Reduction of Nitric Oxide by Tetramesityliridium(IV) and Cobaltocene. Reactions of Hyponitrite Complexes and of the Ether $[Co(\eta^5-C_5H_5)(\eta^4-C_5H_5)](\mu-O-exo)$ with Nitroalkanes, Acids and Amines†

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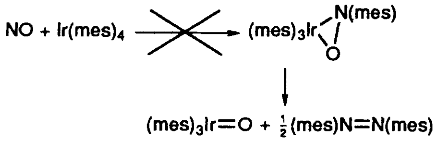
The interactions of either $Ir(mes)_4$ (mes = $C_6H_2Me_3$-2,4,6) or $Co(cp)_2$ (cp = $\eta^5-C_5H_5$) with NO in light petroleum gave unstable solids the IR spectra of which allow them to be formulated as hyponitrite complexes, *e.g.* $[Co(cp)_2]_2(N_2O_2)$ **1**; their reaction with $MeNO_2$ is described. The compound $Co(cp)_2$ with either NO or $Ag_2N_2O_2$ in toluene gave N_2O and the very reactive ether $[Co(cp)(\eta^4-C_5H_5)]_2(\mu-O-exo)$ **2**. This reacts with nitroalkanes where the product depends on the nature of the nitroalkane. Nitromethane produced both $Co(cp)_2^+\ CH_2{=}NO_2^-{\cdot}H_2O$ **3** and $[Co(cp)(\eta^4-C_5H_5)]_2[(\mu-CH(NO_2)-exo]$ **4**, while $Me_2CH(NO_2)$ gave $Co(cp)[\eta^4-C_5H_5(CMe_2NO_2)-exo]$ and $EtNO_2$ corresponding species to **3** and **4** (*i.e.* **6** and **7**). Reactions of **2** with alcohols or phenylacetylene gave mononuclear species of the same type as **4**; treatment with NH_2Ph or $NHPh_2$ also gave similar *exo* complexes **8** and **9** respectively. All these *exo* species reacted with $CHCl_3$ to give the *exo*-CCl_3 compound by facile C–C bond cleavage. Mechanisms for the various reactions are discussed. The structures of compounds **2**–**4**, **8** and **9** have been confirmed by X-ray crystallography: **2** and **4** contain $Co(cp)(\eta^4-C_5H_5)$ moieties bridged by oxygen or $CH(NO_2)$ groups while **8** and **9** are monomers with *exo*-NHPh or -NPh_2 groups. In all cases but one (**2**) there are near-eclipsed C_5CoC_5 geometries; for one of the cobalts in **2** there is a twist of *ca.* 16° from the eclipsed configuration. Compound **3** has $Co(cp)_2^+$ and $CH_2NO_2^-$ ions the latter being involved in strong hydrogen bonding with the H_2O molecule also present in the lattice. In both **8** and **9** there is structural evidence for π interaction between p lone pairs on the planar nitrogen atom and the π system of a phenyl ring.

This study arose from the observation that the paramagnetic (1e) compound $Ir(mes)_4$, where mes = $C_6H_2Me_3$-2,4,6,[1] reacted with nitric oxide in light petroleum to give an unstable solid, which was soluble in nitromethane or acetonitrile giving a solution ^1H NMR spectrum identical to that of the iridium(V) cation[1] $[Ir(mes)_4]^+$.

Previous studies[2] of the reactions of paramagnetic (1e) alkyls and aryls of transition metals with nitric oxide led to insertion of NO into the M–C bond followed by the formation of an M=O bond and RN=NR. However, it was evident that despite the existence of $(mes)_3Ir^V{=}O$[3] the reaction, equation (1), does



(1)

not occur. In view of the limited quantities of $Ir(mes)_4$ available we studied the reaction of NO with $Co(cp)_2$ (cp = $\eta^5-C_5H_5$) which also is paramagnetic (1e) and is readily oxidised to the cobaltocenium ion, $Co(cp)_2^+$.[4]

Studies by Bottomley and co-workers,[5] of paramagnetic η^5-cyclopentadienyl compounds of Ti^{III} and V^{II} showed that the interaction with NO led to compounds with M–O–M bonds. Although the dioxodinitrate(*N*–*N*)(2−) (hyponitrite) ion, $N_2O_2^{2-}$, was considered as a possible intermediate in the reactions, no direct evidence for the formation of this ion was obtained[5c] although N_2O was formed; this gas could be obtained by the reaction (2). Unstable hyponitrite complexes

$$N_2O_2^{2-} \longrightarrow N_2O + O^{2-} \qquad (2)$$

of several transition metals have been obtained in reactions of NO with low-valent metal compounds or in thermal reactions of bis(nitrosyl) complexes.[6] Sodium hyponitrite is made[7] by sodium reduction of NO in reactions presumably involving two one-electron transfers, equations (3)–(5).

$$M^{\bullet} + {}^{\bullet}NO \longrightarrow M^+ + NO^- \qquad (3)$$

$$NO^- + {}^{\bullet}NO \longrightarrow N_2O_2^{\bullet -} \qquad (4)$$

$$N_2O_2^{\bullet -} + M^{\bullet} \longrightarrow 2M^+N_2O_2^{2-} \qquad (5)$$

Results and Discussion

Reaction of $Ir(mes)_4$ *and* $Co(cp)_2$ *with* NO.—The interaction of $Ir(mes)_4$ with NO in light petroleum gives a green-black precipitate the IR spectrum of which, taken as quickly as

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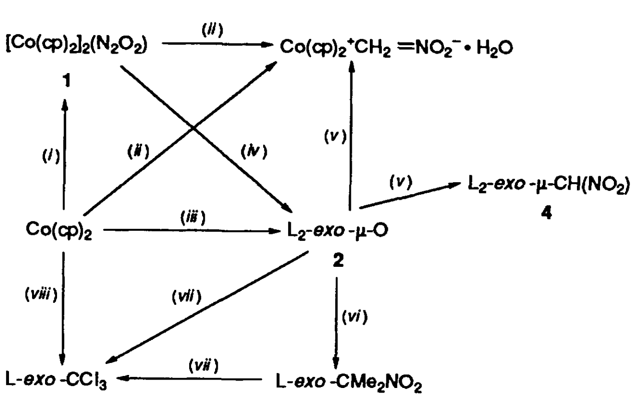
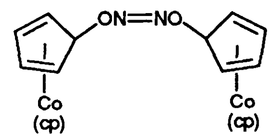
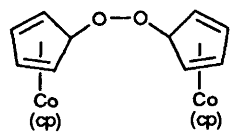
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.



Scheme 1 Main reactions of $Co(cp)_2$ involving NO and nitroalkanes. L = (η^5-C_5H_5)Co(η^4-C_5H_5) unit. (*i*) NO in light petroleum; (*ii*) NO in $MeNO_2$; (*iii*) NO or $Ag_2N_2O_2$ in toluene; (*iv*) toluene; (*v*) $MeNO_2$ in Et_2O; (*vi*) $Me_2CH(NO_2)$ in Et_2O; (*vii*) $CHCl_3$; (*viii*) CCl_4 [50% yield + $Co(cp)_2Cl$]. Nitrous oxide is eliminated in reactions of compound **1** and in (*iii*)



I



II

possible, has three bands (1097, 1022, 802 cm^{-1}) in the regions found[6] for co-ordinated hyponitrites; ionic hyponitrites[8] have two bands around 1058 and 571 cm^{-1}, as we have confirmed also for $Ag_2N_2O_2$. Since three bands are also found for the cobalt compound discussed below we consider that the iridium compound is the oxygen-bridged species $[Ir^V(mes)_4]_2(\mu$-ONNO-$\kappa^2O)$ formed by two one-electron transfers from $Ir(mes)_4$ to NO as in equations (3)–(5).

The interaction of $Co(cp)_2$ (see Scheme 1) in hexane or light petroleum with NO leads rapidly to a beige precipitate. This compound **1** is unstable at room temperature, becoming red-orange (see below), but the IR spectrum, again taken as rapidly as possible, also has three bands at 1088, 1020 and 800 cm^{-1} in addition to bands for cp and η^4-C_5H_5 rings; a structure of the type **I** seems reasonable.

It is surprising considering the extensive work on reactions of NO with $M(cp)_2$ type compounds and especially in view of the innumerable studies[9] on $Co(cp)_2$ that the reaction of the latter with NO appears not to have been reported, perhaps because of the problems encountered in this study. The only comparable reaction is that of $Co(cp)_2$ and O_2 at low temperatures,[10] which gives a very thermally unstable compound (decomp. > −40 °C), formulated only on the basis of its chemical reactions (*cf.* later discussion) as the *exo*-peroxo-bridged η^4-cyclopentadiene cobalt(I) complex **II**. It may be noted here, in view of the similar compounds discussed below, that a variety of *exo*-bridged species are known,[9,10] *e.g.* with μ-CF_2CF_2 and μ-$CH_2C(O)CH_2$; some are noted later.

On standing in toluene compound **1** decomposes with loss of N_2O, confirmed by collection of gas and subsequent gas chromatography–mass spectrometry (GS-MS) study, to give an orange solution containing a cobalt(I) complex **2** described below.

The iridium hyponitrite dissolves in nitromethane with evolution of N_2O as confirmed by mass spectral study but, unlike the cobalt system discussed below, no crystalline product could be obtained; the ^1H NMR spectrum in $CDCl_3$ of the solid residue after pumping off $MeNO_2$ showed only bands for $[Ir(mes)_4]^+$ as noted in the Introduction and the IR spectrum showed OH stretches.

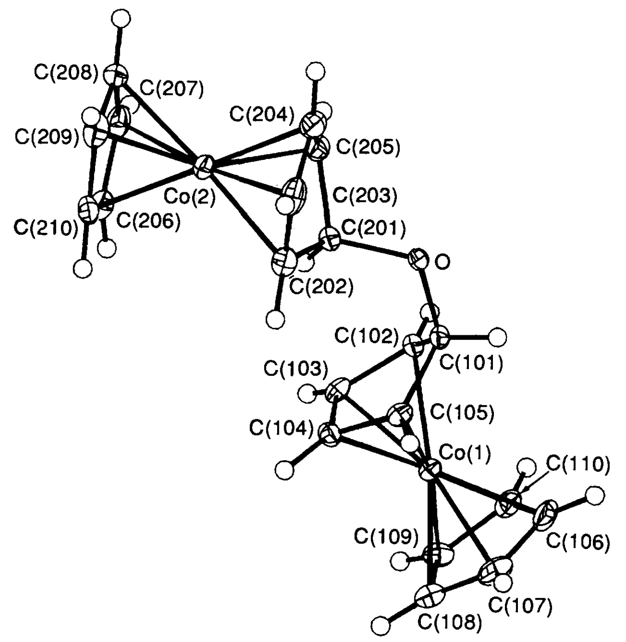
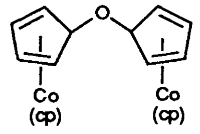


Fig. 1 Structure of the ether $[Co(cp)(\eta^4$-$C_5H_5)]_2(\mu$-O-*exo*) **2**



III

Reaction of $Co(cp)_2$ *and* NO *in Toluene*.—By contrast with the reaction in hexane, in toluene NO reacts immediately to give an orange solution (N_2O is also formed and detected in off-gas by mass spectrometry) from which, on cooling, orange crystals of a compound **2** can be isolated. That a hyponitrite intermediate is involved is confirmed directly by vigorous stirring of a toluene solution of $Co(cp)_2$ with solid $Ag_2N_2O_2$ which again leads to **2** and N_2O.

The compound **2** although stable at room temperature for only *ca.* 1 h can be kept below *ca.* −20 °C and the crystal structure was determined at low temperature. This shows that **2** is the *exo*-μ-O ether **III** and similar to that proposed for the μ-peroxo species noted above. The structure is shown in Fig. 1 and selected bond lengths and angles are given in Table 1. The main feature is the unsymmetrical disposition of the η^4-C_5H_5 groups about the ether linkage which is probably due to steric effects. As a result, the methine H atom on ring 2 [at C(201)] lies approximately over the η^4 ring 1 [C(102)–C(105)] and the C–O–C angle at the ether oxygen at 114.7(3)° is slightly larger than expected. Other points of note relate to the geometries of the distorted rings. Not unexpectedly the η^4 ring has 'slipped' as a result of the loss of bonding to the aliphatic carbons C(101) and C(201) by approximately 0.25 Å. For Co(1) the two rings have a closely eclipsed relative arrangement whereas for Co(2) they are twisted by approximately 16° from an eclipsed configuration. The Co–C bond lengths to the η^5 rings lie in the range 2.037(5)–2.082(5) Å whereas the distances to the η^4 rings are significantly shorter on average and specifically shorter to the central atoms of the 'butadiene' fragment [C(103), C(104) and C(203), C(204)] at 1.967(5)–1.974(5) Å, *cf.* 2.027(5)–2.042(5) Å to C(102), C(105), C(202) and C(205). The C–O distances in the ether link at 1.456(5), 1.475(5) Å are normal. In

Table 1 Selected bond lengths (Å) and angles (°) for compounds **2**–**4**, **8** and **9**

	2	**3**	**4**	**8**	**9**
Co(1)–C(101)	2.497(4)	2.021(4)	2.554(5)	2.552(7)	2.534(3)
Co(1)–C(102)	2.038(5)	2.019(4)	2.027(5)	2.023(7)	2.046(3)
Co(1)–C(103)	1.974(5)	2.017(4)	1.980(5)	1.974(7)	1.985(4)
Co(1)–C(104)	1.968(5)	2.010(4)	1.967(5)	1.981(7)	1.982(4)
Co(1)–C(105)	2.042(5)	2.015(5)	2.008(5)	2.019(8)	2.031(3)
Co(1)–C(106)	2.044(5)	2.010(4)	2.030(5)	2.053(7)	2.070(4)
Co(1)–C(107)	2.037(5)	2.005(4)	2.039(5)	2.063(7)	2.102(4)
Co(1)–C(108)	2.078(5)	2.023(4)	2.092(5)	2.093(7)	2.097(4)
Co(1)–C(109)	2.082(5)	2.022(4)	2.090(5)	2.088(7)	2.040(3)
Co(1)–C(110)	2.046(5)	2.012(4)	2.042(5)	2.042(7)	2.066(4)
Co(2)–C(201)	2.527(5)	—	2.548(5)	—	—
Co(2)–C(202)	2.027(5)	—	2.027(5)	—	—
Co(2)–C(203)	1.967(5)	—	1.964(5)	—	—
Co(2)–C(204)	1.967(5)	—	1.973(5)	—	—
Co(2)–C(205)	2.041(5)	—	2.008(4)	—	—
Co(2)–C(206)	2.055(5)	—	2.030(5)	—	—
Co(2)–C(207)	2.061(5)	—	2.052(5)	—	—
Co(2)–C(208)	2.077(5)	—	2.100(5)	—	—
Co(2)–C(209)	2.078(5)	—	2.081(5)	—	—
Co(2)–C(210)	2.050(5)	—	2.028(6)	—	—
Solvent in lattice					
O(1)–N	—	1.303(4)	—	—	—
O(2)–N	—	1.276(4)	—	—	—
C(11)–N	—	1.308(5)	—	—	—
Bridging atoms					
O(1)–C(101)	1.475(5)	—	—	—	—
O(1)–C(201)	1.456(5)	—	—	—	—
C(1)–C(101)	—	—	1.540(6)	—	—
C(1)–C(201)	—	—	1.554(6)	—	—
Pendant groups					
N–C(1)	—	—	—	1.475(8)	1.508(4)
N–C(11)	—	—	—	1.387(8)	1.400(4)
N–C(21)	—	—	—	—	1.450(4)
N–H	—	—	—	1.05(8)	—
X(1)–C(101)–C(102)	117.3(4)	—	115.4(4)	—	—
X(1)–C(101)–C(105)	117.0(4)	—	113.0(4)	—	—
X(1)–C(201)–C(205)	110.7(4)	—	115.3(4)	—	—
X(1)–C(201)–C(202)	114.7(4)	—	114.7(4)	—	—
C(201)–X(1)–C(101)	114.7(3)	—	112.8(4)	—	—
C(104)–C(105)–C(101)	109.4(4)	—	110.0(4)	—	—
C(103)–C(102)–C(101)	109.9(4)	—	109.8(4)	—	—
C(204)–C(205)–C(201)	110.1(4)	—	109.7(4)	—	—
C(203)–C(202)–C(201)	108.9(4)	—	109.3(4)	—	—
N(1)–C(1)–C(101)	—	—	110.0(4)	—	—
N(1)–C(1)–C(201)	—	—	106.1(3)	—	—
O(2)–N–O(1)	—	117.5(3)	123.4(4)	—	—
O(2)–N–C(11)	—	122.6(4)	117.9(4)	—	—
O(1)–N–C(11)	—	120.0(4)	118.8(4)	—	—
C(2)–C(1)–N	—	—	—	117.7(5)	116.5(2)
C(5)–C(1)–N	—	—	—	113.2(6)	116.4(3)
C(3)–C(2)–C(1)	—	—	—	110.2(6)	110.3(3)
C(4)–C(5)–C(1)	—	—	—	112.1(7)	110.4(3)
C(1)–N–C(11)	—	—	—	122.7(6)	119.0(2)
C(1)–N–C(21)	—	—	—	—	119.2(2)
C(1)–N–H	—	—	—	118(4)	—
C(11)–N–H	—	—	—	114(4)	—

For compounds **3**, **8** and **9**, C(101) to C(110) refer to actual atoms C(1) to C(10); for **2**, **4**, **8** and **9**, C(101) and C(201) (**2** and **4**) are the tilted atoms in the η^4 rings; X is the bridging atom, oxygen in complex **2** and carbon in **4**; for compound **4**, C(11) refers to the actual atom C(1).

the folded η^4 rings the envelope folds are 27.6(3) and 30.2(5)° for rings 1 and 2 respectively; the angles between the η^5 rings and η^4 moieties are close to zero at 3.9(3) and 3.4(4)°.

The IR and ^1H NMR spectra of compound **2** are in accord with the ether structure and are closely similar to those of the cobalt and rhodium cyclopentadiene complexes $M(cp)(\eta^4\text{-}C_5H_5R)$ [M = Co, R = H, Me, $CHCl_2$ or CCl_3, M = Rh, R = H]; the cobalt compounds were made by interaction of

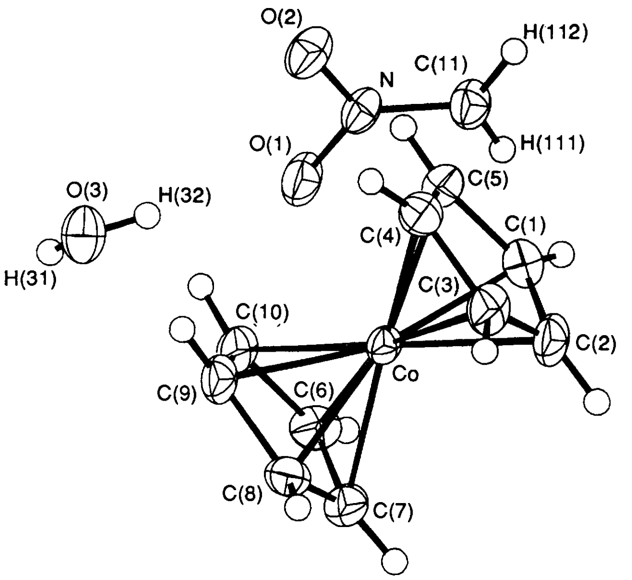


Fig. 2 Asymmetric unit in the structure of $Co(cp)_2{}^+CH_2{=}NO_2{}^-\cdot H_2O$ 3

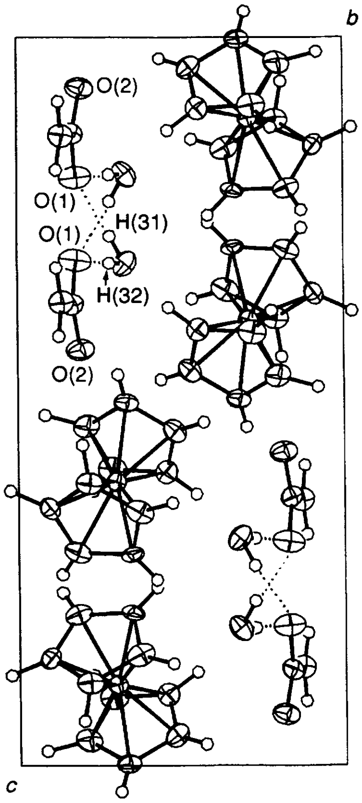


Fig. 3 Packing diagram for compound 3

alkyl halides with Co(cp)$_2$.*[11a] The only difference is that 2 has a band in the IR spectrum at 898 cm^{-1} that can be assigned to the ether, C–O–C, linkage. The ether 2 is exceptionally reactive towards compounds with acidic hydrogens and this behaviour is in striking contrast to the usual low reactivity of ethers, except special cases like alkyl tetrahydropyranyl ethers.[12]

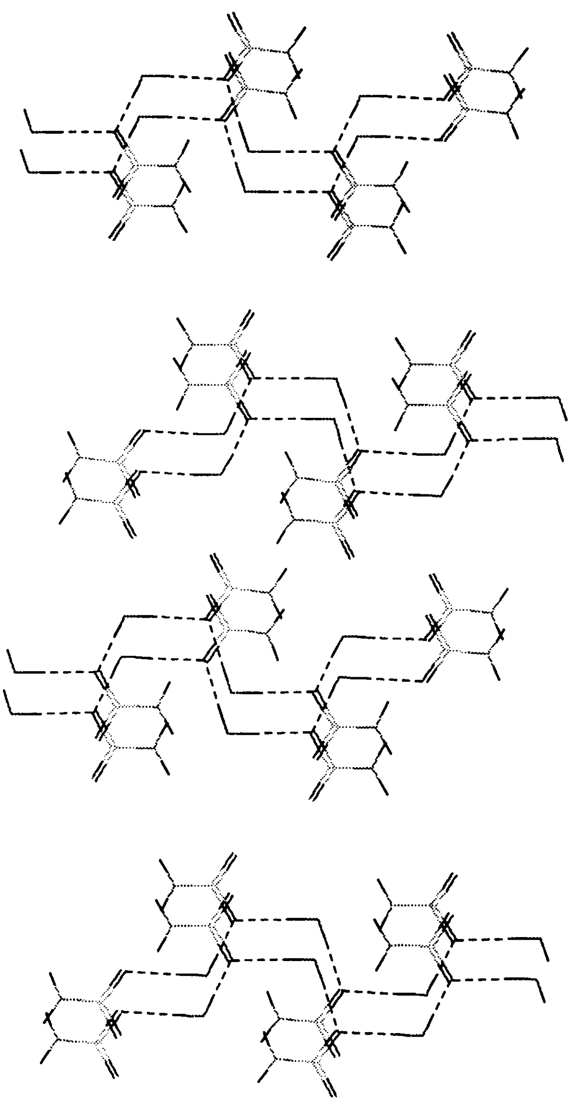
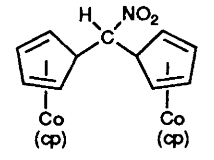


Fig. 4 Hydrogen-bonded ribbons of $H_2O\cdot CH_2NO_2{}^-$ present in the structure of compound 3



IV

Reactions of Compound 2 *with Nitroalkanes.*—Nitromethane reacts rapidly with compound 2 in diethyl ether solutions {*cf.* the reaction of $[Ir(mes)_4]_2(N_2O_2)$ with $MeNO_2$ above} to give two products easily separated by crystallisation. The first isolated is a yellow crystalline solid 3 which is unstable at room temperature or on pumping in vacuum, losing $MeNO_2$. The residue according to IR spectra appears to be $Co(cp)_2{}^+OH^-$. Since the crystal structure of 3 discussed below indicates that it is $Co(cp)_2{}^+CH_2{=}NO_2{}^-\cdot H_2O$ this observation is not surprising. In solution in $CDCl_3$ the ^1H NMR spectrum shows bands for $Co(cp)_2{}^+$ and $MeNO_2$, the latter formed by reaction of $CH_2{=}NO_2{}^-$ and the water of crystallisation.

The structure of compound 3 determined by X-ray crystallography at low temperature is shown in Fig. 2; selected

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* The compound Rh(cp)(C_5H_6) was made by direct interaction of $RhCl_3$ and Na(cp) in the solid state at *ca.* 120 °C in November 1955 at Harvard University by G. W. and characterised by IR and ^1H NMR spectroscopy. These species were first formulated as having *endo*-R groups but later reformulated as *exo* species.[9b] The mechanism of reactions of Co(cp)$_2$ and RX is known to be free radical in nature.[11b]

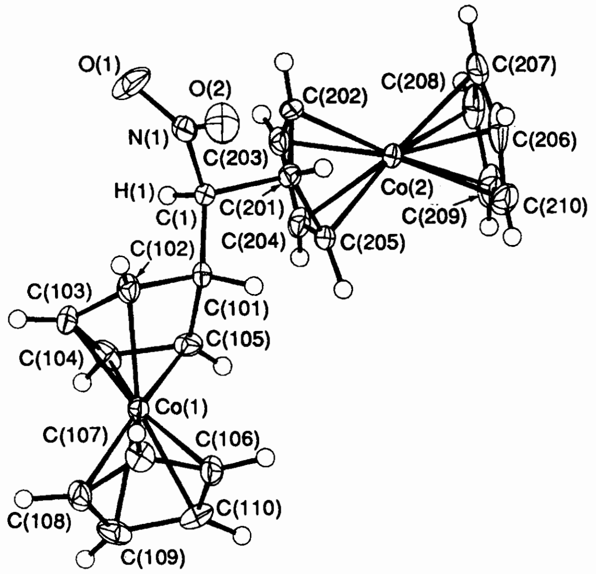
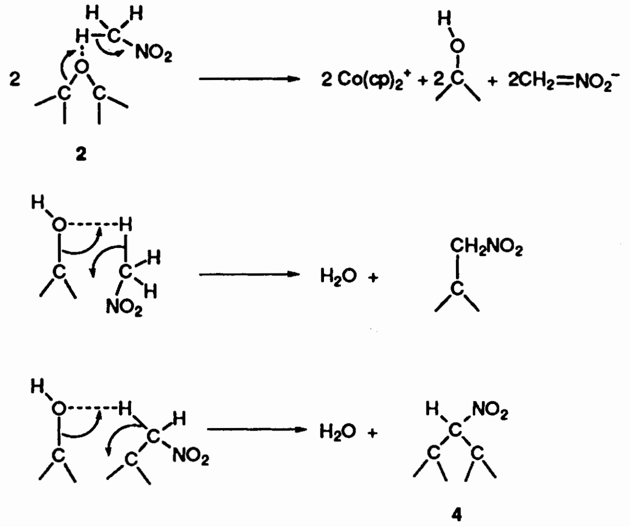


Fig. 5 Structure of $[Co(cp)(\eta^4\text{-}C_5H_5)]_2[\mu\text{-}CH(NO_2)\text{-}exo]$ **4**

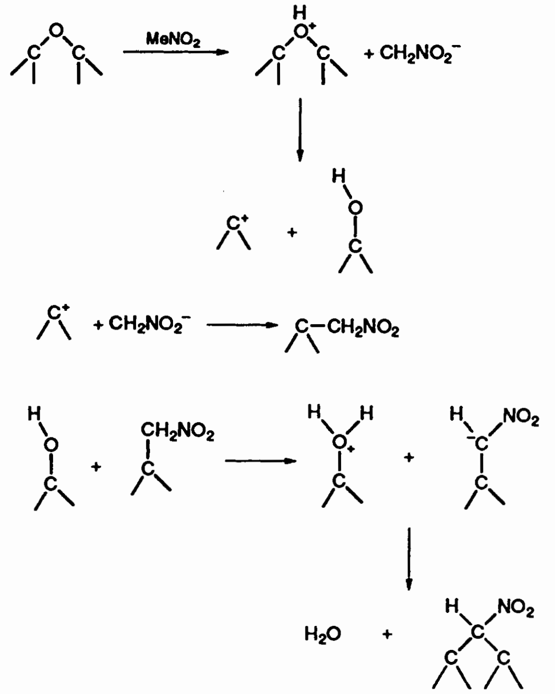
bond lengths and angles are given in Table 1. The rings in the cobaltocenium ion have a near-eclipsed configuration with Co–C bond lengths shorter than in the Co(cp) moiety for compound **2** as expected, 2.005(4)–2.023(4) Å. The compound also contains the methylideneazinate ion $CH_2{=}NO_2^-$ the structure of which has not, to our knowledge, previously been determined.[13] The ion is planar to within limits of experimental error and the geometry agrees with the results of theoretical calculations,[13a] except that our measured C–N bond, which clearly has multiple character, is some 0.04 Å shorter than that predicted using an extended basis set (MP2-HF/6-31G*), but agrees very well with that computed at the Hartree-Fock (HF) level. The two N–O bond lengths are 1.276(4) and 1.303(4) Å, with the former agreeing well with theory. In the crystal structure the $CH_2{=}NO_2^-$ ion is involved in an extended ribbon-like hydrogen bonding system with the water molecule as can be seen in Figs. 3 and 4. The strongest interactions are O(3)–H(32) ··· O(1)–N 1.83 and O(3)–H(31) ··· O(1)–N 1.81 Å. The involvement only of O(1) of the NO_2 group in hydrogen bonding probably accounts for the greater length of O(1)–N.

The second compound **4** formed in the reaction of **2** with $MeNO_2$ is red-orange; this is the *exo*-$CH(NO_2)$ cyclopentadiene cobalt(I) complex shown in **IV**. In addition to the bands characteristic for the cp and η^4-diene rings the IR spectrum shows NO_2 stretches; the ^1H NMR spectrum in C_6D_6 has a triplet for the H of the *exo*-μ-$CH(NO_2)$ group while the *endo*-H atoms of the rings appear as a doublet of triplets, the coupling constant (J = 8.25 Hz) being as expected.

The structure of compound **4** as determined by X-ray diffraction is shown in Fig. 5; selected bond lengths and angles are given in Table 1. It is analogous to that of **2** but with O replaced by a doubly deprotonated $MeNO_2$ group, *i.e.* $CH(NO_2)$. The presence of the latter results in a different conformational arrangement of the η^4-C_5H_5 groups about the C–C bonds of the bridge and it is noteworthy that the C–C–C angle is some 2° less than the C–O–C angle in **2**. The geometries of the Co(cp) and η^4-C_5H_5 fragments are very similar to those in **2** in terms both of bond lengths (Table 1) and folds in the η^4 rings [33.0(5), 32.5(4)°]. However, the angles between the η^5 ring and the η^4 fragment are now 6.4(5) and 6.8(3)°, the slight increase possibly reflecting the greater steric crowding present in **4**. The rings are close to eclipsed in both fragments of the molecule.

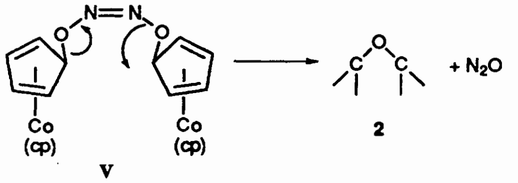


Scheme 2 Interaction of compound **2** with nitromethane. Overall stoichiometry, 2 × **2** + 3 MeNO ⟶ 2 × **3** + **4**



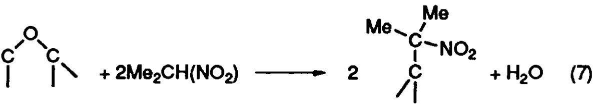
Scheme 3 Carbonium ion route for interaction of compound **2** and $MeNO_2$

Reaction Mechanisms of NO *and* RNO_2 *Reactions*.—Assuming, as suggested above, that the hyponitrite is co-ordinated in compound **1** it seems most likely that the N_2O_2 group is *exo* bound to a η^4-cyclopentadiene ring as in **V** [equation (6)] since ready decomposition to the ether **2** and


(6)

N_2O can then occur. Co-ordination of hyponitrite to cobalt seems highly unlikely. The reaction of **2** with $MeNO_2$ could then proceed as in Scheme 2. An alternative in Scheme 3 involves carbonium ion intermediates. Although the hydroxo species $Co(cp)[\eta^4\text{-}C_5H_5(OH)\text{-}exo]$ shown in Scheme 2 has previously been postulated in the interaction of $Co(cp)_2^+$ salts with concentrated NaOH solutions under forcing conditions to give azulene in low yield[14] there appears to be no other evidence for its existence. The *exo*-hydroxide would doubtless react immediately with $MeNO_2$ to give Co(cp)[η^4-$C_5H_5(CH_2NO_2)$-*exo*] which, with a second molecule of the hydroxide, would produce the unique μ-$CH(NO_2)$ bridge in compound **4**. The water formed in the reactions is then found in the salt **3**.

The formation of the monomeric *exo*-CH_2NO_2 species as an intermediate in Scheme 2 suggested that treatment of compound **2** with $Me_2CH(NO_2)$ would give only a monomer, since further H-atom transfer to give μ-$CH(NO_2)$ could not occur. This was found to be the case and the *exo*-CMe_2NO_2 complex **5** was isolated in essentially quantitative yield according to equation (7). It is of interest that in neat nitroalkanes as solvent $Co(cp)_2$ reacts with NO to give only the $Co(cp)_2{}^+$ salts of the appropriate anion.[15] Presumably the protonation reactions coupled with the driving force of N_2O elimination are more rapid than the reactions of the ether **2** with nitroalkanes.



2 **5**

The ether **2** does, however, react with $EtNO_2$ to give both the $Co(cp)_2{}^+$ salt of $Me(H)C{=}NO_2{}^-$ **6** as well as Co(cp){η^4-$C_5H_5[CH(Me)NO_2$-*exo*]} **7**. The failure to form the analogue of compound **4** despite the presence of a CH group in **7** is presumably due to steric factors. These are perhaps also the reasons why $Me_2CH(NO_2)$ in Et_2O gives only **5** without the formation of the cobaltocenium salt.

Other Reactions of Compound **2**.—There have been previous syntheses of *exo*-η^4-diene cobalt species[9] from CH acids. Thus acetylene reacts with $Co(cp)_2$ to give a dimeric species with an *exo*-CH=CH bridge[16] while secondary phosphine oxides $HP(O)R_2$, *e.g.* R = Bu^n or C_6H_{11}, give Co(cp){η^4-$C_5H_5[P(O)R_2$-*exo*]} and hydrogen at 100–140 °C.[17] However, most species [other than those formed along with Co(cp)X by interaction of $Co(cp)_2$ with halogenoalkanes, see *e.g.* refs. 9(*a*), (*b*) and 11(*a*)] have been obtained by interaction of $Co(cp)_2$ in *the presence of oxygen* with a variety of compounds[9,10] and evidently these reactions involved the labile μ-peroxo species noted earlier. *exo*-Compounds were obtained from $CHCl_3$, MeCN, Me_2HCCN, PhC≡CH, Me_2CO [which gives a CH_2-$C(O)CH_2$ bridge] as well as C_5H_6,[18] C_5H_5Me, indene and methanol.

In addition to confirming the nature of some of these products in reactions of compound **2** other new ones have been obtained. In all cases stoichiometric amounts of the reagent were added to the toluene solution of **2** made *in situ* from NO and $Co(cp)_2$. The compounds were characterised by ^1H NMR spectra in benzene solution. Monomeric species were obtained from PhC≡CH,[10b] MeOH[9c] and adamantan-1-ol. Acetic acid and C_6F_5OH however gave the $Co(cp)_2{}^+$ salts of the anion while $SiHPh_3$ gave $Co(cp)(C_5H_6)$ and $(Ph_3Si)_2O$. There was no reaction with $RhH(CO)(PPh_3)_3$.

While $Co(cp)_2$ can readily be obtained by interaction of $CoCl_2$ with C_5H_6 in the presence of NEt_3 and $NHEt_2$,[19] in toluene compound **2** reacts with NH_2Ph, $NHPh_2$, $NHEt_2$, 1-aminonaphthalene and carbazole. Although the complex from carbazole is insoluble, the other species are moderately soluble in benzene and stable at room temperature. The structures of **8** and **9** (Figs. 6 and 7), the *exo* compounds from aniline and diphenylamine, respectively, have been determined by X-ray crystallography, selected bond lengths and angles are given in Table 1. The structures show that the geometries of the Co(cp)(η^4-C_5H_5) moieties in **8** and **9** are similar to those of the other monomeric compounds of the types discussed earlier.

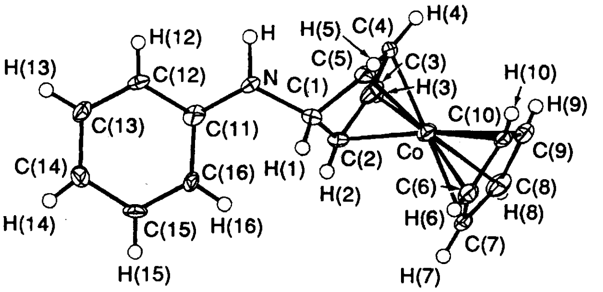


Fig. 6 Structure of Co(cp)[η^4-C_5H_5-(NHPh)-*exo*] **8**

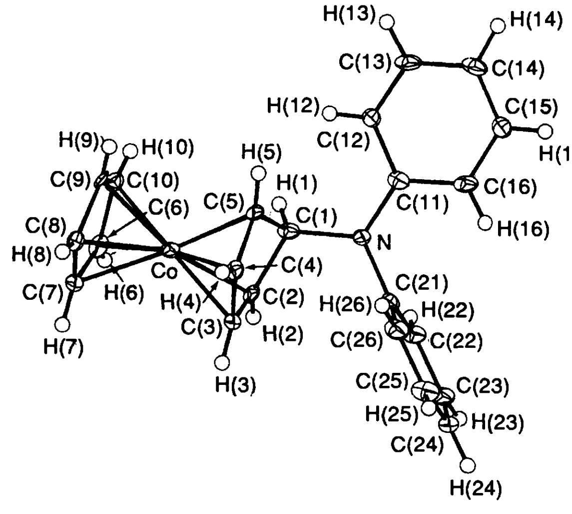


Fig. 7 Structure of Co(cp)[η^4-C_5H_5-(NPh_2)-*exo*] **9**

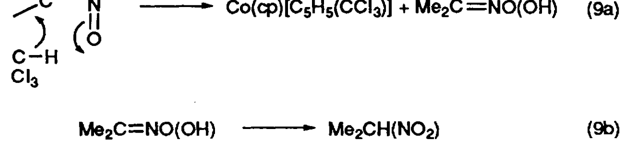
The envelope folds in the η^4 rings are 31.7(6) and 29.3(3)° and the cp/η^4 rings are eclipsed in both molecules. Perhaps the most significant feature in the structures is that in both molecules the geometry about the N atom is planar with the one phenyl ring in **8** and one of the rings in **9** coplanar with the plane of the sp^2 nitrogen. This feature and the shortness of the relevant N–C bond length (especially in **9** where it is 0.05 Å shorter than that to the other ring which is orthogonal to the N plane) indicates some interaction[20] between the π system of the coplanar phenyl ring and the lone pair on the N atom which is in the p orbital perpendicular to the plane.

Since the reaction of compound **2** with an amine is likely to differ from that of CH acids, the attack is more likely to be nucleophilic on the η^4-diene ring than on the ether oxygen atom. A possible pathway is shown in Scheme 4.

Facile C–X *Cleavage*.—Finally, all of the *exo* compounds both mono- and bi-nuclear except $Co(cp)(C_5H_6)$ react rapidly and quantitatively with $CHCl_3$ or $CDCl_3$ at room temperature to give the *exo*-CCl_3 compound[11a] as, *e.g.*, in equation (8).

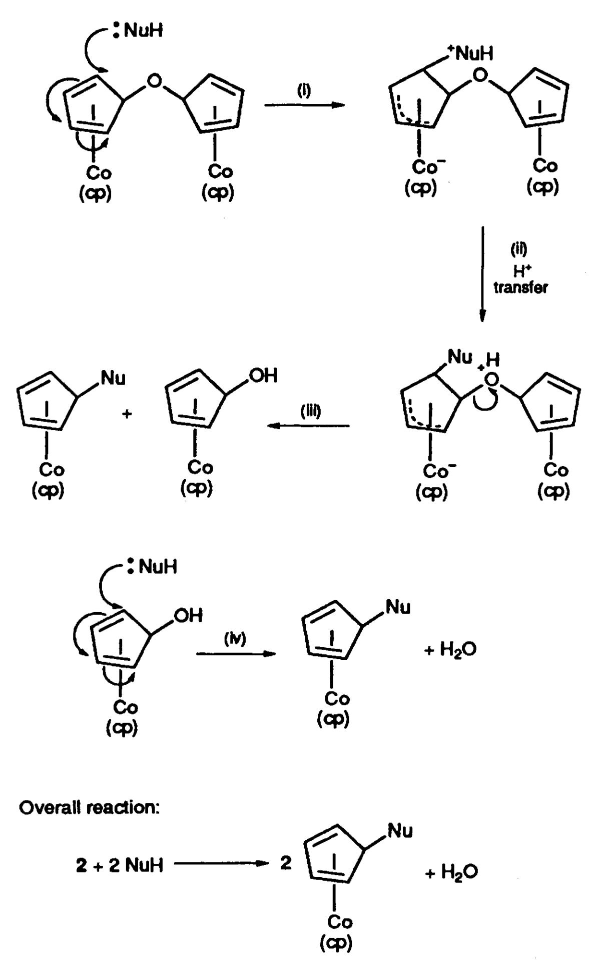
$$Co(cp)(C_5H_5R) + CHCl_3 \longrightarrow Co(cp)[C_5H_5(CCl_3)] + RH \quad (8)$$

Possible mechanisms are of the type shown in equations (9) and (10). It is also of interest that the C–P bond in the

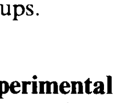


$$\longrightarrow Co(cp)[C_5H_5(CCl_3)] + Me_2C{=}NO(OH) \quad (9a)$$

$$Me_2C{=}NO(OH) \longrightarrow Me_2CH(NO_2) \quad (9b)$$



Scheme 4 Interaction of amines with compound **2**. Reaction (iv) follows a path similar to those in (i)–(iii). Nu = Nucleophile



$\longrightarrow$ Co(cp)[$C_5H_5(CCl_3)$] + PhC≡CH (10)

P(O)R$_2$ species noted above is also cleaved by CDCl$_3$[17] but the products were formulated as having *exo*-CDCl$_2$ groups according to the ^{1}H NMR spectra, which of course would not be definitive. We consider them also to have *exo*-CCl$_3$ groups.

Experimental

Microanalyses for the compounds (with one exception) could not be obtained due to the air and thermal sensitivity. The general techniques used have been described.[1] Infrared spectra (cm^{-1}) are in Nujol mulls. Proton NMR spectra (δ *vs.* SiMe$_4$) were obtained on a JEOL-EX-270 spectrometer at 270 MHz, mass spectra of NO and N$_2$O gas samples on a JEOL JMS-AX 505W spectrometer by the University of London MS Service at King's College.

Commercial samples were from Aldrich. The light petroleum used had b.p. 40–60 °C. Nitric oxide was passed through a copper coil at −78 °C and the purity checked by mass spectrometry. Sodium and silver hyponitrites[7,8] and Co(cp)$_2$[21] were made as described. Nitroalkanes were dried over CaSO$_4$ and distilled under N$_2$. All operations were carried out under purified N$_2$ or Ar or under vacuum.

Interaction of Co(cp)$_2$ *and* NO.—The gas was slowly passed through Co(cp)$_2$ (*ca.* 0.2 g) in light petroleum (30 cm^3) for 5–10 min until the purple colour disappeared and a beige precipitate of compound **1** was formed. After rapid filtration, the IR spectrum showed bands due to hyponitrite (see text) in addition to η^5- and η^4-C$_5$H$_5$ bands; the N$_2$O$_2$ bands disappear when the solid turns red-orange to be replaced by the C–O–C band[22] at *ca.* 900 cm^{-1} due to the ether link in **2**. The gas above the solid after decomposition was N$_2$O.

When a similar reaction was carried out in toluene a small amount of yellow solid was formed and a red-orange solution from which, after filtration, reduction in volume to *ca.* 10 cm^3 and cooling (−20 °C), X-ray-quality crystals of [Co(cp)(η^4-C$_5$H$_5$)]$_2$(μ-O-*exo*) **2** were obtained in > 90% yield. The crystals are stable for weeks at −20 °C. IR (cm^{-1}): Co(cp)(η^4-C$_5$H$_5$) bands[11a] and 898 (C–O–C). ^{1}H NMR (C$_6$D$_6$): δ 4.71 (t, J_{av} = 1.5, 4 H, H^{3,4} of η^4 ring), 4.44 (s, 10 H, cp), 4.03 (t, J_{av} = 2.3, 2 H, *endo* H^1 of η^4 ring), and 3.04 [q, *J* (inner pair) = 2.0, *J* (outer pair) = 2.3 Hz, 4 H, H^{2,5} of η^4 ring]. This spectrum is identical to that of the complex obtained from decomposition of **1** in toluene at room temperature. Compound **2** was also obtained essentially quantitatively when a mixture of Ag$_2$N$_2$O$_2$ (*ca.* 0.07 g) and Co(cp)$_2$ (*ca.* 0.09 g) in toluene (30 cm^3) was stirred very vigorously for 1 h; N$_2$O was lost and the solution became red-orange with formation of a black precipitate of silver. After filtration and reduction in volume, compound **2** was obtained in > 80% yield on cooling to −20 °C.

Reactions with Nitroalkanes.—(*a*) *Compounds* **3** *and* **4**. A fresh sample of compound **2** (*ca.* 0.06 g) was dissolved in MeNO$_2$ (*ca.* 2 cm^3) and the orange solution layered with Et$_2$O. After *ca.* 48 h at −20 °C yellow crystals of **3** (*ca.* 0.04 g, yield *ca.* 98%) were collected. The filtrate was evaporated in vacuum and the residue dissolved in toluene; cooling at −20 °C gave orange-red crystals of **4** (0.03 g, yield *ca.* 98%). X-Ray-quality crystals of **3** were obtained by recrystallisation from MeNO$_2$–Et$_2$O and of **4** from toluene. Compound **3**: IR (cm^{-1}) 3400 (br, H$_2$O), *ca.* 1200 (C=NO$_2^-$)[23a] and strong bands[23b] at 1417, 1012 and 868 [Co(cp)$_2^+$]; ^{1}H NMR (CDCl$_3$) δ 5.8 (s, cp) and 4.3 (MeNO$_2$ from reaction with H$_2$O, see text). Compound **4**: IR (cm^{-1}) cp and η^4-C$_5$H$_5$ bands; 1528, 1360 (NO$_2$);[15] ^{1}H NMR (C$_6$D$_6$) δ 4.77 (m, 4 H, H^{3,4} of η^4 ring), 4.38 (s, 10 H, cp), 2.99 (d of pseudo-t, 2 H, J_d = 8.25, J_t = 2.31, *endo*-H^1), 2.44 (m, 2 H, H^2 or H^5), 2.38 (m, 2 H, H^2 or H^5) and 2.36 [t, 1 H, *J* = 8.25 Hz, CH(NO$_2$)].

(*b*) Compound **5**. As in (*a*) but compound **2** (*ca.* 0.07 g) was dissolved with stirring in Me$_2$CH(NO$_2$) (20 cm^3); reduction in volume and cooling to −20 °C gave a quantitative yield of orange crystals of **5**. IR (cm^{-1}) 1575, 1151 (NO$_2$); cp and η^4-C$_5$H$_5$ bands. ^{1}H NMR (C$_6$D$_6$): δ 4.74 (t, br, 2 H, H^{3,4} of η^4 ring); 4.34 (s, 5 H, cp), 3.20 (t, br, 1 H, *endo*-H^1), 2.42 (q, br, 2 H, H^{2,5}) and 0.85 (s, 6 H, Me$_2$CNO$_2$).

(*c*) Interaction of NO and Co(cp)$_2$ in either neat MeNO$_2$ or Me$_2$CH(NO$_2$) gave a quantitative yield of the respective salts on work-up; both are unstable when solvent is removed. The characterisation was by IR and NMR spectra.

(*d*) The reaction of compound **2** and EtNO$_2$ was carried out as in (*a*) but **2** (0.16 g) was dissolved in EtNO$_2$ (3 cm^3) and Et$_2$O was added to precipitate the yellow salt **6** in quantitative yield (0.1 g). Evaporation of the mother-liquor and dissolution of the residue in toluene gave a quantitative yield (0.11 g) of orange Co(cp){η^4-C$_5$H$_5$[CH(Me)NO$_2$-*exo*]} **7**. Compound **6**: IR (cm^{-1}) 1552, 1260, 1370 and Co(cp)$_2^+$ bands; ^{1}H NMR (CDCl$_3$) δ 5.93 (cp), 3.24 (q, *J* = 7.26, CH$_2$) and 0.62 (t, *J* = 7.26, CH$_3$), both for EtNO$_2$. Compound **7**: IR (cm^{-1}) 1543, 1325, 1174 plus cp and η^4-C$_5$H$_5$ bands; ^{1}H NMR (C$_6$D$_6$) δ 4.75 (m, 1 H, H^3 or H^4 of η^4 ring), 4.70 (m, 1 H, H^3 or H^4), 4.34 (s, 5 H, cp), 3.05 [d of q, 1 H, *J* = 6.6 for q, 7.6 for d, C*H*(Me)NO$_2$], 2.85 (d of pseudo-t, 1 H, *J* = 7.59 for d, 2.64, 2.31 Hz for t), 2.50 and 2.19 (m, 1 H, H^2 or H^5 of η^4 ring).

Table 2 Crystal data and structure refinement for compounds **2**–**4**, **8** and **9**

	2	**3**	**4**	**8**	**9**
Formula	$C_{20}H_{20}Co_2O$	$C_{11}H_{14}CoNO_3$	$C_{21}H_{21}Co_2NO_2$	$C_{16}H_{16}CoN$	$C_{22}H_{20}CoN$
M_r	394.22	267.17	437.25	281.23	357.32
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	$P2_1/a$	$P2_1/a$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	11.537(4)	7.520(1)	5.615(1)	5.756(9)	8.036(8)
b/Å	10.197(2)	17.904(4)	11.920(2)	9.43(2)	11.060(3)
c/Å	13.265(2)	8.433(1)	13.583(3)	12.23(2)	11.363(2)
α/°	90(0)	90(0)	104.05(1)	98.7(1)	118.97(6)
β/°	96.81(2)	108.13(2)	94.42(1)	88.7(1)	108.94(4)
γ/°	90(0)	90(0)	91.12(1)	106.26(8)	88.34(4)
U/Å^3	1549.5(7)	1079.0(3)	878.6(3)	629.8(2)	825.6(9)
Z	4	4	2	2	2
D_c/Mg m^{-3}	1.690	1.645	1.653	1.483	1.437
$F(000)$	808	552	448	292	372
μ(Mo-Kα)/mm^{-1}	2.141	1.537	1.903	1.341	1.040
Reflections collected	5050	5473	2769	2096	2962
Independent reflections (R_{int})	2471 (0.0485)	2774 (0.0664)	2440 (0.0487)	1689 (0.0651)	2284 (0.0329)
Maximum, minimum absorption correction factors	0.775, 0.597	1.293, 1.059	0.834, 0.573	—	—
Data, parameters	2465, 288	2756, 201	2428, 310	1687, 227	2284, 297
Goodness of fit, F^2	0.383	0.417	0.337	0.382	0.381
Final R indices $R1$, $wR2$					
$[I > 2\sigma(I)]$	0.0320, 0.0800	0.0392, 0.0747	0.0356, 0.0863	0.0403, 0.0945	0.0348, 0.0884
(all data)	0.0566, 0.1230	0.0848, 0.1334	0.0505, 0.1592	0.0698, 0.1538	0.0406, 0.0996
Largest difference peak and hole/e Å^{-3}	0.376, −0.511	0.552, −0.539	0.334, −0.390	0.543, −0.238	0.395, −0.266

Goodness of fit, $S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{\frac{1}{2}}$ where n = number of reflections and p = total number of parameters; $R1 = \Sigma|F_o - F_c|/\Sigma F_o$; $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$ where $w = 1/[\sigma^2(F_o)^2 + (xP)^2]$ with $x = 0$ for compound **2** and 0.1 for **3**, **4**, **8** and **9** and $P = [\max(F_o^2, 0) + 2F_c^2]/3$.

Reactions of Compound **2** *with Other Substrates*.—All reactions were performed in the same manner from compound **2** prepared *in situ*: NO was passed slowly through a stirred toluene solution of $Co(cp)_2$ (0.1 g in *ca*. 20 cm^3) for 5–10 min as previously described. After filtration, the required amount of purified substrate [corresponding to 90% yield of **2** from $Co(cp)_2$] was added at room temperature. The formation of product was immediate with yields quantitative according to NMR spectroscopy, except in the cases of adamantan-1-ol (80) and PhC≡CH (23%). All products were crystallised from toluene; in the case of carbazole the product precipitated from the reaction mixture. Proton NMR data, in C_6D_6 unless otherwise indicated, for new compounds are as follows.

Compound **8**: δ 6.3–7.1 (m, 5 H, aromatic), 4.70 (pseudo-t, br, 2 H, J_t = 1.98, $H^{3,4}$), 4.49 (s, 5 H, cp), 4.00 (d of pseudo-t, J_d = 8.59, J_t = 1.98 and 2.64, *endo*-H^1), 2.95 (q, 2 H, J = 1.98, $H^{2,5}$) and 2.93 (d, br, 1 H, J *ca*. 8 Hz, NH).

Compound **9** (in $C_6D_5CD_3$): δ 6.8–7.15 (m, 10 H, aromatic), 4.70 (s, br, 1 H, *endo*-H^1), 4.49 (s, br, 7 H, cp and $H^{3,4}$) and 2.91 (s, br, 2 H, $H^{2,5}$); at −15 to −65 °C, δ 7.16–6.8 (m, 10 H, aromatic), 4.68 (s, br, 1 H, *endo*-H^1), 4.45 (s, 5 H, cp), 4.41 (s, br, 2 H, $H^{3,4}$) and 2.87 (s, br, 2 H, $H^{2,5}$).

Co(cp)[η^4-$C_5H_5(NHC_{10}H_7)$-*exo*]: δ 7.4–6.8 (m, 7 H, aromatic), 4.74 (pseudo-t, 2 H, J 1.98 and 1.65 Hz, $H^{3,4}$), 4.50 (s, 5 H, cp), 4.22 (d pseudo-t, 1 H, J_d = 7.9, J_t = 2.31, *endo*-H^1), 3.72 (d, br, 1 H, J_d = 7.9, NH), 3.06 (q, 2 H, J = 1.98 between inner pairs, 2.31 Hz between outer pairs, $H^{2,5}$).

Co(cp)[η^4-$C_5H_5(NEt_2)$-*exo*]: δ 4.86 (pseudo-t, 2 H, J = 1.98 and 2.65 Hz, $H^{3,4}$), 4.49 (s, 5 H, cp), 3.74 (pseudo-t, 1 H, J = 2.31 and 1.98, *endo*-H^1), 2.80 (q, 2 H, J = 2.65 between inner pairs, 2.31 between outer pairs, $H^{2,5}$) 2.23 (q, 4 H, J = 7.26, CH_2CH_3) and 0.92 (t, 6 H, J = 7.26 Hz, CH_2CH_3).

Co(cp)[η^4-$C_5H_5(OC_{10}H_{15})$-*exo*]: δ 4.76 (t, 2 H, J = 1.65, $H^{3,4}$), 4.50 (s, 5 H, cp), 4.27 (pseudo-t, 1 H, J = 2.64 and 2.31, *endo*-H^1), 3.05 (q, 2 H, J = 1.65 between inner pairs, 2.31 between outer pairs, $H^{2,5}$), 1.91 (s, br, 3 H, bridgehead H of adamantyl), 1.74 (d, 6 H, J = 2.96, adamantyl) and 1.45 (pseudo-t, 6 H, J = 2.97 and 3.29 Hz, adamantyl).

Data not previously reported for known compounds: Co(cp)[η^4-C_5H_5(OMe)-*exo*],[9c] δ 4.75 (t, br, 2 H, $H^{3,4}$ of η^4 ring), 4.44 (s, 5 H, cp), 4.05 (t, br, 1 H, *endo*-H^1), 3.06 (q, br, 2 H, $H^{2,5}$) and 2.94 (s, 3 H, OCH_3); Co(cp)[η^4-C_5H_5(C≡CPh)-*exo*],[10b] δ 7.33 (m, 2 H, Ph), 6.83 (m, 3 H, Ph), 5.03 (t, 2 H, J = 1.98, $H^{3,4}$), 4.40 (s, 5 H, cp), 3.66 (pseudo-t, 1 H, J = 2.64 and 2.31, *endo*-H^1) and 2.68 (q, 2 H, J = 1.98 Hz, $H^{2,5}$).

With $SiPh_3H$ to give Co(cp)(η^4-C_5H_6).[11a] At 270 MHz: δ 5.23 (m, 2 H, $H^{3,4}$), 4.56 (s, 5 H, cp), 2.64 (d pseudo-t, 1 H, J_d = 13.87, J_t = 1.98, *endo*-H^1), 2.40 (q, br, 2 H, $H^{2,5}$) and 2.05 (d pseudo-t, 1 H, J_d = 13.88, J_t = 1.99 Hz, *exo*-H^1). Other product: $(Ph_3Si)_2O$; δ 7.0–7.7 (m, aromatic H).

With $MeCO_2H$ (in $CDCl_3$). δ 5.82 (s, cp), 2.11 (CO_2Me).

With C_6F_5OH (in $CDCl_3$). δ 5.81 (s, cp). ^{19}F (referenced to $CFCl_3$): δ −171.0 (m, br, *o*-, *m*-F) and −188.4 (m, br, *p*-F).

With carbazole. The red solid was insoluble in C_6D_6 and $C_6D_5CD_3$ but in $CDCl_3$ the compound Co(cp)[η^4-$C_5H_5(CCl_3)$-*exo*] was formed (Found: C, 74.7; H, 4.8; N, 4.5. $C_{22}H_{18}CoN$ requires C, 74.4; H, 5.1; N, 4.0%). FAB mass spectrum in 3-nitrobenzyl alcohol: *m*/*z* 189, $Co(cp)_2^+$.

Reactions of exo-R *Compounds with* $CHCl_3$ *or* $CDCl_3$.—All the nitro compounds when dissolved in the minimum amount of chloroform at room temperature were converted quantitatively into the nitroalkane and Co(cp)[$C_5H_5(CCl_3)$-*exo*] the spectra of which were identical to those of authentic samples.[11a] ^1H NMR ($CDCl_3$): δ 5.28 (t, 2 H, J = 1.98, H^3 and H^4), 4.82 (s, 5 H, cp), 3.76 (t, 1 H, J = 2.31, H^1) and 3.00 (q, 2 H, J = 1.65 between inner pairs, 2.31 Hz between outer pairs, H^2 and H^5).

All of the other compounds except Co(cp)(η^4-C_5H_6) reacted similarly.

Reaction of $Ir(mes)_4$ *and* NO.—Nitric oxide was slowly passed into $Ir(mes)_4$ (*ca*. 0.15 g) in light petroleum (*ca*. 30 cm^3) until the initial dark brown colour disappeared (*ca*. 20 min) and a dark green-black precipitate formed. This was collected rapidly and the IR spectrum showed broad bands at 1097, 1022 and 802 cm^{-1}. The solid was soluble in MeCN or $MeNO_2$ when

Table 3 Fractional atomic coordinates (× 10^4)

Atom	x	y	z	Atom	x	y	z
Compound **2**							
Co(1)	4 656(1)	2 319(1)	5 907(1)	C(201)	2 715(4)	3 068(5)	2 810(3)
Co(2)	1 966(1)	2 088(1)	1 107(1)	C(202)	1 738(4)	2 074(5)	2 599(4)
C(101)	3 311(4)	3 540(4)	4 622(3)	C(203)	794(5)	2 666(5)	1 975(4)
C(102)	4 598(4)	3 374(5)	4 597(3)	C(204)	1 264(5)	3 747(5)	1 486(4)
C(103)	4 862(5)	2 034(5)	4 467(4)	C(205)	2 469(5)	3 796(5)	1 834(4)
C(104)	3 914(4)	1 295(5)	4 749(3)	C(206)	3 079(5)	633(5)	748(4)
C(105)	3 076(4)	2 202(5)	5 038(4)	C(207)	3 157(5)	1 725(5)	99(4)
C(106)	4 740(5)	3 312(6)	7 252(4)	C(208)	2 027(4)	1 948(5)	−448(4)
C(107)	4 309(5)	2 035(6)	7 361(4)	C(209)	1 272(4)	982(5)	−135(4)
C(108)	5 171(5)	1 115(5)	7 143(4)	C(210)	1 902(4)	186(5)	604(4)
C(109)	6 135(4)	1 835(5)	6 892(4)	O	2 607(3)	3 931(3)	3 668(2)
C(110)	5 874(5)	3 195(5)	6 938(4)				
Compound **3**							
Co	1 494(1)	6 113(1)	2 935(1)	C(8)	−594(6)	6 477(2)	932(5)
C(1)	4 125(6)	5 979(3)	4 495(6)	C(9)	−1 334(6)	6 136(2)	2 108(6)
C(2)	4 103(6)	5 942(3)	2 815(7)	C(10)	−632(7)	6 524(2)	3 642(6)
C(3)	2 904(7)	5 347(2)	2 042(6)	C(11)	4 440(6)	6 357(3)	8 673(6)
C(4)	2 174(6)	5 025(2)	3 246(6)	O(1)	1 652(5)	6 930(2)	8 253(5)
C(5)	2 936(6)	5 416(2)	4 757(6)	O(2)	1 736(5)	5 701(2)	8 115(4)
C(6)	519(7)	7 105(2)	3 414(6)	O(3)	−2 178(5)	6 886(2)	6 767(4)
C(7)	552(6)	7 077(2)	1 761(6)	N	2 624(5)	6 320(2)	8 346(4)
Compound **4**							
Co(1)	1 926(1)	1 771(1)	4 005(1)	C(108)	1 130(10)	1 233(5)	2 427(3)
Co(2)	3 779(1)	2 716(1)	9 364(1)	C(109)	2 588(9)	443(5)	2 747(4)
O(1)	1 964(7)	5 795(3)	7 036(3)	C(110)	1 444(9)	18(4)	3 487(4)
O(2)	−1 243(7)	4 713(3)	6 892(3)	C(201)	2 175(9)	3 371(4)	7 797(3)
N	949(8)	4 851(3)	6 926(3)	C(202)	3 562(9)	4 105(4)	8 751(3)
C(1)	2 414(8)	3 805(4)	6 818(3)	C(203)	5 895(9)	3 708(4)	8 822(3)
C(101)	1 532(8)	2 894(4)	5 838(3)	C(204)	5 848(9)	2 551(4)	8 232(3)
C(102)	1 196(9)	3 340(4)	4 882(3)	C(205)	3 459(8)	2 272(4)	7 835(3)
C(103)	3 417(9)	3 351(4)	4 442(4)	C(206)	961(11)	2 333(5)	10 092(4)
C(104)	4 828(9)	2 540(5)	4 809(4)	C(207)	2 582(10)	3 147(5)	10 793(4)
C(105)	3 417(9)	2 069(4)	5 440(4)	C(208)	4 762(10)	2 617(5)	10 863(4)
C(106)	−778(9)	550(4)	3 603(3)	C(209)	4 575(11)	1 528(5)	10 227(4)
C(107)	−960(9)	1 315(4)	2 964(4)	C(210)	2 235(12)	1 349(5)	9 750(4)
Compound **8**							
Co	3 842(1)	7 402(1)	2 370(1)	C(8)	4 028(12)	8 706(8)	1 112(5)
N	2 739(9)	6 499(6)	5 413(4)	C(9)	4 981(14)	7 482(8)	742(5)
C(1)	2 421(12)	6 708(7)	4 260(5)	C(10)	3 119(12)	6 144(8)	840(5)
C(2)	3 468(13)	8 261(7)	3 962(5)	C(11)	1 505(11)	7 055(6)	6 285(5)
C(3)	5 890(12)	8 477(8)	3 677(5)	C(12)	2 054(12)	6 952(7)	7 380(5)
C(4)	6 218(11)	7 019(7)	3 351(5)	C(13)	805(11)	7 470(7)	8 268(5)
C(5)	3 927(13)	6 025(9)	3 473(6)	C(14)	−1 021(13)	8 114(7)	8 083(5)
C(6)	1 060(13)	6 545(8)	1 225(5)	C(15)	−1 569(11)	8 238(7)	7 000(5)
C(7)	1 592(11)	8 114(7)	1 423(5)	C(16)	−344(11)	7 726(7)	6 117(5)
Compound **9**							
Co	110(1)	2 351(1)	4 889(1)	C(11)	−6 225(4)	2 047(3)	2 230(3)
N	−5 131(3)	1 304(3)	2 794(3)	C(12)	−5 766(4)	3 495(4)	2 828(4)
C(1)	−3 260(4)	1 988(3)	3 832(4)	C(13)	−6 851(4)	4 233(4)	2 280(4)
C(2)	−2 149(4)	1 138(3)	4 411(3)	C(14)	−8 448(4)	3 564(4)	1 120(4)
C(3)	−1 116(4)	391(3)	3 545(3)	C(15)	−8 921(4)	2 144(4)	534(4)
C(4)	−1 009(4)	1 080(3)	2 784(3)	C(16)	−7 846(4)	1 384(4)	1 064(4)
C(5)	−1 970(4)	2 224(3)	3 214(3)	C(21)	−5 614(4)	−194(3)	2 133(3)
C(6)	1 441(4)	3 378(4)	7 094(4)	C(22)	−6 512(4)	−688(3)	2 715(4)
C(7)	2 594(4)	2 543(4)	6 397(4)	C(23)	−6 996(4)	−2 128(3)	2 109(4)
C(8)	2 825(4)	3 006(3)	5 492(4)	C(24)	−6 593(4)	−3 067(4)	902(4)
C(9)	1 801(4)	4 103(3)	5 615(4)	C(25)	−5 706(4)	−2 579(4)	320(4)
C(10)	976(4)	4 359(3)	6 629(4)	C(26)	−5 225(4)	−1 139(4)	938(4)

N_2O was evolved; evaporation or dilution with Et_2O gave no crystalline product only a solid the ^1H NMR spectrum of which was identical to that observed previously[1] for $[Ir(mes)_4]^+$. ^1H NMR (CD_3CN): δ 6.73 (s, br, 2 H, aromatic), 2.43 (s, 3 H, *p*-Me) and 2.19 (s, br, 6 H, *o*-Me). This green-black product was also formed using cyclohexane or toluene as solvent.

Crystal Structure Determinations of Compounds **2**–**4**, **8** *and* **9**.—The X-ray measurements were made on crystals handled under standard Schlenk procedures and mounted on glass fibres using silicone oil as both a coating and adhesive medium. The unit-cell and intensity data for crystals **2**–**4** were obtained at 150 K, those for the thermally unstable crystals **8** and **9** at 120 K, using a Delft-Instruments FAST TV area detector diffractometer and graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å) following previously described procedures.[24] Structures **2**, **3**, **8** and **9** were solved by direct methods whilst that for compound **4** was derived *via* a Patterson solution. All refinements were by full-matrix least squares on F^2 (SHELX 92).[25] The data for compounds **2**–**4** were corrected for absorption using the program DIFABS[26] adapted for FAST geometry.[27] The non-hydrogen atoms were refined anisotropically and all of the hydrogen atoms in compounds **2**, **3**, **8** and **9** were located from the difference map and freely refined. The cp rings in all of the compounds were refined without geometrical restraints. However, in compound **4**, whilst most of the hydrogens in the structure were experimentally located from the difference map, and were freely refined, three hydrogens were placed in theoretical positions: H(1) (on the bridging group) was refined as a tertiary hydrogen in the riding mode and with a fixed thermal parameter: the cp hydrogens H(207) and H(208) were refined as riding model aromatic C–H with the H atoms on the external bisector of the C–C–C angles. The crystal data and refinement details are listed in Table 2, fractional atomic coordinates in Table 3.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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References

1 R. S. Hay-Motherwell, G. Wilkinson, B. Hussain-Bates and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1992, 3477.

2 F. Bottomley, in *Reactions of Coordinated Ligands*, ed. P. S. Braterman, Plenum, New York, 1986, vol. 2, ch. 3, sect. 6; F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, 5th edn., Wiley, New York, 1988, p. 1311; A. Guttierrez, G. Wilkinson, B. Hussain-Bates and M. B. Hursthouse, *Polyhedron*, 1990, **9**, 2081.

3 R. S. Hay-Motherwell, G. Wilkinson, B. Hussain-Bates and M. B. Hursthouse, *Polyhedron*, 1993, **12**, 2009.

4 G. Wilkinson, *J. Am. Chem. Soc.*, 1952, **74**, 6146.

5 (*a*) F. Bottomley and I. J. B. Lin, *J. Chem. Soc., Dalton Trans.*, 1981, 271; F. Bottomley, J. Darkwa and P. S. White, *J. Chem. Soc., Dalton Trans.*, 1985, 1435; *Organometallics*, 1985, **4**, 691; (*b*) F. Bottomley, personal communication.

6 D. A. Muccigrosso, F. Mares, S. E. Diamond and J. P. Solar, *Inorg. Chem.*, 1983, **22**, 960 and refs. therein; S. Bhaduri, B. F. G. Johnson, A. Pickard, P. R. Raithby, G. M. Sheldrick and C. I. Zuccaro, *J. Chem. Soc., Chem. Commun.*, 1977, 354; S. Bhaduri, I. Bratt, B. F. G. Johnson, A. Khair, J. A. Siegel, R. Waller and C. I. Zuccaro, *J. Chem. Soc., Dalton Trans.*, 1981, 234.

7 G. D. Mendenhall, *J. Am. Chem. Soc.*, 1974, **96**, 5000.

8 L. Kuhn and E. R. Lippincott, *J. Am. Chem. Soc.*, 1956, **78**, 1820; D. J. Millen, C. N. Polydoropoulis and D. Watson, *J. Chem. Soc.*, 1960, 689.

9 (*a*) J. E. Sheats, *J. Organomet. Chem. Library*, 1979, **7**, 461; (*b*) R. D. W. Kemmitt and D. R. Russell, in *Comprehensive Organometallic Chemistry*, eds. G. Wilkinson, F. G. A. Stone and E. W. Abel, Pergamon, Oxford, 1982, vol. 5, sect. 34.4.4; (*c*) H. Bönnemann, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 248.

10 (*a*) H. Kojima, S. Takahashi and N. Hagihara, *J. Chem. Soc., Chem. Commun.*, 1973, 230; *Tetrahedron Lett.*, 1973, 1991; (*b*) H. Kojima, S. Takahashi, H. Yamazaki and N. Hagihara, *Bull. Chem. Soc. Jpn.*, 1970, **43**, 2272.

11 (*a*) M. L. H. Green, L. Pratt and G. Wilkinson, *J. Chem. Soc.*, 1959, 3753; (*b*) G. E. Herberich and J. Schwarzer, *Angew. Chem., Int. Ed. Engl.*, 1970, **9**, 897.

12 R. T. Morrison and R. N. Boyd, *Organic Chemistry*, 4th edn., Allyn and Bacon, Boston, 1983.

13 See (*a*) K. Lammerstein and B. V. Prasad, *J. Am. Chem. Soc.*, 1993, **115**, 2348; (*b*) A. T. Nielsen, in *The Chemistry of the Nitro and Nitroso Groups*, ed. H. Feuer, Interscience, New York, 1969, Part 1; (*c*) G. Klebe, K. H. Böhn, M. Marsch and G. Boche, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 78 and refs. therein; (*d*) J. A. Cook, M. G. B. Drew and D. A. Rice, *J. Chem. Soc., Dalton Trans.*, 1975, 1973; B. N. Diel and H. Hope, *Inorg. Chem.*, 1978, **17**, 4448; (*e*) J. Yarwood and W. T. Orville-Thomas, *J. Chem. Soc.*, 1963, 5991.

14 C. J. Attridge, S. J. Baker and A. W. Parkins, *Organomet. Chem. Synth.*, 1971, **1**, 183.

15 See M. T. Reetz, T. Knauf, U. Minet and C. Bingel, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1373.

16 Y. Wakatsuki and H. Yamazaki, *Synthesis*, 1976, 26.

17 W. Kläui and C. E. Song, *Inorg. Chem.*, 1989, **28**, 3845.

18 H. Bönnemann, M. Radermacher, C. Krüger and H. J. Klaus, *Helv. Chim. Acta*, 1983, **66**, 185.

19 J. M. Birmingham, D. Seyferth and G. Wilkinson, *J. Am. Chem. Soc.*, 1954, **76**, 4179.

20 N. Allinger and E. Eliel, *Top. Stereochem.*, 1971, **6**, 19; see also A. N. Sobolev, V. K. Belsky, I. P. Romm, N. Yu Chernikova and E. N. Guryanova, *Acta Crystallogr., Sect. C.*, 1985, **41**, 967; H. Bock, I. Göbel, C. Näther, Z. Havlas, A. Gavezzotti and G. Filippini, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1755.

21 J. J. Eisch and R. B. King, *Organometallic Syntheses*, ed. R. B. King, Academic Press, New York, 1965, vol. 1.

22 L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Chapman and Hall, London, 1975.

23 (*a*) M. J. Brooks and N. Jonathan, *Spectrochim. Acta, Part A*, 1969, **25**, 187; C. N. R. Rao, ref. 13(*b*), ch. 2, p. 88; (*b*) D. Hartley and M. J. Ware, *J. Chem. Soc. A*, 1969, 138.

24 A. A. Danopoulos, G. Wilkinson, B. Hussain-Bates and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1991, 1855.

25 G. M. Sheldrick, University of Göttingen, 1992.

26 N. P. C. Walker and D. Stuart, *Acta Crystallogr., Sect. A.*, 1983, **39**, 158.

27 A. Karaulov, University of Wales, Cardiff, 1991.

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