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Cyclopentadienyl nitrosyl compounds of chromium: aqueous solution chemistry, π bonding and nitric oxide loss†

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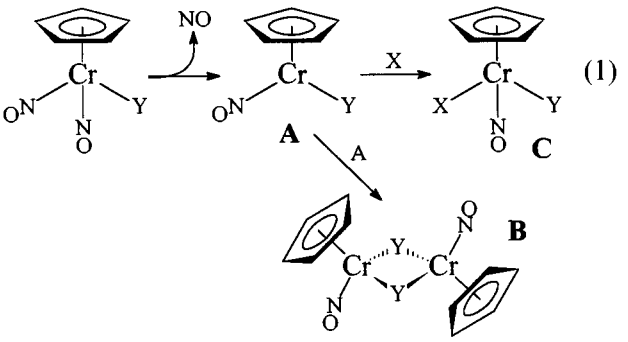
The complex $[Cr(\eta\text{-}C_5H_5)(NO)_2(CF_3SO_3)]$ **1** was synthesised in order to explore the relationship between π-donor ligands and nitrosyl lability and to investigate the aqueous chemistry of the $[Cr(\eta\text{-}C_5H_5)(NO)_2]^+$ fragment. Treatment of **1** with σ-donor ligands gave $[Cr(\eta\text{-}C_5H_5)(NO)_2(L)][CF_3SO_3]$ salts. Potentiometric titrations and ^{1}H NMR spectroscopic studies of **1** provided evidence for the existence of $[Cr(\eta\text{-}C_5H_5)(NO)_2(H_2O)]^+$ and $[Cr(\eta\text{-}C_5H_5)(NO)_2(OH)]$ in aqueous solution. When generated *in situ*, $[Cr(\eta\text{-}C_5H_5)(NO)_2(OH)]$ reacted with acetylacetone, pyridinecarboxylic acid, or salicylaldehyde to form paramagnetic, mononitrosyl complexes, which were independently synthesised from the mononitrosyl precursor $[Cr(\eta\text{-}C_5H_5)(NO)(\mu\text{-}I)]_2$. The solid-state molecular structures of $[Cr(\eta\text{-}C_5Me_5)(NO)_2(CF_3SO_3)]$ **2**, $[Cr(\eta\text{-}C_5H_5)(NO)_2(N_2C_5H_7)]$ **9** and $[Cr(\eta\text{-}C_5H_5)(NO)(O_2C_5H_7)]$ **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, $\beta = 91.760(7)°$, $Z = 4$, space group $P2_1/n$; crystals of **9** are monoclinic, $a = 18.3382(4)$, $b = 11.1774(3)$, $c = 12.9102(1)$ Å, $\beta = 121.386(1)°$, $Z = 8$, 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[2] reported the synthesis of $[Cr(\eta\text{-}C_5H_5)(NO)_2Cl]$, one of the first well characterized organometallic complexes of chromium.[3] The compound is slightly water soluble, and upon treatment with aqueous $AgNO_3$ forms solutions of $[Cr(\eta\text{-}C_5H_5)(NO)_2(H_2O)]^+$ [4] {originally formulated as $[Cr(\eta\text{-}C_5H_5)(NO)_2]^+$}.[2] The remarkable water stability of the $[Cr(\eta\text{-}C_5H_5)(NO)_2]^+$ fragment is demonstrated by the isolation of $[Cr(\eta\text{-}C_5H_5)(NO)_2X]$ (X = halide or pseudohalide) complexes upon addition of KX salts to *in situ* generated $[Cr(\eta\text{-}C_5H_5)(NO)_2(H_2O)]^+$ followed by $CHCl_3$ extraction.[2]

Subsequent metathesis studies of $[Cr(\eta\text{-}C_5H_5)(NO)_2Cl]$ have been performed in anhydrous organic solvents.[5–8] Under these conditions, several alkyl complexes of the type $[Cr(\eta\text{-}C_5H_5)(NO)_2R]$ (*e.g.*, R = Me,[5a] Et,[5a] CH_2Ph,[5b] Bu^i,[5c] CH_2SiMe_3 [5d] and CH_2X [5e]) have been synthesised. The electron-donating ability of the alkyl groups is apparent in the shift of ν(NO) from 1815 and 1710 cm^{-1} for $[Cr(\eta\text{-}C_5H_5)(NO)_2Cl]$ to ≈ 1780 and 1670 cm^{-1} for $[Cr(\eta\text{-}C_5H_5)(NO)_2R]$ as measured by solution IR spectroscopy (CH_2Cl_2).[5] The results of the alkylation reactions contrasts with metathesis reactions of $[Cr(\eta\text{-}C_5H_5)(NO)_2Cl]$ with Y^- sources (Y = SR, NR_2 or OR) which depend on the electronic nature of the Y^- group. All known compounds of the composition $[Cr(\eta\text{-}C_5H_5)(NO)_2Y]$ contain strongly electron-withdrawing substituents (*e.g.*, Y = SCN,[2] SO_2CH_3,[5b] SCF_3,[6a] $OSO_2C_6H_4Me$,[6c] NCO [6b] and NO_2 [2,6d]). However, if Y contains electron-donating substituents (*e.g.*, Y = SPh,[7b] OMe,[7g] OEt,[7e] OPr^i,[8b] NMe_2 [7d] or NPh_2 [8a]) the products isolated *have lost one nitric oxide ligand*, as illustrated in equation (1). These reactions likely proceed *via* the intermediate $[Cr(\eta\text{-}C_5H_5)(NO)Y]$ **A**, which then either dimerises to $[Cr(\eta\text{-}C_5H_5)(NO)(\mu\text{-}Y)]_2$ **B**,[7] or forms chromium(II) species $[Cr(\eta\text{-}C_5R_5)(NO)(X)Y]$ **C**,[8] *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 π-*acceptor* nitrosyl ligand being triggered by *increased* electron donation



from the Y^- ligand. Furthermore, $[Cr(\eta\text{-}C_5H_5)(NO)_2X]$ complexes containing strong σ-donor alkyl ligands display no propensity to lose NO.[5] The observed reactivity is limited to π-donor Y^- ligands because $[Cr(\eta\text{-}C_5H_5)(NO)_2]^+$ is a π-loaded fragment. The cyclopentadienyl and nitrosyl ligands each form one σ and two π interactions, leaving no empty orbital available on the $M(1\sigma,2\pi)_3$ fragment to accept π donation from the Y^- ligand.[9] This unfavourable filled/filled π-interaction is relieved by loss of nitric oxide. Related ligand-loss reactions have also been attributed to the repulsion between filled p orbitals on π-donor ligands and filled metal orbitals.[10] These reactions typically involve the dissociation of two-electron donor ligands such as CO [11a] or PPh_3,[11b,c] 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*.[12] Several features make $[Cr(\eta\text{-}C_5H_5)(NO)_2X]$ complexes particularly suitable as model compounds for the study of NO release from transition metals. These Cr^0, d^6 complexes‡ are diamagnetic with two equivalents

† Dedicated to the memory of Professor Sir Geoffrey Wilkinson.
π Bonding and reactivity in transition-metal nitrosyl complexes. Part 4.[1]

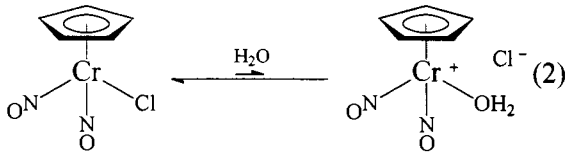
‡ Linear dinitrosyl compounds of Cr^0 are more accurately described as having a $\{Cr(NO)_2\}^6$ electronic configuration using Enemark–Feltham notation.[13]

of NO per Cr atom, and the paramagnetic Cr^{I}, d^5 mononitrosyl compounds that would be the products expected upon loss of NO radical have been shown to be unusually inert.[14] We have recently investigated the oxidatively-triggered NO release from $[Cr(\eta\text{-}C_5H_5)(NO)Cl_2]^-$ in organic solvents.[15] Given the stability of the $[Cr(\eta\text{-}C_5H_5)(NO)_2]^+$ fragment in aqueous solution,[2] we hypothesised that treatment of aqueous $[Cr(\eta\text{-}C_5H_5)(NO)_2(H_2O)]^+$ with base should form $[Cr(\eta\text{-}C_5H_5)(NO)_2(OH)]$. 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

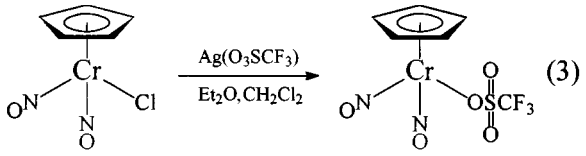
Synthesis of $[Cr(\eta\text{-}C_5R_5)(NO)_2(CF_3SO_3)]$

The slight water solubility of $[Cr(\eta\text{-}C_5H_5)(NO)_2Cl]$ initially reported by Piper and Wilkinson[2] is presumably due to hydrolysis of the Cr–Cl bond as illustrated in equation (2).



(2)

Similar reactions have been studied in detail for $[M(\eta\text{-}C_5H_5)_2Cl_2]$ complexes (M = Ti, Zr, V or Mo).[16] More recent investigations of aqueous organometallic chemistry[17] have relied on the trifluoromethanesulfonate ($CF_3SO_3^-$) ligand which dissociates more readily from the metal centre.[18] As shown in equation (3), $[Cr(\eta\text{-}C_5H_5)(NO)_2(CF_3SO_3)]$ **1** can be



(3)

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synthesised by treatment of $[Cr(\eta\text{-}C_5H_5)(NO)_2Cl]$ with $Ag(CF_3SO_3)$, in a manner analogous to previous chloride abstraction reactions with $AgPF_6$[19] and $AgBF_4$.[20] 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_2Cl_2.

Complex **1** is soluble in CH_2Cl_2, CH_3CN, alcohols, water, ethers and aromatic solvents, and is isolated as large, air-stable, black crystals. The single resonance in the ^1H 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^{-1} (CH_2Cl_2) as compared to the Cl precursor reflects the greater electron-withdrawing properties of the $CF_3SO_3^-$ ligand.[15] The Nujol mull IR spectrum also contains six bands between 1000 and 1350 cm^{-1}, consistent with the presence of a covalently bound $CF_3SO_3^-$ ligand.[21]

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_3SCF_3 bond in **1**, the related $[Cr(\eta\text{-}C_5Me_5)(NO)_2(CF_3SO_3)]$ **2** was synthesised. As expected, the pentamethylcyclopentadienyl ligand imparted increased solubility and crystallinity to the complex,[22] 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 $CF_3SO_3^-$ 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 $[Cr(\eta\text{-}C_5Me_5)(NO)_2(CF_3SO_3)]$ **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.

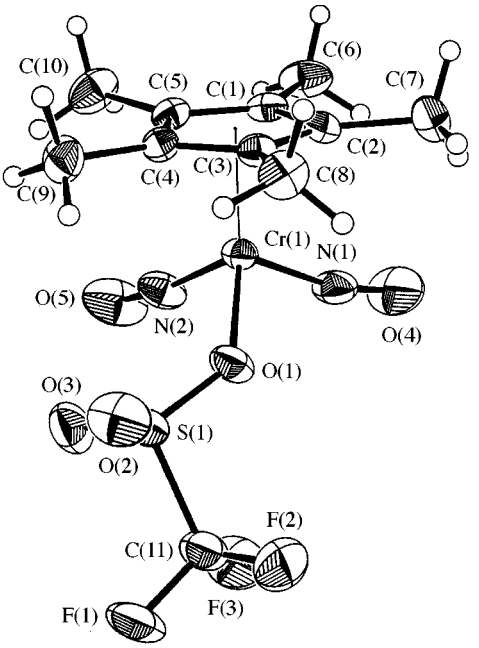
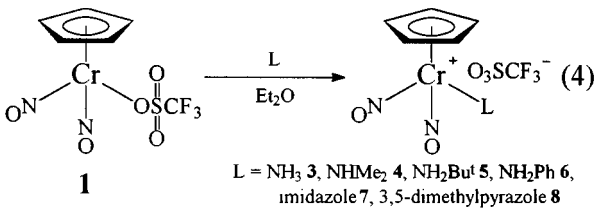


Fig. 1 The solid-state molecular structure of $[Cr(\eta\text{-}C_5Me_5)(NO)_2(CF_3SO_3)]$ **2**, 50% probability ellipsoids

Reaction of 1 with σ-donor ligands

To test the ability of the $CF_3SO_3^-$ 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 $[Cr(\eta\text{-}C_5H_5)(NO)_2(L)][CF_3SO_3]$ (L = NH_3 **3**, $NHMe_2$ **4**, NH_2Bu^t **5**, NH_2Ph **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 $[Cr(\eta\text{-}C_5H_5)(NO)_2(CF_3SO_3)]$



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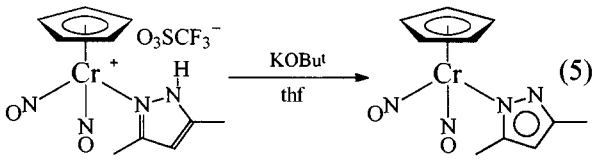
may be used for these reactions, or **1** may be generated *in situ* from $[Cr(\eta\text{-}C_5H_5)(NO)_2Cl]$ and $Ag(CF_3SO_3)$ in diethyl ether.

Compound **6** was treated with $LiBu^n$ or KBu^t in (tetrahydrofuran) thf in an attempt to generate the neutral dinitrosyl amide complex $[Cr(\eta\text{-}C_5H_5)(NO)_2(NHPh)]$ at low temperatures by deprotonation. Monitoring this reaction by solution IR spectroscopy did not reveal any ν(NO) bands consistent with $[Cr(\eta\text{-}C_5H_5)(NO)_2(NHPh)]$. Instead, the ν(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 $LiBu^n$ or KBu^t displayed new ν(NO) bands at 1817 and 1712 cm^{-1} (CH_2Cl_2), but the presumed $[Cr(\eta\text{-}C_5H_5)(NO)_2(N_2C_3H_3)]$ product cannot be separated from the CF_3SO_3-containing by-product. In contrast, the neutral 3,5-dimethylpyrazolyl product $[Cr(\eta\text{-}C_5H_5)(NO)_2(N_2C_5H_7)]$ **9** can be isolated in a pure state due to its greater solubility [equation (5)].



8 **9**

Complex **9** is relatively air-stable in the solid state, and is soluble in thf, CH_2Cl_2, C_6H_6 and Et_2O. The shift in ν(NO) from 1839 and 1722 cm^{-1} (Nujol) for cationic **8** to 1800 and 1686 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 C_5H_5 ligand. This contrasts with the short Cr–N bonds and electronically-enforced ON–Cr–NR_2 coplanarity recently observed for $[Cr(\eta\text{-}C_5H_5)(NO)(NR_2)]$-containing species which possess a Cr–N π bond,[1] 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 $[Cr(\eta\text{-}C_5H_5)(NO)_2(N_2C_3HR_2)]$ complexes (R = H or Me) is due to the aromatic nature of the heterocyclic ring. Disruption of the Cr–NO π bonds is avoided by delocalising the filled N p orbital electron density over the N_2C_3 moiety. The strong π-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 decomposition even when the neutral amide complex is generated under relatively mild conditions.

Table 2 Bond lengths (Å) and angles (°) for $[Cr(\eta\text{-}C_5H_5)(NO)_2(N_2C_5H_7)]$ **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)		

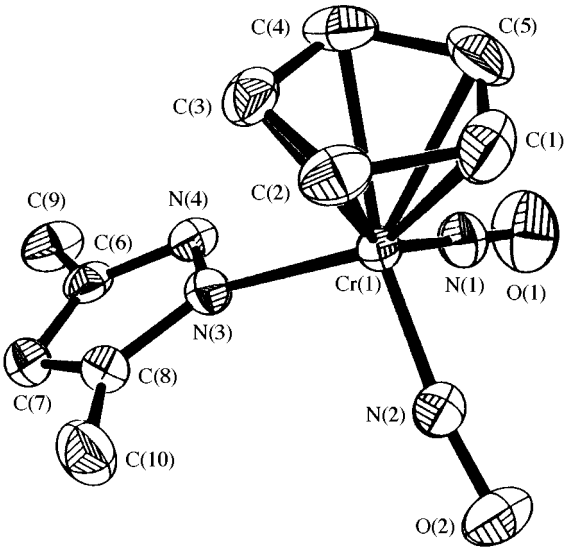
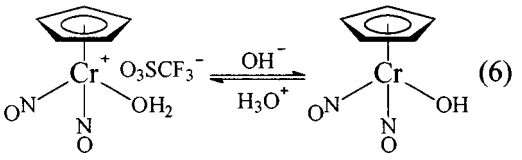


Fig. 2 The solid-state molecular structure of $[Cr(\eta\text{-}C_5H_5)(NO)_2(N_2C_5H_7)]$ **9**, 50% probability ellipsoids

Aqueous chemistry of $[Cr(\eta\text{-}C_5H_5)(NO)_2]^+$

With samples of **1** in hand, we could now investigate the aqueous chemistry of the $[Cr(\eta\text{-}C_5H_5)(NO)_2]^+$ fragment, to determine if a pH-dependent release of NO would be observed.

As expected, **1** is much more water soluble than $[Cr(\eta\text{-}C_5H_5)(NO)_2Cl]$ due to the readily displaced $CF_3SO_3^-$ ligand.[18] When dissolved in D_2O, **1** shows a single peak in its ^1H NMR spectrum at δ 5.90 that is attributable to the $(\eta\text{-}C_5H_5)$ ligand of $[Cr(\eta\text{-}C_5H_5)(NO)_2(D_2O)][CF_3SO_3]$. However, in basic D_2O–NaOD solutions, a new cyclopentadienyl peak at δ 5.75 is the only signal observed; most likely corresponding to the neutral hydroxide complex, $[Cr(\eta\text{-}C_5H_5)(NO)_2(DH)]$. Potentiometric titration of **1** in H_2O using dilute NaOH and HO_3SCF_3 solutions determined a pK_a value of 6.8 for $[Cr(\eta\text{-}C_5H_5)(NO)_2(H_2O)][CF_3SO_3]$. Consistent with this value, both the δ 5.75 and 5.90 cyclopentadienyl peaks are present in relatively equal proportions in the ^1H NMR spectrum when the pH is 6.6. These observations indicate the presence of a pH-dependent equilibrium between $[Cr(\eta\text{-}C_5H_5)(NO)_2(H_2O)][CF_3SO_3]$ and $[Cr(\eta\text{-}C_5H_5)(NO)_2(OH)]$, as shown in equation (6).



(6)

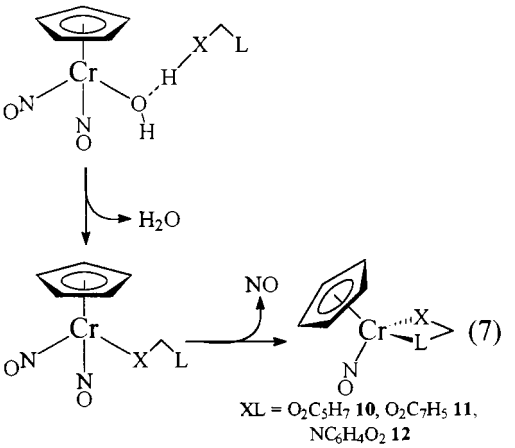
Thus, aqueous solutions of **1** are unexpectedly stable over a range of pH values, with the ^1H NMR spectra remaining unchanged for weeks at room temperature under N_2. No evidence of hydrolysis of the cyclopentadienyl ligand is observed even at low pH.[16] Even more surprisingly, no evidence for NO loss from $[Cr(\eta\text{-}C_5H_5)(NO)_2(OH)]$ 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 $[Cr(\eta\text{-}C_5H_5)(NO)_2(OH)]$. The Lewis basicity of the hydroxide oxygen atom in $[Cr(\eta\text{-}C_5H_5)(NO)_2(OH)]$ has been previously established by the isolation of $[Cr(\eta\text{-}C_5H_5)(NO)_2(HO\cdots A)]$ adducts with Lewis acids {A = BPh_3 or $[Cr(\eta\text{-}C_5H_5)(NO)_2]^+$}[23] from the basic, aqueous work up of $[Cr(\eta\text{-}C_5H_5)(NO)_2(BF_4)]$. Also worthy of note is the IR monitoring of the reaction of EtO^- and $[Cr(\eta\text{-}C_5H_5)(NO)_2Cl]$ in ethanol which indicates that the species $[Cr(\eta\text{-}C_5H_5)(NO)_2(OEt)]$ is stable until the protic solvent is removed *in vacuo*.[7e] Attempts to induce NO loss by generating $[Cr(\eta\text{-}C_5H_5)(NO)_2(OH)]$ in aprotic solvents such as thf by reaction of $[Cr(\eta\text{-}C_5H_5)(NO)_2(CF_3SO_3)]$ with CsOH instead led to the formation of $[\{Cr(\eta\text{-}C_5H_5)(NO)_2\}_2(\mu\text{-}OH)]^+[CF_3SO_3]^-$, identified in solution by IR spectroscopy by comparison with the known BF_4^- and BPh_4^- analogues.[23] In the absence of a hydrogen-bonding solvent, the initially generated $[Cr(\eta\text{-}C_5H_5)(NO)_2(OH)]$ species displaces the $CF_3SO_3^-$ 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.[24] 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 π donation, and so strong H-bonding interactions are formed to relieve the resulting filled/filled repulsions.[10] Of particular interest are the studies of Simpson and Bergman[25] who invoke this type of hydrogen bonded species as intermediates in the exchange reactions of alkoxides by protonolysis.

Synthesis of $[Cr(\eta\text{-}C_5H_5)(NO)(LX)]$

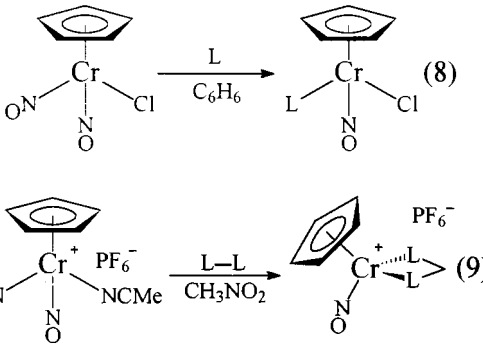
While hydrogen bonding prevents one potential route to nitric oxide loss by attenuating the electron density at the hydroxide oxygen of $[Cr(\eta\text{-}C_5H_5)(NO)_2(OH)]$, it presents a second possible route through protonolysis with potentially chelating ligands. Thus, when treated with acids such as acetylacetone, salicylaldehyde or picolinic acid (pyridinecarboxylic acid) (HXL), *in situ* generated solutions of $[Cr(\eta\text{-}C_5H_5)(NO)_2(OH)]$ react slowly to give the *mononitrosyl* products $[Cr(\eta\text{-}C_5H_5)(NO)(LX)]$ (LX = $O_2C_5H_7$ **10**, $O_2C_7H_5$ **11**, $NC_6H_4O_2$ **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



(7)

XL = $O_2C_5H_7$ **10**, $O_2C_7H_5$ **11**, $NC_6H_4O_2$ **12**

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)[26] and (9)[19] dis-

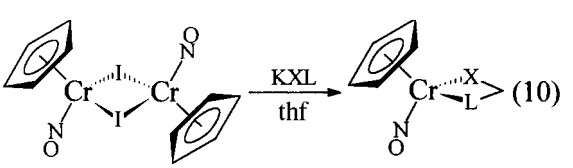


(8)

(9)

play previous examples of substitution of nitric oxide from $[Cr(\eta\text{-}C_5H_5)(NO)_2]$-containing species by σ-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 $[Cr(\eta\text{-}C_5H_5)(NO)(\mu\text{-}I)]_2$[27] and KLX salts in thf [equation (10)]. Compounds



(10)

10–**12** are air stable as solids and their ν(NO) (1647, 1659 and 1666 cm^{-1}, respectively), solubility and other physical properties are similar to related, stable 17-valence-electron Cr^I mononitrosyl complexes.[14,15] 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 $[Cr(\eta\text{-}C_5H_5)(NO)(O_2C_5H_7)]$ **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: $x, \frac{1}{2}-y, z$.

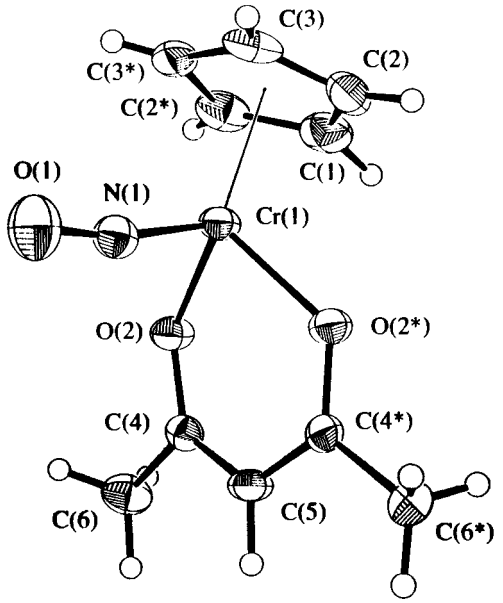
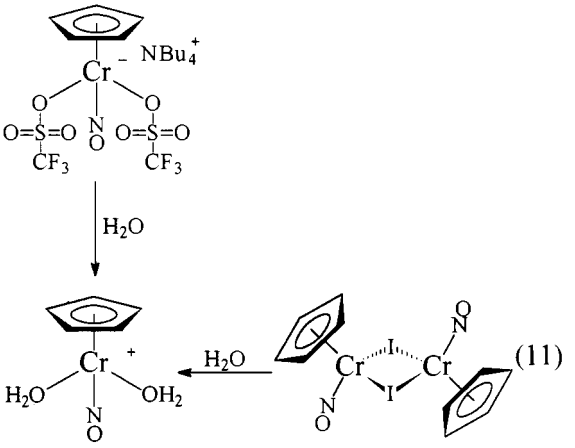


Fig. 3 The solid-state molecular structure of $[Cr(\eta\text{-}C_5H_5)(NO)(O_2C_5H_7)]$ **10**, 50% probability ellipsoids

nitrosyl ligand, the Cr atom, one C atom in the C_5H_5 ring and the methine C atom of the acetylacetonate ligand.

Aqueous chemistry of $[Cr(\eta\text{-}C_5H_5)(NO)(H_2O)_2]^+$

Since paramagnetic compounds of formula $[Cr(\eta\text{-}C_5H_5)(NO)L_2]^+$ have recently been demonstrated to be remarkably inert,[14] we sought to expand this class of complexes to the bis(aqua) mononitrosyl cation $[Cr(\eta\text{-}C_5H_5)(NO)(H_2O)_2]^+$ which may be synthesised in two ways, as shown in equation (11). Suspensions of $[Cr(\eta\text{-}C_5H_5)(NO)(\mu\text{-}I)]_2$ in hot water slowly react to give green solutions of $[Cr(\eta\text{-}C_5H_5)(NO)(H_2O)_2]^+$, while $[NBu^n_4][Cr(\eta\text{-}C_5H_5)(NO)(CF_3SO_3)_2]$ dissolves in water at room temperature over 5 min to provide the same complex. Addition of aqueous $NaBPh_4$ to concentrated solutions of $[Cr(\eta\text{-}C_5H_5)(NO)(H_2O)_2]^+$ causes the precipitation of $[Cr(\eta\text{-}C_5H_5)(NO)(H_2O)_2][BPh_4]$ **13** as analytically pure microcrystals. Unfortunately, the pK_a of $[Cr(\eta\text{-}C_5H_5)(NO)(H_2O)_2]^+$ could not be determined due to the instability of its conjugate base. At pH > 7 solutions of $[Cr(\eta\text{-}C_5H_5)(NO)(H_2O)_2]^+$ precipitate $[Cr(\eta\text{-}C_5H_5)(NO)(\mu\text{-}OH)]_2$ **14** in low yields. Apparently, any hydrogen-bonding interactions that may exist between the expected $[Cr(\eta\text{-}C_5H_5)(NO)(OH)(H_2O)]$ product and the aqueous solvent are insufficient to prevent loss of H_2O and subsequent aggregation reactions. This reactivity contrasts with



the stability of $[Cr(\eta\text{-}C_5H_5)(NO)_2(OH)]$, as expected upon formal replacement of a nitrosyl ligand with an aqua ligand, which should be a much better leaving group. Solutions of $[Cr(\eta\text{-}C_5H_5)(NO)(H_2O)_2]^+$ 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 $[Cr(\eta\text{-}C_5H_5)(NO)_2]^+$ fragment has been known since the original synthesis of this class of compounds by Piper and Wilkinson[2] in 1956. Subsequent studies directed at the metathesis of the Cl^- ligand of $[Cr(\eta\text{-}C_5H_5)(NO)_2Cl]$ with π-donor ligands report only *mono*-nitrosyl products.[7,8] Prompted by these two observations, we postulated that π donation from the hydroxide ligand of $[Cr(\eta\text{-}C_5H_5)(NO)_2(OH)]$ might trigger nitric oxide release under physiologically relevant conditions. This mode of NO loss was not observed, as $[Cr(\eta\text{-}C_5H_5)(NO)_2(OH)]$ 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 $[Cr(\eta\text{-}C_5H_5)(NO)_2(OH)]$ 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 $[Cr(\eta\text{-}C_5H_5)(NO)(\mu\text{-}I)]_2$ in aqueous solution and organic solvents.

Our future work in this area will continue along three lines: $[Cr(\eta\text{-}C_5H_5)(NO)_2X]$ derivatives with pendant σ-donor ligands capable of nitrosyl displacement will be synthesised; alternative routes to $[Cr(\eta\text{-}C_5H_5)(NO)_2(H_2O)]^+$ and $[Cr(\eta\text{-}C_5H_5)(NO)_2(OH)]$ in organic solvents will be investigated; sterically-stabilized, 17-electron species of formula $[Cr(\eta\text{-}C_5R_5)(NO)(NR_2)]$ will be generated from $[Cr(\eta\text{-}C_5Me_5)(NO)(\mu\text{-}Cl)]_2$[15] and $[Cr(\eta\text{-}C_5H_5)(NO)(NPr^i_2)X]$ precursors.[28]

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.[29] The complexes $[Cr(\eta\text{-}C_5H_5)(NO)_2Cl]$,[2,30] $[Cr(\eta\text{-}C_5Me_5)(NO)_2Cl]$,[20] $[Cr(\eta\text{-}C_5H_5)(NO)I]_2$[27] and $[NBu^n_4][Cr(\eta\text{-}C_5H_5)(NO)(CF_3SO_3)_2]$[15] 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_5H_5)(NO)$_2$(CF_3SO_3)] 1. To [Cr(η-C_5H_5)(NO)$_2$Cl] (0.655 g, 3.08 mmol) and Ag(CF_3SO_3) (0.793 g, 3.09 mmol) was added CH_2Cl_2 (15 cm^3) followed by diethyl ether (15 cm^3). The solution was stirred for 15 min, and then filtered to remove AgCl. The Celite pad was washed with diethyl ether (4 × 5 cm^3). The volume of the solution was reduced slightly *in vacuo*, then hexanes (15 cm^3) 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_5H_5)(NO)$_2$(CF_3SO_3)] **1** (0.874 g, 87%) (Found: C, 22.3; H, 1.57; N, 8.49%; M^+ 326. $C_6H_5CrF_3N_2O_5S$ requires C, 22.1; H, 1.55; N, 8.59%; *M* 326); ν_{max}/cm^{-1} (Nujol) 1834 and 1729 (NO); (CH_2Cl_2) 1836 and 1730; δ_H($CDCl_3$) 5.82 (5 H, s, C_5H_5); *m*/*z* 326 (M^+), 296 (M^+ − NO), 266 (M^+ − 2NO).

[Cr(η-C_5Me_5)(NO)$_2$(CF_3SO_3)] 2. To [Cr(η-C_5Me_5)(NO)$_2$Cl] (0.110 g, 0.38 mmol) and Ag(CF_3SO_3) (0.100 g, 0.39 mmol) was added diethyl ether (30 cm^3). The solution was stirred for 15 min, and then filtered to remove AgCl. The Celite pad was washed with diethyl ether (3 × 10 cm^3). The volume of the solution was reduced *in vacuo* to ≈5 cm^3 and cooled to −30 °C overnight to provide dark brown *crystals* of [Cr(η-C_5Me_5)(NO)$_2$(CF_3SO_3)] **2** (0.125 g, 82% (Found: C, 33.3; H, 3.87; N, 6.88%; M^+ 396. $C_{11}H_{15}CrF_3N_2O_5S$ requires C, 33.3; H, 3.81; N, 7.07%; *M* 396); ν_{max}/cm^{-1} (Nujol) 1794 and 1708 (NO); (CH_2Cl_2) 1801 and 1702; δ_H($CDCl_3$) 1.86 (15 H, s, C_5Me_5); *m*/*z* 396 (M^+), 366 (M^+ − NO), 336 (M^+ − 2NO).

[Cr(η-C_5H_5)(NO)$_2$(NH_3)][CF_3SO_3] 3. To a stirred solution of [Cr(η-C_5H_5)(NO)$_2$(CF_3SO_3)] (0.334 g, 1.02 mmol) in diethyl ether (35 cm^3) was added an excess of CH_2Cl_2 saturated with NH_3 (≈5 cm^3). 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^3). Drying *in vacuo* provided the green *powder* [Cr(η-C_5H_5)(NO)$_2$(NH_3)][CF_3SO_3] **3** (0.206 g, 60%) (Found: C, 21.2; H, 2.23; N, 12.2. $C_6H_8CrF_3N_3O_5S$ requires C, 21.0; H, 2.35; N, 12.2%); ν_{max}/cm^{-1} (Nujol) 1824 and 1735 (NO); (CH_2Cl_2) 1830 and 1727; δ_H[$(CD_3)_2CO$] 3.72 (3 H, br s, NH_3) and 6.14 (5 H, s, C_5H_5); δ_C[$(CD_3)_2CO$] 104.3 (C_5H_5); *m*/*z* 194 (M^+); 149 (M^-).

[Cr(η-C_5H_5)(NO)$_2$($NHMe_2$)][CF_3SO_3] 4. To a stirred solution of [Cr(η-C_5H_5)(NO)$_2$(CF_3SO_3)] (0.331 g, 1.01 mmol) in diethyl ether (35 cm^3) was added an excess of CH_2Cl_2 saturated with $NHMe_2$ (≈4 cm^3). 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^3). Drying *in vacuo* provided the green *powder* [Cr(η-C_5H_5)(NO)$_2$($NHMe_2$)][CF_3SO_3] **4** (0.159 g, 42%) (Found: C, 25.8; H, 3.12; N, 11.2. $C_8H_{12}CrF_3N_3O_5S$ requires C, 25.9; H, 3.26; N, 11.3%); ν_{max}/cm^{-1} (Nujol) 1826 and 1709 (NO); (CH_2Cl_2) 1825 and 1723; δ_H($CDCl_3$) 2.77 [6 H, d, NH(CH_3)$_2$], 5.52 [1 H, br s, N*H*(CH_3)$_2$] and 5.96 (5 H, s, C_5H_5); *m*/*z* 222 (M^+), 192 (M^+ − NO); 149 (M^-).

[Cr(η-C_5H_5)(NO)$_2$(NH_2Bu^t)][CF_3SO_3] 5. To a stirred solution of [Cr(η-C_5H_5)(NO)$_2$(CF_3SO_3)] (0.163 g, 0.50 mmol) in diethyl ether (30 cm^3) was added an excess of NH_2Bu^t (0.25 cm^3, 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^3). Drying *in vacuo* provided the green *powder* [Cr(η-C_5H_5)(NO)$_2$(NH_2Bu^t)][CF_3SO_3] **5** (0.104 g, 52%) (Found: C, 30.4; H, 4.30; N, 10.3. $C_{10}H_{16}CrF_3N_3O_5S$ requires C, 30.1; H, 4.04; N, 10.5%); ν_{max}/cm^{-1} (Nujol) 1818 and 1700 (NO); (CH_2Cl_2) 1822 and 1720; δ_H($CDCl_3$) 1.34 (9 H, s, $NH_2C(CH_3)_3$), 4.16 (2 H, s, NH_2Bu^t) and 5.94 (5 H, s, C_5H_5); δ_c($CDCl_3$) 30.0 (NH_2Bu^t), 45.1 (NH_2Bu^t) and 103.3(C_5H_5); *m*/*z* 250 (M^+), 220 (M^+ − NO), 190 (M^+ − 2NO); 149 (M^-).

[Cr(η-C_5H_5)(NO)$_2$(NH_2Ph)][CF_3SO_3] 6. To a stirred solution of [Cr(η-C_5H_5)(NO)$_2$(CF_3SO_3)] (0.163 g, 0.50 mmol) in diethyl ether (20 cm^3) was added an excess of NH_2Ph (0.20 cm^3, 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^3). Drying *in vacuo* provided the green microcrystalline *powder* [Cr(η-C_5H_5)(NO)$_2$(NH_2Ph)][CF_3SO_3] **6** (0.170 g, 80%) (Found: C, 34.3; H, 2.88; N, 10.0. $C_{12}H_{12}CrF_3N_3O_5S$ requires C, 34.4; H, 2.88; N, 10.0%); ν_{max}/cm^{-1} (Nujol) 1823 and 1710 (NO); (CH_2Cl_2) 1830 and 1728; δ_H($CDCl_3$) 5.82 (5 H, s, C_5H_5) and 6.38–7.22 (5 H, m, NH_2Ph); δ_c($CDCl_3$) 102.8 (C_5H_5), 119.9 (NH_2Ph), 125.3 (NH_2Ph) and 129.5 (NH_2Ph); *m*/*z* 270 (M^+), 240 (M^+ − NO), 210 (M^+ − 2NO); 149 (M^-).

[Cr(η-C_5H_5)(NO)$_2$($N_2C_3H_4$)][CF_3SO_3] 7. To a stirred solution of [Cr(η-C_5H_5)(NO)$_2$(CF_3SO_3)] (0.165 g, 0.51 mmol) in diethyl ether (20 cm^3) was added imidazole (0.046 g, 0.53 mmol) in diethyl ether (20 cm^3). 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^3). Drying *in vacuo* provided the green *powder* [Cr(η-C_5H_5)(NO)$_2$($N_2C_3H_4$)][CF_3SO_3] **7** (0.167 g, 83%) (Found: C, 27.7; H, 2.31; N, 13.9. $C_9H_9CrF_3N_4O_5S$ requires C, 27.4; H, 2.30; N, 14.2%); ν_{max}/cm^{-1} (Nujol) 1824 and 1720 (NO); (CH_2Cl_2) 1832 and 1730; δ_H(CD_3CN) 5.88 (5 H, s, C_5H_5), 6.95 (1 H, s, CH), 7.29 (1 H, s, CH), 7.86 (1 H, s, CH); δ_c(CD_3CN) 104.7 (C_5H_5), 120.1 (CH), 132.3 (CH) and 141.7 (CH); *m*/*z* 357 (M^+), 327 (M^+ − NO), 297 (M^+ − 2NO); 149 (M^-).

[Cr(η-C_5H_5)(NO)$_2$($N_2C_5H_8$)][CF_3SO_3] 8. To a stirred solution of [Cr(η-C_5H_5)(NO)$_2$(CF_3SO_3)] (0.065 g, 0.20 mmol) in diethyl ether (20 cm^3) was added 3,5-dimethylpyrazole (0.022g, 0.23 mmol) in diethyl ether (10 cm^3). 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^3). Drying *in vacuo* provided the green *powder* [Cr(η-C_5H_5)(NO)$_2$($N_2C_5H_8$)][CF_3SO_3] **8** (0.071 g, 76%) (Found: C, 31.5; H, 3.21; N, 13.1. $C_{11}H_{13}CrF_3N_4O_5S$ requires C, 31.3; H, 3.10; N, 13.3%); ν_{max}/cm^{-1} (Nujol) 1839 and 1722 (NO); (CH_2Cl_2) 1835 and 1730; δ_H(CD_3CN) 2.16 (3 H, s, CH_3), 2.28 (3 H, s, CH_3), 5.89 (5 H, s, C_5H_5) and 6.15 (1 H, s, CH); δ_c(CD_3CN) 10.9 (CH_3), 14.6 (CH_3), 104.7 (C_5H_5), 109.0 (CH), 147.3 (*C*CH_3) and 156.4 (*C*CH_3); *m*/*z* 273 (M^+), 243 (M^+ − NO); 149 (M^-).

[Cr(η-C_5H_5)(NO)$_2$($N_2C_5H_7$)] 9. To [Cr(η-C_5H_5)(NO)$_2$($N_2C_5H_8$)][CF_3SO_3] (0.232 g, 0.55 mmol) and KBu^t (0.068 g, 0.61 mmol) was added tetrahydrofuran (≈10 cm^3) *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^3) and filtered. The Celite pad was washed with diethyl ether (3 × 5 cm^3). 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_5H_5)(NO)$_2$($N_2C_5H_7$)] **9** (0.070 g, 47%) (Found: C, 43.4; H, 4.33; N, 19.8%; M^+ 272. $C_{10}H_{12}CrN_4O_2$ requires C, 44.1; H, 4.44; N, 20.6%; *M* 272); ν_{max}/cm^{-1} (Nujol) 1800 and 1686 (NO); (Et_2O) 1808 and 1701; δ_H(C_6D_6) 2.19 (3 H,

s, CH_3), 2.53 (3 H, s, CH_3), 4.79 (5 H, s, C_5H_5) and 6.18 (1 H, s, CH); $\delta_c(C_6D_6)$ 14.7 (CH_3), 15.0 (CH_3), 102.8 (C_5H_5), 105.3 (CH), 149.3 (CCH_3) and 149.8 (CCH_3); *m/z* 272 (M^+), 242 ($M^+ - NO$), 212 ($M^+ - 2NO$).

[Cr(η-C_5H_5)(NO)($O_2C_5H_7$)] 10. *Method 1.* To [Cr(η-C_5H_5)-(NO)$_2$(CF_3SO_3)] (0.038 g, 0.117 mmol) and $CsOH·H_2O$ (0.020 g, 0.12 mmol) was added water (10 cm^3). The solution was stirred for 30 min, and acetylacetone (0.020 cm^3, 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_5H_5)(NO)($O_2C_5H_7$)] **10** (0.012 g, 42%) (Found: C, 48.5; H, 4.96; N, 5.57%; M^+ 246. $C_{10}H_{12}CrNO_3$ requires C, 48.8; H, 4.91; N, 5.96%; *M* 246); ν_{max}/cm^{-1} (Nujol) 1647 (NO); (CH_2Cl_2) 1656; *m/z* 246 (M^+), 216 ($M^+ - NO$).

Method 2. To a stirred solution of [NBu_4][Cr(η-C_5H_5)-(NO)(CF_3SO_3)$_2$] (0.118 g, 0.182 mmol) in water (5 cm^3) was added acetylacetone (0.025 cm^3, 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_5H_5)(NO)-($O_2C_5H_7$)] **10** by infrared spectroscopy and mass spectrometry (0.089 g, 52%) (Found M^+ 246; $C_{10}H_{12}CrNO_3$ requires *M* 246); ν_{max}/cm^{-1} (Nujol) 1647 (NO).

Method 3. Tetrahydrofuran (≈5 cm^3) was vacuum transferred onto [Cr(η-C_5H_5)(NO)(μ-I)]$_2$ (0.083 g, 0.151 mmol) and K($O_2C_5H_7$) (0.052 g, 0.377 mmol). Diethyl ether (5 cm^3) 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^3). The solution was reduced *in vacuo* to one-third volume and hexanes added (10 cm^3). The solution was cooled to −30 °C overnight, to provide green *crystals*, which were identified as [Cr(η-C_5H_5)(NO)-($O_2C_5H_7$)] **10** by infrared spectroscopy, mass spectrometry and single-crystal X-ray diffraction (0.051 g, 68%) (Found M^+ 246; $C_{10}H_{12}CrNO_3$ requires *M* 246); ν_{max}/cm^{-1} (Nujol) 1648 (NO).

[Cr(η-C_5H_5)(NO)($O_2C_7H_5$)] 11. This compound was prepared by the methods used for **10**, substituting salicylaldehyde for acetylacetone to give [Cr(η-C_5H_5)(NO)($O_2C_7H_5$)] **11** (84%) (Found: C, 53.6; H, 3.79; N, 5.15%; M^+ 268. $C_{12}H_{10}CrNO_3$ requires C, 53.7; H, 3.76; N, 5.22%; *M* 268); ν_{max}/cm^{-1} (Nujol) 1659 (NO); (Et_2O) 1677; *m/z* 268 (M^+), 238 ($M^+ - NO$).

[Cr(η-C_5H_5)(NO)($NC_6H_4O_2$)] 12. This compound was prepared by the methods used for **10**, substituting picolinic acid for acetylacetone to give [Cr(η-C_5H_5)(NO)($NC_6H_4O_2$)] **12** (59%) (Found: C, 48.9; H, 3.36; N, 10.4; M^+ 269. $C_{11}H_9CrN_2O_3$ requires C, 49.1; H, 3.37; N, 10.4; *M* 269); ν_{max}/cm^{-1} (Nujol) 1666 (NO); (CH_2Cl_2) 1683; *m/z* 269 (M^+), 239 ($M^+ - NO$), 195 ($M^+ - NO - C_5H_5$).

[Cr(η-C_5H_5)(NO)(H_2O)$_2$][BPh_4] 13. A suspension of [Cr(η-C_5H_5)(NO)(μ-I)]$_2$ (0.260 g, 0.474 mmol) in water (10 cm^3) was stirred and heated to 70 °C for 30 min. The clear green solution was filtered, and to the filtrate was added $NaBPh_4$ (0.680 g, 1.99 mmol) in water (5 cm^3). A microcrystalline solid immediately formed, and was collected by filtration, washed with water (2 × 5 cm^3) then with hexanes (4 × 5 cm^3) to give [Cr(η-C_5H_5)(NO)(H_2O)$_2$][BPh_4] **13** (0.280 g, 53%) (Found: C, 69.5; H, 5.86; N, 2.80. $C_{29}H_{29}BCrNO_3$ requires C, 69.3; H, 5.82; N, 2.80%); ν_{max}/cm^{-1} (Nujol) 1692 (NO).

[Cr(η-C_5H_5)(NO)(μ-OH)]$_2$ 14. A suspension of [Cr(η-C_5H_5)-(NO)(μ-I)]$_2$ (0.150 g, 0.273 mmol) in water (10 cm^3) 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^3) to yield a metallic brown *powder* [Cr(η-C_5H_5)(NO)(μ-OH)]$_2$ **14** (0.020 g, 22%) (Found: C, 36.35; H, 3.80; N, 8.38; M^+ = 328. $C_{10}H_{12}Cr_2N_2O_4$ requires C, 36.6; H, 3.66; N, 8.54; *M* = 328); ν_{max}/cm^{-1} (Nujol) 1595 (NO); *m/z* 328 (M^+), 298 ($M^+ - NO$), 268 ($M^+ - 2NO$).

X-Ray crystallographic analysis of [Cr(η-C_5Me_5)(NO)$_2$-(CF_3SO_3)] 2

Crystal data. $C_{11}H_{15}CrF_3N_2O_5S$, *M* = 396.30, space group $P2_1/n$ (no. 14), monoclinic, *a* = 8.575(1), *b* = 8.642(1), *c* = 21.8626(9) Å, β = 91.760(7), *U* = 1619.4(3) $Å^3$ (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_c = 1.625 g cm^{-3}, *F*(000) = 808. Brown prisms, crystal dimensions 0.20 × 0.40 × 0.40 mm, μ(Mo-Kα) = 8.65 cm^{-1}.

Data collection and processing.[29] Rigaku AFC6S diffractometer, ω–2θ scan mode, ω-scan width 1.21 + 0.35 tan θ, ω-scan speed 16° min^{-1} (up to 8 rescans), graphite-monochromated Mo-Kα radiation; 5007 unique reflections measured (1 < θ < 30°, *h*,*k*, ± *l*), 2546 having $I \geqslant 3\sigma(I)$. 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, $B_{iso} = 1.2B$(parent atom)]. Statistical weights = $4F_o/\sigma^2(F^2)$.[29] Final $R = \Sigma||F_o|-|F_c||/\Sigma|F_o| = 0.039$, $R' = (\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2)^{\frac{1}{2}} = 0.039$ for 2546 reflections with $I \geqslant 3\sigma(I)$. 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^5-C_5H_5)(NO)$_2$-($N_2C_5H_7$)] 9

Crystal Data. $C_{10}H_{12}CrN_4O_2$, *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) $Å^3$ [by least-squares refinement on F^2 for three sets of 20 frames with 2.16 < 2θ < 25.03°, λ = 0.71073 Å, *T* = 173(2) K], *Z* = 8, D_c = 1.519 g cm^{-3}, *F*(000) = 1120. Green blocks, crystal dimensions 0.45 × 0.42 × 0.30 mm, μ(Mo-Kα) = 0.956 mm^{-1}.

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_{int} = 0.0229). No intensity checks were made. Absorption correction = semiempirical.[31]

Structure analysis and refinement. The structure was solved by direct methods and refined by full-matrix least squares on F^2.[32] Statistical weights = $[\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$, where $P = (F_o^2 + F_c^2)/3$, *A* = 0.0384 and *B* = 5.3763. Final *R*1 = 0.0318, *wR*2 = 0.0815 for 2072 reflections with $I \geqslant 2\sigma(I)$, goodness of fit on F^2 = 1.021. Bond lengths and bond angles appear in Table 2.

X-Ray crystallographic analysis of [Cr(η^5-C_5H_5)(NO)-($O_2C_5H_7$)] 10

Crystal data. $C_{10}H_{12}CrNO_3$, *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) $Å^3$ (by least-squares refinement on setting angles for 25 reflections with 17° < 2θ < 28°, λ = 0.71069 Å,

$T = 21$ °C), $Z = 4$, $D_c = 1.539$ g cm^{-3}, $F(000) = 508$. Green plates, crystal dimensions 0.07 × 0.30 × 0.30 mm, μ(Mo-Kα) = 10.62 cm^{-1}.

Data collection and processing.[29] Rigaku AFC6S diffractometer, ω–2θ scan mode, ω-scan width 1.21 + 0.35 tan θ, ω-scan speed 16° min^{-1} (up to 8 rescans), graphite-monochromated Mo-Kα radiation; 1822 unique reflections measured ($1 < \theta < 30°$, h,k,l), 787 having $I \geqslant 3\sigma(I)$. 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 Å, $B_{iso} = 1.2B$(parent atom)]. Statistical weights = $4F_o/\sigma^2(F^2)$.[29] Final $R = \Sigma||F_o|-|F_c||/\Sigma|F_o| = 0.037$, $R' = (\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2)^{\frac{1}{2}} = 0.033$ for 787 reflections with $I \geqslant 3\sigma(I)$. Computer programs and source of scattering factors are given in ref. 29. Bond lengths and bond angles appear in Table 3.

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