2</sub>Cl<sub>2</sub>) 1822 and 1720; δ<sub>H</sub>(CDCl<sub>3</sub>) 1.34 (9 H, s, NH<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>), 4.16 (2 H, s, NH<sub>2</sub>Bu<sup>t</sup>) and 5.94 (5 H, s, C<sub>5</sub>H<sub>5</sub>); δ<sub>C</sub>(CDCl<sub>3</sub>) 30.0 (NH<sub>2</sub>Bu<sup>t</sup>), 45.1 (NH<sub>2</sub>Bu<sup>t</sup>) and 103.3 (C<sub>5</sub>H<sub>5</sub>); *m/z* 250 (*M*<sup>+</sup>), 220 (*M*<sup>+</sup> - NO), 190 (*M*<sup>+</sup> - 2NO); 149 (*M*<sup>+</sup>).

**[Cr(η-C<sub>5</sub>H<sub>5</sub>)(NO)<sub>2</sub>(NH<sub>2</sub>Ph)] [CF<sub>3</sub>SO<sub>3</sub>] 6.** To a stirred solution of [Cr(η-C<sub>5</sub>H<sub>5</sub>)(NO)<sub>2</sub>(CF<sub>3</sub>SO<sub>3</sub>)] (0.163 g, 0.50 mmol) in diethyl ether (20 cm<sup>3</sup>) was added an excess of NH<sub>2</sub>Ph (0.20 cm<sup>3</sup>, 2.2 mmol). A green powder immediately precipitated from solution, which was stirred for 5 min. The pale yellow supernatant solution was removed by cannulation, and the solid was washed with hexanes (2 × 7 cm<sup>3</sup>). Drying *in vacuo* provided the green microcrystalline powder [Cr(η-C<sub>5</sub>H<sub>5</sub>)(NO)<sub>2</sub>(NH<sub>2</sub>Ph)] [CF<sub>3</sub>SO<sub>3</sub>] **6** (0.170 g, 80%) (Found: C, 34.3; H, 2.88; N, 10.0. C<sub>12</sub>H<sub>12</sub>CrF<sub>3</sub>N<sub>3</sub>O<sub>5</sub>S requires C, 34.4; H, 2.88; N, 10.0%); *v*<sub>max</sub>/cm<sup>-1</sup> (Nujol) 1823 and 1710 (NO); (CH<sub>2</sub>Cl<sub>2</sub>) 1830 and 1728; δ<sub>H</sub>(CDCl<sub>3</sub>) 5.82 (5 H, s, C<sub>5</sub>H<sub>5</sub>) and 6.38-7.22 (5 H, m, NH<sub>2</sub>Ph); δ<sub>C</sub>(CDCl<sub>3</sub>) 102.8 (C<sub>5</sub>H<sub>5</sub>), 119.9 (NH<sub>2</sub>Ph), 125.3 (NH<sub>2</sub>Ph) and 129.5 (NH<sub>2</sub>Ph); *m/z* 270 (*M*<sup>+</sup>), 240 (*M*<sup>+</sup> - NO), 210 (*M*<sup>+</sup> - 2NO); 149 (*M*<sup>+</sup>).

**[Cr(η-C<sub>5</sub>H<sub>5</sub>)(NO)<sub>2</sub>(N<sub>2</sub>C<sub>3</sub>H<sub>4</sub>)] [CF<sub>3</sub>SO<sub>3</sub>] 7.** To a stirred solution of [Cr(η-C<sub>5</sub>H<sub>5</sub>)(NO)<sub>2</sub>(CF<sub>3</sub>SO<sub>3</sub>)] (0.165 g, 0.51 mmol) in diethyl ether (20 cm<sup>3</sup>) was added imidazole (0.046 g, 0.53 mmol) in diethyl ether (20 cm<sup>3</sup>). A green powder immediately precipitated from solution. The pale yellow supernatant solution was removed by cannulation, and the solid was washed with diethyl ether (3 × 5 cm<sup>3</sup>). Drying *in vacuo* provided the green powder [Cr(η-C<sub>5</sub>H<sub>5</sub>)(NO)<sub>2</sub>(N<sub>2</sub>C<sub>3</sub>H<sub>4</sub>)] [CF<sub>3</sub>SO<sub>3</sub>] **7** (0.167 g, 83%) (Found: C, 27.7; H, 2.31; N, 13.9. C<sub>9</sub>H<sub>9</sub>CrF<sub>3</sub>N<sub>4</sub>O<sub>5</sub>S requires C, 27.4; H, 2.30; N, 14.2%); *v*<sub>max</sub>/cm<sup>-1</sup> (Nujol) 1824 and 1720 (NO); (CH<sub>2</sub>Cl<sub>2</sub>) 1832 and 1730; δ<sub>H</sub>(CD<sub>3</sub>CN) 5.88 (5 H, s, C<sub>5</sub>H<sub>5</sub>), 6.95 (1 H, s, CH), 7.29 (1 H, s, CH), 7.86 (1 H, s, CH); δ<sub>C</sub>(CD<sub>3</sub>CN) 104.7 (C<sub>5</sub>H<sub>5</sub>), 120.1 (CH), 132.3 (CH) and 141.7 (CH); *m/z* 357 (*M*<sup>+</sup>), 327 (*M*<sup>+</sup> - NO), 297 (*M*<sup>+</sup> - 2NO); 149 (*M*<sup>+</sup>).

**[Cr(η-C<sub>5</sub>H<sub>5</sub>)(NO)<sub>2</sub>(N<sub>2</sub>C<sub>5</sub>H<sub>8</sub>)] [CF<sub>3</sub>SO<sub>3</sub>] 8.** To a stirred solution of [Cr(η-C<sub>5</sub>H<sub>5</sub>)(NO)<sub>2</sub>(CF<sub>3</sub>SO<sub>3</sub>)] (0.065 g, 0.20 mmol) in diethyl ether (20 cm<sup>3</sup>) was added 3,5-dimethylpyrazole (0.022 g, 0.23 mmol) in diethyl ether (10 cm<sup>3</sup>). A green powder immediately precipitated from solution. The pale yellow supernatant solution was removed by cannulation, and the solid was washed with diethyl ether (3 × 5 cm<sup>3</sup>). Drying *in vacuo* provided the green powder [Cr(η-C<sub>5</sub>H<sub>5</sub>)(NO)<sub>2</sub>(N<sub>2</sub>C<sub>5</sub>H<sub>8</sub>)] [CF<sub>3</sub>SO<sub>3</sub>] **8** (0.071 g, 76%) (Found: C, 31.5; H, 3.21; N, 13.1. C<sub>11</sub>H<sub>13</sub>CrF<sub>3</sub>N<sub>4</sub>O<sub>5</sub>S requires C, 31.3; H, 3.10; N, 13.3%); *v*<sub>max</sub>/cm<sup>-1</sup> (Nujol) 1839 and 1722 (NO); (CH<sub>2</sub>Cl<sub>2</sub>) 1835 and 1730; δ<sub>H</sub>(CD<sub>3</sub>CN) 2.16 (3 H, s, CH<sub>3</sub>), 2.28 (3 H, s, CH<sub>3</sub>), 5.89 (5 H, s, C<sub>5</sub>H<sub>5</sub>) and 6.15 (1 H, s, CH); δ<sub>C</sub>(CD<sub>3</sub>CN) 10.9 (CH<sub>3</sub>), 14.6 (CH<sub>3</sub>), 104.7 (C<sub>5</sub>H<sub>5</sub>), 109.0 (CH), 147.3 (CCH<sub>3</sub>) and 156.4 (CCH<sub>3</sub>); *m/z* 273 (*M*<sup>+</sup>), 243 (*M*<sup>+</sup> - NO); 149 (*M*<sup>+</sup>).

**[Cr(η-C<sub>5</sub>H<sub>5</sub>)(NO)<sub>2</sub>(N<sub>2</sub>C<sub>5</sub>H<sub>7</sub>)] 9.** To [Cr(η-C<sub>5</sub>H<sub>5</sub>)(NO)<sub>2</sub>(N<sub>2</sub>C<sub>5</sub>H<sub>8</sub>)] [CF<sub>3</sub>SO<sub>3</sub>] (0.232 g, 0.55 mmol) and KOBu<sup>t</sup> (0.068 g, 0.61 mmol) was added tetrahydrofuran (≈ 10 cm<sup>3</sup>) *via* vacuum transfer. The solution was stirred for 80 min in an acetone-dry ice bath, and then the solution was taken to dryness *in vacuo*. The residue was extracted with diethyl ether (15 cm<sup>3</sup>) and filtered. The Celite pad was washed with diethyl ether (3 × 5 cm<sup>3</sup>). The volume of the combined filtrates was reduced *in vacuo*, and the solution was cooled to -30 °C overnight, to provide black-green crystals of [Cr(η-C<sub>5</sub>H<sub>5</sub>)(NO)<sub>2</sub>(N<sub>2</sub>C<sub>5</sub>H<sub>7</sub>)] **9** (0.070 g, 47%) (Found: C, 43.4; H, 4.33; N, 19.8%; *M*<sup>+</sup> 272. C<sub>10</sub>H<sub>12</sub>CrN<sub>4</sub>O<sub>2</sub> requires C, 44.1; H, 4.44; N, 20.6%; *M* 272); *v*<sub>max</sub>/cm<sup>-1</sup> (Nujol) 1800 and 1686 (NO); (Et<sub>2</sub>O) 1808 and 1701; δ<sub>H</sub>(C<sub>6</sub>D<sub>6</sub>) 2.19 (3 H,

s, CH<sub>3</sub>), 2.53 (3 H, s, CH<sub>3</sub>), 4.79 (5 H, s, C<sub>5</sub>H<sub>5</sub>) and 6.18 (1 H, s, CH); δ<sub>c</sub>(C<sub>6</sub>D<sub>6</sub>) 14.7 (CH<sub>3</sub>), 15.0 (CH<sub>3</sub>), 102.8 (C<sub>5</sub>H<sub>5</sub>), 105.3 (CH), 149.3 (CCH<sub>3</sub>) and 149.8 (CCH<sub>3</sub>); *m/z* 272 (*M*<sup>+</sup>), 242 (*M*<sup>+</sup> - NO), 212 (*M*<sup>+</sup> - 2NO).

**[Cr(η-C<sub>5</sub>H<sub>5</sub>)(NO)(O<sub>2</sub>C<sub>5</sub>H<sub>7</sub>)] 10.** *Method 1.* To [Cr(η-C<sub>5</sub>H<sub>5</sub>)-(NO)<sub>2</sub>(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>] (0.038 g, 0.117 mmol) and CsOH·H<sub>2</sub>O (0.020 g, 0.12 mmol) was added water (10 cm<sup>3</sup>). The solution was stirred for 30 min, and acetylacetone (0.020 cm<sup>3</sup>, 0.20 mmol) was added *via* syringe. The solution was allowed to stir for 2 d while a green powder precipitated from solution. The solid was collected by filtration in air, washed with cold water and dried *in vacuo* to provide the green powder [Cr(η-C<sub>5</sub>H<sub>5</sub>)(NO)(O<sub>2</sub>C<sub>5</sub>H<sub>7</sub>)] **10** (0.012 g, 42%) (Found: C, 48.5; H, 4.96; N, 5.57%; *M*<sup>+</sup> 246. C<sub>10</sub>H<sub>12</sub>CrNO<sub>3</sub> requires C, 48.8; H, 4.91; N, 5.96%; *M* 246); *v*<sub>max</sub>/cm<sup>-1</sup> (Nujol) 1647 (NO); (CH<sub>2</sub>Cl<sub>2</sub>) 1656; *m/z* 246 (*M*<sup>+</sup>), 216 (*M*<sup>+</sup> - NO).

*Method 2.* To a stirred solution of [NBu<sub>4</sub>][Cr(η-C<sub>5</sub>H<sub>5</sub>)-(NO)(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>] (0.118 g, 0.182 mmol) in water (5 cm<sup>3</sup>) was added acetylacetone (0.025 cm<sup>3</sup>, 0.243 mmol). Within 1 min, a green solid precipitated out of solution. After 1 h, the solid was collected by filtration in air, washed with water and dried *in vacuo*. The green powder was identified as [Cr(η-C<sub>5</sub>H<sub>5</sub>)(NO)(O<sub>2</sub>C<sub>5</sub>H<sub>7</sub>)] **10** by infrared spectroscopy and mass spectrometry (0.089 g, 52%) (Found *M*<sup>+</sup> 246; C<sub>10</sub>H<sub>12</sub>CrNO<sub>3</sub> requires *M* 246); *v*<sub>max</sub>/cm<sup>-1</sup> (Nujol) 1647 (NO).

*Method 3.* Tetrahydrofuran (≈5 cm<sup>3</sup>) was vacuum transferred onto [Cr(η-C<sub>5</sub>H<sub>5</sub>)(NO)(μ-I)]<sub>2</sub> (0.083 g, 0.151 mmol) and K(O<sub>2</sub>C<sub>5</sub>H<sub>7</sub>) (0.052 g, 0.377 mmol). Diethyl ether (5 cm<sup>3</sup>) was added and the solution was stirred for 12 h. The solution was filtered through alumina (1 × 2 cm) and the column was washed with diethyl ether (2 × 10 cm<sup>3</sup>). The solution was reduced *in vacuo* to one-third volume and hexanes added (10 cm<sup>3</sup>). The solution was cooled to -30 °C overnight, to provide green crystals, which were identified as [Cr(η-C<sub>5</sub>H<sub>5</sub>)(NO)(O<sub>2</sub>C<sub>5</sub>H<sub>7</sub>)] **10** by infrared spectroscopy, mass spectrometry and single-crystal X-ray diffraction (0.051 g, 68%) (Found *M*<sup>+</sup> 246; C<sub>10</sub>H<sub>12</sub>CrNO<sub>3</sub> requires *M* 246); *v*<sub>max</sub>/cm<sup>-1</sup> (Nujol) 1648 (NO).

**[Cr(η-C<sub>5</sub>H<sub>5</sub>)(NO)(O<sub>2</sub>C<sub>7</sub>H<sub>5</sub>)] 11.** This compound was prepared by the methods used for **10**, substituting salicylaldehyde for acetylacetone to give [Cr(η-C<sub>5</sub>H<sub>5</sub>)(NO)(O<sub>2</sub>C<sub>7</sub>H<sub>5</sub>)] **11** (84%) (Found: C, 53.6; H, 3.79; N, 5.15%; *M*<sup>+</sup> 268. C<sub>12</sub>H<sub>10</sub>CrNO<sub>3</sub> requires C, 53.7; H, 3.76; N, 5.22%; *M* 268); *v*<sub>max</sub>/cm<sup>-1</sup> (Nujol) 1659 (NO); (Et<sub>2</sub>O) 1677; *m/z* 268 (*M*<sup>+</sup>), 238 (*M*<sup>+</sup> - NO).

**[Cr(η-C<sub>5</sub>H<sub>5</sub>)(NO)(NC<sub>6</sub>H<sub>4</sub>O<sub>2</sub>)] 12.** This compound was prepared by the methods used for **10**, substituting picolinic acid for acetylacetone to give [Cr(η-C<sub>5</sub>H<sub>5</sub>)(NO)(NC<sub>6</sub>H<sub>4</sub>O<sub>2</sub>)] **12** (59%) (Found: C, 48.9; H, 3.36; N, 10.4; *M*<sup>+</sup> 269. C<sub>11</sub>H<sub>9</sub>CrN<sub>2</sub>O<sub>3</sub> requires C, 49.1; H, 3.37; N, 10.4; *M* 269); *v*<sub>max</sub>/cm<sup>-1</sup> (Nujol) 1666 (NO); (CH<sub>2</sub>Cl<sub>2</sub>) 1683; *m/z* 269 (*M*<sup>+</sup>), 239 (*M*<sup>+</sup> - NO), 195 (*M*<sup>+</sup> - NO - C<sub>5</sub>H<sub>5</sub>).

**[Cr(η-C<sub>5</sub>H<sub>5</sub>)(NO)(H<sub>2</sub>O)<sub>2</sub>][BPh<sub>4</sub>]] 13.** A suspension of [Cr(η-C<sub>5</sub>H<sub>5</sub>)(NO)(μ-I)]<sub>2</sub> (0.260 g, 0.474 mmol) in water (10 cm<sup>3</sup>) was stirred and heated to 70 °C for 30 min. The clear green solution was filtered, and to the filtrate was added NaBPh<sub>4</sub> (0.680 g, 1.99 mmol) in water (5 cm<sup>3</sup>). A microcrystalline solid immediately formed, and was collected by filtration, washed with water (2 × 5 cm<sup>3</sup>) then with hexanes (4 × 5 cm<sup>3</sup>) to give [Cr(η-C<sub>5</sub>H<sub>5</sub>)(NO)(H<sub>2</sub>O)<sub>2</sub>][BPh<sub>4</sub>]] **13** (0.280 g, 53%) (Found: C, 69.5; H, 5.86; N, 2.80. C<sub>29</sub>H<sub>29</sub>BCrNO<sub>3</sub> requires C, 69.3; H, 5.82; N, 2.80%); *v*<sub>max</sub>/cm<sup>-1</sup> (Nujol) 1692 (NO).

**[Cr(η-C<sub>5</sub>H<sub>5</sub>)(NO)(μ-OH)]<sub>2</sub> 14.** A suspension of [Cr(η-C<sub>5</sub>H<sub>5</sub>)-(NO)(μ-I)]<sub>2</sub> (0.150 g, 0.273 mmol) in water (10 cm<sup>3</sup>) was stirred and heated to 70 °C for 30 min. The clear green solution was filtered, and to the filtrate was added 1 M NaOH until the pH was 8.6. Within 10 min, brown powder started to precipitate

from solution. After being stirred for 12 h, the solution was filtered in air, and washed with water (2 × 5 cm<sup>3</sup>) to yield a metallic brown powder [Cr(η-C<sub>5</sub>H<sub>5</sub>)(NO)(μ-OH)]<sub>2</sub> **14** (0.020 g, 22%) (Found: C, 36.35; H, 3.80; N, 8.38; *M*<sup>+</sup> = 328. C<sub>10</sub>H<sub>12</sub>Cr<sub>2</sub>N<sub>2</sub>O<sub>4</sub> requires C, 36.6; H, 3.66; N, 8.54; *M* = 328); *v*<sub>max</sub>/cm<sup>-1</sup> (Nujol) 1595 (NO); *m/z* 328 (*M*<sup>+</sup>), 298 (*M*<sup>+</sup> - NO), 268 (*M*<sup>+</sup> - 2NO).

#### X-Ray crystallographic analysis of [Cr(η-C<sub>5</sub>Me<sub>5</sub>)(NO)<sub>2</sub>-(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>] 2

**Crystal data.** C<sub>11</sub>H<sub>15</sub>CrF<sub>3</sub>N<sub>2</sub>O<sub>5</sub>S, *M* = 396.30, space group *P*<sub>2</sub><sub>1</sub>/*n* (no. 14), monoclinic, *a* = 8.575(1), *b* = 8.642(1), *c* = 21.8626(9) Å, β = 91.760(7), *U* = 1619.4(3) Å<sup>3</sup> (by least-squares refinement on the setting angles for 25 reflections with 20 < 2θ < 29°, λ = 0.71069 Å, *T* = 21 °C), *Z* = 4, *D*<sub>c</sub> = 1.625 g cm<sup>-3</sup>, *F*(000) = 808. Brown prisms, crystal dimensions 0.20 × 0.40 × 0.40 mm, μ(Mo-Kα) = 8.65 cm<sup>-1</sup>.

**Data collection and processing.**<sup>29</sup> Rigaku AFC6S diffractometer, ω-2θ scan mode, ω-scan width 1.21 + 0.35 tan θ, ω-scan speed 16° min<sup>-1</sup> (up to 8 rescans), graphite-monochromated Mo-Kα radiation; 5007 unique reflections measured (1 < θ < 30°, *h*, *k*, ± *l*), 2546 having *I* ≥ 3σ(*I*). Absorption correction: azimuthal scans for three reflections (relative transmission factors 0.880–1.000). The intensities of three standard reflections, measured each 200 reflections, decayed linearly by 2.6% (correction applied).

**Structure analysis and refinement.** Direct methods followed by Fourier synthesis. Full-matrix least squares with all non-hydrogen atoms anisotropic and hydrogen atoms in calculated positions [C-H = 0.98 Å, *B*<sub>iso</sub> = 1.2*B*(parent atom)]. Statistical weights = 4*F*<sub>o</sub><sup>2</sup>/σ<sup>2</sup>(*F*<sup>2</sup>).<sup>29</sup> Final *R* = Σ||*F*<sub>o</sub> - *F*<sub>c</sub>||/Σ|*F*<sub>o</sub>| = 0.039, *R*' = (Σw(|*F*<sub>o</sub> - *F*<sub>c</sub>|)<sup>2</sup>/Σw|*F*<sub>o</sub>|<sup>2</sup>)<sup>1/2</sup> = 0.039 for 2546 reflections with *I* ≥ 3σ(*I*). Computer programs and source of scattering factors are given in ref. 29. Bond lengths and bond angles appear in Table 1.

#### X-Ray crystallographic analysis of [Cr(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(NO)<sub>2</sub>-(N<sub>2</sub>C<sub>5</sub>H<sub>7</sub>)] 9

**Crystal Data.** C<sub>10</sub>H<sub>12</sub>CrN<sub>4</sub>O<sub>2</sub>, *M* = 272.24, space group *C*2/*c* (no. 15), monoclinic, *a* = 18.3382(4), *b* = 11.1774(3), *c* = 12.9102(1) Å, β = 121.386(1)°, *U* = 2380.31(8) Å<sup>3</sup> [by least-squares refinement on *F*<sup>2</sup> for three sets of 20 frames with 2.16 < 2θ < 25.03°, λ = 0.71073 Å, *T* = 173(2) K], *Z* = 8, *D*<sub>c</sub> = 1.519 g cm<sup>-3</sup>, *F*(000) = 1120. Green blocks, crystal dimensions 0.45 × 0.42 × 0.30 mm, μ(Mo-Kα) = 0.956 mm<sup>-1</sup>.

**Data collection and processing.** Siemens SMART Platform CCD diffractometer, hemisphere collection (randomly oriented region of reciprocal space surveyed to the extent of 1.3 hemispheres to a resolution of 0.84 Å. Three major swaths of frames were collected with 0.30° steps in ω); 5803 reflections collected with 2072 independent reflections (*R*<sub>int</sub> = 0.0229). No intensity checks were made. Absorption correction = semiempirical.<sup>31</sup>

**Structure analysis and refinement.** The structure was solved by direct methods and refined by full-matrix least squares on *F*<sup>2</sup>.<sup>32</sup> Statistical weights = [σ<sup>2</sup>(*F*<sub>o</sub><sup>2</sup>) + (*AP*)<sup>2</sup> + *BP*]<sup>-1</sup>, where *P* = (*F*<sub>o</sub><sup>2</sup> + *F*<sub>c</sub><sup>2</sup>)/3, *A* = 0.0384 and *B* = 5.3763. Final *R*1 = 0.0318, *wR*2 = 0.0815 for 2072 reflections with *I* ≥ 2σ(*I*), goodness of fit on *F*<sup>2</sup> = 1.021. Bond lengths and bond angles appear in Table 2.

#### X-Ray crystallographic analysis of [Cr(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(NO)-(O<sub>2</sub>C<sub>5</sub>H<sub>7</sub>)] 10

**Crystal data.** C<sub>10</sub>H<sub>12</sub>CrNO<sub>3</sub>, *M* = 246.21, space group *Pnma* (no. 62), orthorhombic, *a* = 17.373(2), *b* = 8.833(1), *c* = 6.926(2) Å, *U* = 1062.8(7) Å<sup>3</sup> (by least-squares refinement on setting angles for 25 reflections with 17° < 2θ < 28°, λ = 0.71069 Å,

$T = 21\text{ }^\circ\text{C}$ ),  $Z = 4$ ,  $D_c = 1.539\text{ g cm}^{-3}$ ,  $F(000) = 508$ . Green plates, crystal dimensions  $0.07 \times 0.30 \times 0.30\text{ mm}$ ,  $\mu(\text{Mo-K}\alpha) = 10.62\text{ cm}^{-1}$ .

**Data collection and processing.**<sup>29</sup> Rigaku AFC6S diffractometer,  $\omega$ - $2\theta$  scan mode,  $\omega$ -scan width  $1.21 + 0.35 \tan \theta$ ,  $\omega$ -scan speed  $16^\circ\text{ min}^{-1}$  (up to 8 rescans), graphite-monochromated Mo-K $\alpha$  radiation; 1822 unique reflections measured ( $1 < \theta < 30^\circ$ ,  $h, k, l$ ), 787 having  $I \geq 3\sigma(I)$ . Absorption correction: azimuthal scans for three reflections (relative transmission factors 0.756–1.000). The intensities of three standard reflections, measured each hour of X-ray exposure time, decayed linearly by 2.0% (linear decay correction applied).

**Structure analysis and refinement.** Direct methods followed by Fourier synthesis. The molecule lies on a crystallographic mirror plane. Full-matrix least squares with all non-hydrogen atoms anisotropic and hydrogen atoms in calculated positions [ $C-H = 0.98\text{ \AA}$ ,  $B_{\text{iso}} = 1.2B(\text{parent atom})$ ]. Statistical weights =  $4F_o/\sigma^2(F_o)$ .<sup>29</sup> Final  $R = \sum||F_o| - |F_c||/\sum|F_o| = 0.037$ ,  $R' = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2} = 0.033$  for 787 reflections with  $I \geq 3\sigma(I)$ . Computer programs and source of scattering factors are given in ref. 29. Bond lengths and bond angles appear in Table 3.

CCDC reference number 186/598.

## Acknowledgements

We are grateful to the Natural Sciences and Engineering Research Council of Canada for support of this work in the form of grants (to P. L.). We also acknowledge Dr. Michael J. Shaw for preliminary investigation of the aqueous mononitrosyl chromium chemistry.

## References

- 1 Part 3, J. Kuzelka, P. Legzdins, S. J. Rettig and K. M. Smith, *Organometallics*, in the press.
- 2 T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 1956, **2**, 38.
- 3 E. Uhlig, *Organometallics*, 1993, **12**, 4751 and refs. therein.
- 4 G. Wilkinson and F. A. Cotton, *Prog. Inorg. Chem.*, 1959, **1**, 1.
- 5 (a) T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 1956, **3**, 104; (b) J. A. Hanna and A. Wojcicki, *Inorg. Chim. Acta*, 1974, **9**, 55; (c) J. K. Hoyano, P. Legzdins and J. T. Malito, *J. Chem. Soc., Dalton Trans.*, 1975, 1022; (d) P. Legzdins, G. B. Richter-Addo, B. Wassink, F. W. B. Einstein, R. H. Jones and A. C. Willis, *J. Am. Chem. Soc.*, 1989, **111**, 2097; (e) J. L. Hubbard and W. K. McVicar, *Organometallics*, 1990, **9**, 2683.
- 6 (a) R. B. King and N. Welcman, *Inorg. Chem.*, 1969, **8**, 2540; (b) M. A. Bush and G. A. Sim, *J. Chem. Soc. A*, 1970, 605; (c) B. W. Hames and P. Legzdins, *Organometallics*, 1982, **1**, 116; (d) J. L. Hubbard, C. R. Zoch and W. L. Elcesser, *Inorg. Chem.*, 1993, **32**, 3333.
- 7 (a) M. Ahmad, R. Bruce and G. Knox, *Z. Naturforsch., Teil B*, 1966, **21**, 289; (b) A. T. McPhail and G. A. Sim, *J. Chem. Soc. A*, 1968, 1858; (c) M. A. Bush, G. A. Sim, G. R. Knox, M. Ahmad and C. G. Robertson, *Chem. Commun.*, 1969, 74; (d) M. A. Bush and G. A. Sim, *J. Chem. Soc. A*, 1970, 611; (e) B. W. S. Kolthammer, P. Legzdins and J. T. Malito, *Inorg. Chem.*, 1977, **16**, 3173; (f) M. H. Chisholm, F. A. Cotton, M. W. Extine and D. C. Rideout, *Inorg.*

- Chem.*, 1979, **18**, 120; (g) A. D. U. Hardy and G. A. Sim, *Acta Crystallogr., Sect. B*, 1979, **35**, 1463.
- 8 (a) G. A. Sim, D. I. Woodhouse and G. R. Knox, *J. Chem. Soc., Dalton Trans.*, 1979, 83; (b) J. L. Hubbard and W. K. McVicar, *Inorg. Chem.*, 1992, **31**, 910.
- 9 S. R. Huber, T. C. Baldwin and D. E. Wigley, *Organometallics*, 1993, **12**, 91.
- 10 K. G. Caulton, *Nouv. J. Chim.*, 1994, **18**, 25.
- 11 (a) M. T. Ashby, J. H. Enemark and D. L. Lichtenberger, *Inorg. Chem.*, 1988, **27**, 191; (b) M. A. Dewey, D. A. Knight, A. Arif and J. A. Gladysz, *Chem. Ber.*, 1992, **125**, 815; (c) M. A. Dewey, G. A. Stark and J. A. Gladysz, *Organometallics*, 1996, **15**, 4798.
- 12 M. J. Clarke and J. B. Gaul, *Struct. Bonding (Berlin)*, 1993, **81**, 147; P. Legzdins, C. C. Y. Pang and M. J. Shaw, *US Pat.*, 5 631 284, 1997.
- 13 J. H. Enemark and R. D. Feltham, *Coord. Chem. Rev.*, 1974, **13**, 339.
- 14 P. Legzdins, W. S. McNeil, R. J. Batchelor and F. W. B. Einstein, *J. Am. Chem. Soc.*, 1995, **117**, 10 521 and refs. therein.
- 15 P. Legzdins, W. S. McNeil, S. J. Rettig and K. M. Smith, *J. Am. Chem. Soc.*, 1997, **119**, 3513.
- 16 J. H. Toney and T. J. Marks, *J. Am. Chem. Soc.*, 1985, **107**, 947; J. H. Toney, C. P. Brock and T. J. Marks, *J. Am. Chem. Soc.*, 1986, **108**, 7263; L. Y. Kuo, M. G. Kanatzidis, M. Sabat, A. L. Tipton and T. J. Marks, *J. Am. Chem. Soc.*, 1991, **113**, 9027.
- 17 U. Koelle, *Coord. Chem. Rev.*, 1994, **135**, 623 and refs. therein.
- 18 L. Wang, R. S. Lu, R. Bau and T. C. Flood, *J. Am. Chem. Soc.*, 1993, **115**, 6999; M. S. Eisen, A. Haskel, H. Chen, M. M. Olmstead, D. P. Smith, M. F. Maestre and R. H. Fish, *Organometallics*, 1995, **14**, 2806; A. Svetlanova-Larsen, C. R. Zoch and J. L. Hubbard, *Organometallics*, 1996, **15**, 3076.
- 19 F. J. Regina and A. Wojcicki, *Inorg. Chem.*, 1980, **19**, 3803.
- 20 P. Legzdins and D. T. Martin, *Organometallics*, 1983, **2**, 1785; P. Legzdins, G. B. Richter-Addo, F. W. B. Einstein and R. H. Jones, *Organometallics*, 1990, **9**, 431.
- 21 G. A. Lawrance, *Chem. Rev.*, 1986, **86**, 17.
- 22 C. M. Fendrick, L. D. Schertz, E. A. Mintz and T. J. Marks, *Inorg. Synth.*, 1992, **29**, 193.
- 23 P. Legzdins, D. T. Martin, C. R. Nurse and B. Wassink, *Organometallics*, 1983, **2**, 1238.
- 24 H. E. Bryndza, L. K. Fong, R. A. Paciello, W. Tam and J. E. Bercaw, *J. Am. Chem. Soc.*, 1987, **109**, 1444; R. G. Bergman, *Polyhedron*, 1995, **14**, 3227; G. M. Kapteijn, A. Dervisi, D. M. Grove, H. Kooijman, M. T. Lakin, A. L. Spek and G. van Koten, *J. Am. Chem. Soc.*, 1995, **117**, 10 939; G. M. Kapteijn, D. M. Grove, H. Kooijman, W. J. J. Smeets, A. L. Spek and G. van Koten, *Inorg. Chem.*, 1996, **35**, 526; G. M. Kapteijn, M. P. R. Spee, D. M. Grove, H. Kooijman, A. L. Spek and G. van Koten, *Organometallics*, 1996, **15**, 1405.
- 25 R. D. Simpson and R. G. Bergman, *Organometallics*, 1992, **11**, 3980; 1993, **12**, 781.
- 26 E. O. Fischer and H. Strametz, *J. Organomet. Chem.*, 1967, **10**, 323.
- 27 P. Legzdins and C. R. Nurse, *Inorg. Chem.*, 1985, **24**, 327.
- 28 W. W. Lukens, M. R. Smith and R. A. Andersen, *J. Am. Chem. Soc.*, 1996, **118**, 1719 and refs. therein.
- 29 P. Legzdins, S. R. Rettig, K. J. Ross, R. J. Batchelor and F. W. B. Einstein, *Organometallics*, 1995, **14**, 5579.
- 30 J. K. Hoyano, P. Legzdins and J. T. Malito, *Inorg. Synth.*, 1978, **18**, 126.
- 31 SMART V4.0, Siemens Industrial Automation Inc., Madison, WI, 1990.
- 32 SHELXTL-Plus V5.0, Siemens Industrial Automation Inc., Madison, WI, 1994.

Received 23rd May 1997; Paper 7/03595K