X-Ray Crystal Structure of Chloro(cyclo-octa-1,5-diene)[4-dimethylamino-2-methyl(nitroso)benzene-*N*′]rhodium(I)† and a Nuclear Magnetic Resonance Study of Nitroso-rhodium Co-ordination

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Complexes [RhCl(cod)L] [cod = cyclo-octa-1,5-diene; L = 4-dimethylamino(nitroso)benzene or 4-dimethylamino-2-methyl(nitroso)benzene] have been prepared. On the basis of the temperature-dependent ^{1}H and ^{13}C n.m.r. spectra of these complexes and of a mixture of [{RhCl(cod)}$_2$] and 4-dimethylamino-2,6-dimethyl(nitroso)benzene in [^{2}H$_1$]chloroform, the nitroso nitrogen–rhodium bonding is discussed and thermodynamic parameters for the dissociation equilibria of the complexes [RhCl(cod)L] have been determined. A single-crystal *X*-ray structure analysis has been performed for [RhCl(cod)(2-Me-4-$Me_2NC_6H_3NO$)]. The crystals are triclinic, space group $P\bar{1}$, with $Z = 2$, $a = 11.431(6)$, $b = 9.305(6)$, $c = 8.429(3)$ Å, $\alpha = 89.28(5)$, $\beta = 82.24(4)$, and $\gamma = 103.15(5)°$. Block-diagonal least-squares refinement based on 4 405 independent reflections with $|F_o| > 3\sigma(F)$ converged at $R = 0.043$. The geometry around the rhodium atom is square planar with co-ordination of the nitroso-nitrogen and chlorine atoms as well as two cod olefin bonds.

Metal complexes with C-nitroso ligands have attracted attention from the following viewpoints. The nitroso group is isoelectronic with dioxygen and C-nitroso compounds can form adducts with metalloproteins and metalloporphyrins,[1] like dioxygen. Some metal complexes with C-nitroso ligands have been proposed as reaction intermediates,[2–4] and some transition-metal complexes exhibit unique reactions through active metal–nitrogen and/or –oxygen bonds.[5–9]

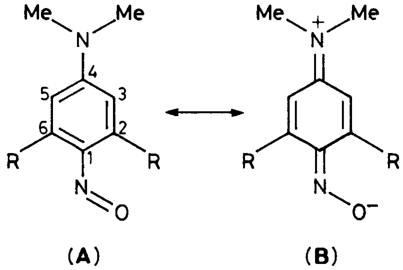
As for the binding modes of C-nitroso ligands to metals, unidentate N-bonding for [$PdCl_2(C_6H_5NO)_2$][10] and [$CoCl_2$(4-$Me_2NC_6H_4NO)_2$],[11] O-bonding for [$SnMe_2Cl_2$(4-$Me_2NC_6H_4NO)_2$],[12] and a bridging geometry containing both N- and O-bonding for [$Pd_3(PBu^t{}_3)_3(C_6H_5NO)_3$][13] have been revealed by *X*-ray crystallography.

Although nitrosobenzene is a weak base, the donor strength of the nitroso group is increased by introduction of a strongly electron-donating *para* substituent.[14] In 4-dimethylamino(nitroso)benzene and its methyl-substituted analogues a contribution of canonical structure (**B**) may increase the electron density on the oxygen atom. Moreover, methyl substituents at the 2 and/or 6 positions may favour oxygen–metal bonding owing to steric hindrance by methyl groups to nitrogen–metal co-ordination, in spite of the preferred metal to nitroso-nitrogen bonding observed for a palladium[10] and a cobalt complex.[11]

This paper reports the co-ordination properties of 4-dimethylamino(nitroso)benzene and its methyl-substituted analogues toward dichlorobis(cyclo-octa-1,5-diene)dirhodium(I) on the basis of ^{1}H and ^{13}C n.m.r. spectra, together with the *X*-ray molecular structure of chloro(cyclo-octa-1,5-diene)[4-dimethylamino-2-methyl(nitroso)benzene]rhodium(I).

Experimental

Materials.—4-Dimethylamino(nitroso)benzene (4-$Me_2NC_6H_4NO$), 4-dimethylamino-2-methyl(nitroso)benzene (2-Me-4-$Me_2NC_6H_3NO$), and 4-dimethylamino-2,6-dimethyl(nitroso)benzene (2,6-Me_2-4-$Me_2NC_6H_2NO$) were prepared by nitrosation of *N*,*N*-dimethylaniline, 3-*N*,*N*-trimethylaniline, and 3,5,*N*,*N*-tetramethylaniline with sodium nitrite, respectively, as described previously.[15] Dichlorobis(cyclo-octa-1,5-diene)dirhodium(I), [{RhCl(cod)}$_2$], was prepared according to the literature.[16]



(**A**) (**B**)

Preparations of [RhCl(cod)(4-$Me_2NC_6H_4NO$)] (**1**) *and* [RhCl(cod)(2-Me-4-$Me_2NC_6H_3NO$)] (**2**).—A dichloromethane (5 cm^3) solution of [{RhCl(cod)}$_2$] (160 mg, 330 μmol) was added with stirring to a dichloromethane (5 cm^3) solution of 4-$Me_2NC_6H_4NO$ (100 mg, 670 μmol), followed by addition of light petroleum (b.p. 40—60 °C, 10 cm^3). The solution was allowed to stand in a refrigerator overnight to afford dark brown needles of complex (**1**), which were collected by filtration and dried *in vacuo* (78% yield) (Found: C, 48.15; H, 5.70; N, 6.95. Calc. for $C_{16}H_{22}ClN_2ORh$: C, 48.45; H, 5.60; N, 7.05%).

Similarly, the reaction of [{RhCl(cod)}$_2$] with 2-Me-4-$Me_2NC_6H_3NO$ in dichloromethane, followed by recrystallization from dichloromethane–light petroleum (1 : 1 v/v), afforded dark red plates of complex (**2**) (60% yield) (Found: C, 49.50; H, 5.90; N, 6.90. Calc. for $C_{17}H_{24}ClN_2ORh$: C, 49.70; H, 5.90; N, 6.80%).

Although a similar reaction of [{RhCl(cod)}$_2$] with a large excess of 2,6-Me_2-4-$Me_2NC_6H_2NO$ in dichloromethane was attempted, only [{RhCl(cod)}$_2$] was recovered as crystals.

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Table 1. Atomic co-ordinates (× 10^4; H, × 10^3) for [RhCl(cod)(2-Me-4-$Me_2NC_6H_3NO$)] (**2**) with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Rh	2 698.4(3)	2 516.9(3)	1 940.8(3)	H(2)	136(4)	277(5)	−8(5)
Cl	2 711(1)	1 942(1)	4 692(1)	H(3)	441(4)	147(5)	235(5)
O	2 468(3)	5 466(3)	2 374(4)	H(4)	273(3)	−6(5)	195(5)
N(1)	1 832(3)	4 186(4)	2 495(4)	H(5—1)	229(4)	−97(6)	−37(6)
N(2)	−3 154(3)	3 009(4)	4 199(4)	H(5—2)	348(5)	13(6)	−128(6)
C(1)	3 246(4)	3 142(5)	−419(5)	H(6—1)	184(5)	109(7)	−202(7)
C(2)	2 105(4)	2 482(5)	−311(5)	H(6—2)	111(5)	49(7)	−44(7)
C(3)	4 155(4)	1 148(5)	1 283(5)	H(7—1)	536(5)	165(6)	−54(6)
C(4)	3 095(4)	460(5)	1 179(5)	H(7—2)	570(4)	323(6)	33(6)
C(5)	2 666(5)	23(6)	−410(6)	H(8—1)	494(4)	396(5)	−149(5)
C(6)	1 851(4)	960(6)	924(6)	H(8—2)	427(5)	258(6)	−206(6)
C(7)	5 019(4)	2 298(6)	−83(7)	H(10)	31(4)	158(6)	320(6)
C(8)	4 413(4)	3 088(6)	−1 221(5)	H(11)	−162(4)	133(5)	395(5)
C(9)	581(3)	3 991(4)	2 852(4)	H(13)	−164(3)	558(5)	332(5)
C(10)	−70(3)	2 533(4)	3 251(5)	H(15—1)	98(4)	676(6)	123(6)
C(11)	−1 296(3)	2 194(4)	3 700(5)	H(15—2)	104(5)	714(6)	312(6)
C(12)	−1 945(3)	3 318(4)	3 757(4)	H(15—3)	0(4)	736(6)	231(6)
C(13)	−1 293(3)	4 782(4)	3 301(5)	H(16—1)	−465(4)	151(6)	509(6)
C(14)	−48(3)	5 150(4)	2 857(5)	H(16—2)	−365(5)	96(7)	413(7)
C(15)	542(4)	6 739(5)	2 350(6)	H(16—3)	−357(5)	151(6)	574(6)
C(16)	−3 812(4)	1 558(5)	4 846(6)	H(17—1)	−375(4)	457(6)	328(6)
C(17)	−3 834(4)	4 163(5)	4 271(6)	H(17—2)	−463(5)	379(6)	432(6)
H(1)	324(4)	449(5)	−26(5)	H(17—3)	−366(5)	468(6)	506(7)

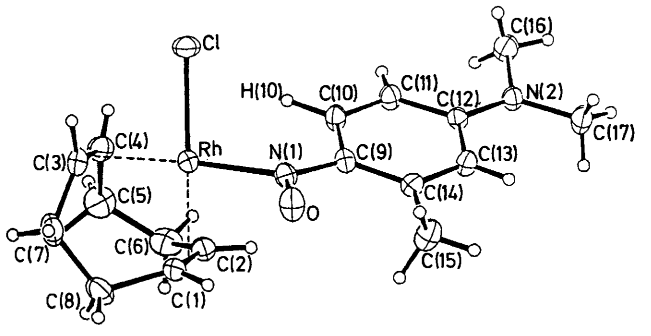


Figure 1. The molecular structure of [RhCl(cod)(2-Me-4-$Me_2NC_6H_3$-NO)] (**2**) with the atom-labelling scheme

X-Ray Crystal-structure Determination of [RhCl(cod)(2-Me-4-$Me_2NC_6H_3NO$)] (**2**).—Accurate cell constants were determined by least-squares refinement of the angular co-ordinates of 25 independent reflections with 2θ values from 17 to 26°, measured on a Rigaku four-circle automated diffractometer. Intensities were collected in the range $4 < 2\theta < 60°$ for a crystal with approximate dimensions 0.10 × 0.25 × 0.40 mm, using graphite-monochromated Mo-K_α radiation ($\lambda = 0.710\,69$ Å). An ω—2θ scan mode was used at a 2θ scan rate of 4° min^{-1} and scan width in 2θ of (1.0 + 0.35 tanθ)°. Five check reflections were monitored after every 50 reflections. No significant variation in their intensities was observed throughout the data collection. Lorentz and polarization factors were applied. No absorption correction was made. The space group $P\bar{1}$ proved to be correct, based on a successful analysis. Of 5 042 independent measured reflections, 4 405 with $|F_o| > 3\sigma(F)$ were used for solving and refining the structure.

Crystal data. $C_{17}H_{24}ClN_2ORh$, $M = 410.75$, triclinic, space group $P\bar{1}$, $a = 11.431(6)$, $b = 9.305(6)$, $c = 8.429(3)$ Å, $\alpha = 89.28(5)$, $\beta = 82.24(4)$, $\gamma = 103.15(5)°$, $U = 864.2(10)$ Å^3, $Z = 2$, $D_c = 1.579(2)$ g cm^{-3}, $F(000) = 420.0$, μ(Mo-K_α) = 12.2 cm^{-1}.

The structure was solved by the conventional heavy-atom procedure and atomic parameters were refined by the block-diagonal least-squares method. From Fourier and Fourier difference maps, the positions of all the atoms were determined. Final refinement, with anisotropic thermal parameters for non-hydrogen atoms and isotropic thermal parameters for hydrogen atoms, converged at $R = 0.043$ and $R' = 0.049$, using the weighting scheme $1/w = \sigma^2(F_o) + 0.0005F_o^2$. The final Fourier-difference map showed no positive maxima > 0.7 e Å^{-3} except in the vicinity of the rhodium atom (1.1 e Å^{-3}). Atomic scattering factors used in the refinement were taken from ref. 17. The fractional atomic co-ordinates with estimated standard deviations are listed in Table 1.

Crystallographic calculations were performed using the programs of Professor K. Nakatsu, Kwansei Gakuin University, on an ACOS 930s computer at the Crystallographic Research Centre, Institute for Protein Research, Osaka University. Figure 1 was drawn by the local version of ORTEP II.[18]

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

N.M.R. Measurements.—Proton n.m.r. spectra were recorded on a JEOL JNM-PS-100 spectrometer with a variable-temperature probe and a temperature control. The temperature of the probe was calibrated from the signals of methanol.[19] Carbon-13 n.m.r. spectra were measured at 100.4 MHz using the pulse Fourier-transform technique on a JEOL JNM-GSX-400 spectrometer. The chemical shifts were measured relative to tetramethylsilane as internal standard in both ^1H and ^{13}C n.m.r. spectra.

Results and Discussion

Crystal Structure of [RhCl(cod)(2-Me-4-$Me_2NC_6H_3NO$)] (**2**).—The molecular structure is illustrated in Figure 1, together with the atom-labelling scheme. No unusual intermolecular contacts are observed. The nitroso-nitrogen and chlorine atoms as well as the cod olefin bonds ligate the rhodium atom, forming a square-planar geometry around the metal. Selected bond lengths and angles with estimated standard deviations are listed in Table 2.

The nitroso nitrogen atom is co-ordinated to the rhodium

Table 2. Selected bond distances (Å) and angles (°) for complex (**2**) with e.s.d.s in parentheses

Rh–Cl	2.376(1)	C(1)–C(8)	1.518(6)
Rh–N(1)	2.050(4)	C(2)–C(6)	1.493(7)
Rh–C(1)	2.113(4)	C(3)–C(4)	1.359(6)
Rh–C(2)	2.098(4)	C(3)–C(7)	1.498(6)
Rh–C(3)	2.142(5)	C(4)–C(5)	1.516(7)
Rh–C(4)	2.151(5)	C(5)–C(6)	1.512(9)
Rh–C(1:2)	1.955(4)	C(7)–C(8)	1.527(8)
Rh–C(3:4)	2.036(5)		
C(1)–C(2)	1.393(5)	Rh ··· H(10)	2.73(4)
Cl–Rh–N(1)	91.8(1)	C(4)–C(3)–C(7)	126.5(7)
Rh–N(1)–O	117.1(2)	C(3)–C(4)–C(5)	122.7(4)
Rh–N(1)–C(9)	124.5(3)	C(4)–C(5)–C(6)	112.5(4)
C(1:2)–Rh–C(3:4)	87.4(2)	C(2)–C(6)–C(5)	113.5(4)
C(2)–C(1)–C(8)	124.2(4)	C(3)–C(7)–C(8)	113.7(4)
C(1)–C(2)–C(6)	125.5(4)	C(1)–C(8)–C(7)	113.0(4)

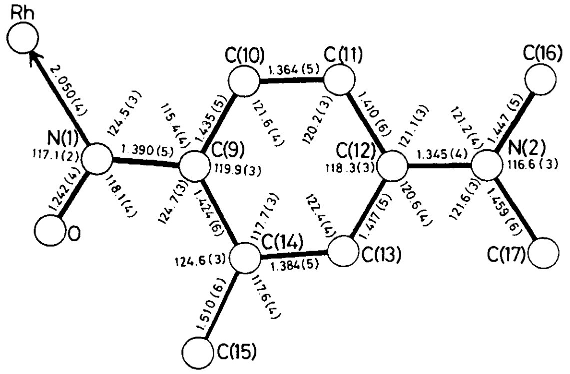


Figure 2. Geometry of the ligand moiety of complex (**2**) with bond distances (Å) and angles (°)

atom as in $[CoCl_2(4\text{-}Me_2NC_6H_4NO)_2]$[11] and $[PdCl_2(C_6H_5NO)_2]$,[10] but in contrast to the metal–oxygen bonding of $[SnMe_2Cl_2(4\text{-}Me_2NC_6H_4NO)_2]$.[12] The Rh–N distance [2.050(4) Å] is close to those in rhodium complexes of quinolin-8-olate [2.098(9) Å],[19] substituted pyridinecarbaldimine [2.068(6) Å],[20] pyrrole- and pyridine-carbaldimines [2.061(5), 2.119(4)[21] and 2.086(11), 2.086(9) Å,[22] respectively].

The cod molecule ligates the rhodium atom with its customary 'tub' conformation, and the olefin bonds are located approximately perpendicular to the co-ordination plane constructed from Cl, Rh, and N(1) atoms; the dihedral angle between the C(1)–C(2)–C(3)–C(4) plane (±0.048 Å) and the N(1)–Rh–Cl plane is 88.7°. The distances between the rhodium atom and the olefin bond centres of the cod molecule [Rh–C(1:2) 1.955(4) and Rh–C(3:4) 2.036(5) Å] are close to those [1.982(11) and 2.014(14) Å] reported previously.[20] The distances in complex (**2**) are at the short end of the range (2.00—2.16 Å) found in heavy-metal complexes with cod.[23] These short distances seem to arise from the *trans* influence of the nitrogen and chlorine atoms of complex (**2**). Moreover, the difference in the *trans* influences of these atoms is reflected in the Rh–C(olefin) bonds;[24] the shorter Rh–C(1) and –C(2) distances [2.113(4) and 2.098(4) Å] compared with the Rh–C(3) and –C(4) distances [2.142(5) and 2.151(5) Å] are associated with the difference in distances C(1)–C(2) [1.393(5) Å] and C(3)–C(4) [1.359(6) Å].

The carbon atoms of the ligand six-membered ring are almost coplanar (±0.009 Å). However, the NO group deviates from the ring plane with an O–N(1)–C(9) twist angle of 11.0°. This is in contrast to the small twists of the NO groups in $[CoCl_2(4\text{-}Me_2NC_6H_4NO)_2]$ (5.4 and 7.2°).[11] This somewhat larger twist in the present complex reasonably arises from a steric repulsion between the nitroso and 2-substituted methyl groups. As illustrated in Figure 2, the C–C bond distances of the ligand six-membered ring show an appreciable quinoid distortion, indicating a significant contribution of the dipolar resonance form (**B**) caused by the electron-donating dimethylamino group. In accord with this, the N(1)–C(9) distance [1.390(5) Å] is shortened and the N(1)–O distance [1.242(4) Å] lengthened compared with those of $[PdCl_2(C_6H_5NO)_2]$[N–C 1.411(3) and N–O 1.209(3) Å].[10] This effect is also found in $[CoCl_2(4\text{-}Me_2NC_6H_4NO)_2]$,[11] in which the N–O bond is much longer [1.267(5) Å] and the N–C bond appreciably shorter [1.360(6) Å] than the corresponding bonds of $[PdCl_2(C_6H_5NO)_2]$.

It is noteworthy that the present complex shows an unusual contact between the rhodium atom and a hydrogen atom of the ligand six-membered ring [Rh ··· H(10) 2.73(4) Å]. This causes an unusual low-field shift of the ^1H n.m.r. signal, as described below. Similar metal–proton contacts were reported for $[RuCl_2(PPh_3)_3]$ (Ru ··· H 2.59 Å),[25] $[Pd\{P(C_6H_{11})_3\}_2]$ (Pd ··· H 2.73 Å),[26] $[Pd(PPhBu^t{}_2)_2]$ (Pd ··· H 2.73 and 2.79 Å),[27] and $[PdCl_2\{(Pr_2C{=}NO)_2CH_2\}]$ (Pd ··· H 2.46 Å).[28]

N.M.R. Spectra.—Figure 3 shows the ^1H n.m.r. spectra of complex (**1**) in [$^2H_1$]chloroform. At −35 °C all the signals of the protons of the six-membered ring appear separately due to the hindered rotation of the N(1)–O group around the N(1)–C(9) bond through the contribution of the dipolar electronic structure (**B**). The signals are similar to that of uncomplexed ligand[15] and are assigned as in Figure 3. Atom H^6, however, appears at extremely low field (δ 10.08). This proton is considered to be located near the rhodium atom which is bonded to the nitroso-nitrogen atom, as can be seen in the molecular structure of complex (**2**). Thus, the paramagnetic anisotropic effect of the metal acts on this proton. Such large low-field shifts of protons located near heavy metal atoms were reported for $[Pd\{P(C_6H_{11})_3\}_2]$,[26] $[Pd(PPhBu^t{}_2)_2]$,[27] and $[PdCl_2\{(Pr_2C{=}NO)_2CH_2\}]$.[28] With increase in temperature, the signals of H^3 and H^5 coalesce at 10 °C, as do those of H^2 and H^6 at 24 °C, as illustrated in Figure 3. This is due to the rapid rotation around the C–NO bond.[15,29]

Olefin-proton signals of the co-ordinated cod molecule are observed at δ 3.60 and 4.86. Although spin couplings between the rhodium atom and these protons are not obvious, the ^{13}C n.m.r. spectrum of complex (**1**) measured in [$^2H_1$]chloroform exhibits the cod olefin-carbon signals as two doublets at δ 77.8 and 90.2 p.p.m. with separations of 13.4 and 8.5 Hz, respectively, owing to the $^1J(^{103}Rh-^{13}C)$ coupling. The former signal is reasonably assigned to carbons *trans* to the chlorine atom and the latter to carbons *trans* to the nitrogen atom, since C(1) and C(2) of complex (**2**) ligate the rhodium atom rather strongly compared with C(3) and C(4) (see Figure 1 and Table 2). The observed $^1J(^{103}Rh-^{13}C)$ values are close to the value (14.0 Hz) obtained for $[\{RhCl(cod)\}_2]$ and those (7.9—14.5 Hz) reported for rhodium complexes of pyrrole- and pyridine-carbaldimines.[22]

Figure 4 shows the ^1H n.m.r. spectra of complex (**2**) in [$^2H_1$] chloroform. Although broad signals are observed at 24 °C, only the signals due to the complex appear at −35 °C. That of H^6 also occurs at extremely low field (δ 10.35) owing to the paramagnetic effect of the rhodium atom co-ordinated to the nitroso-nitrogen atom. This is in great contrast to the corresponding chemical shift (δ 6.71) of the free ligand. Although the methyl signal of the free ligand occurs at low field (δ 3.15) due to the paramagnetic effect of the nitroso-nitrogen atom, complex formation with rhodium through the nitrogen atom leads to a drastic rearrangement of the nitroso group from (**C**) to (**D**), and the methyl signal appears at an appreciably higher field (δ 2.25)

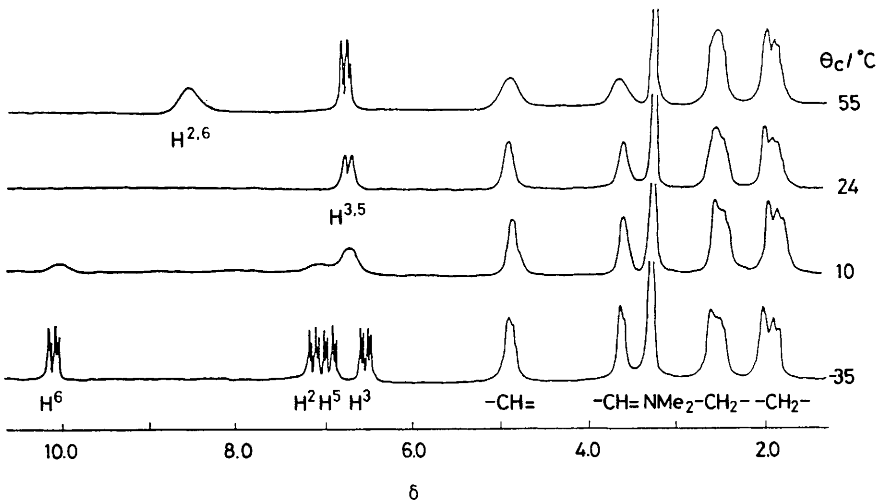


Figure 3. Proton n.m.r. spectra of [RhCl(cod)(4-$Me_2NC_6H_4NO$)] (**1**) in [$^2H_1$] chloroform

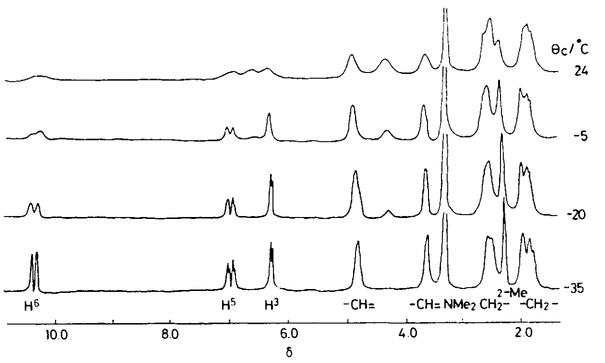
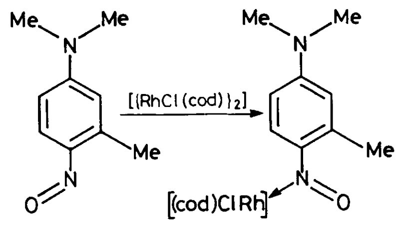


Figure 4. Proton n.m.r. spectra of a [$^2H_1$]chloroform solution of [RhCl(cod)(2-Me-4-$Me_2NC_6H_3NO$)] (**2**) (3.91×10^{-2} mol kg^{-1})



(**C**) (**D**)

owing to the disappearance of the anisotropic effect of the nitroso-nitrogen atom. The ^{13}C n.m.r. spectrum of complex (**2**) measured in [$^2H_1$]chloroform at −30 °C shows signals of the co-ordinated cod olefin carbons at δ 78.7 and 88.6 p.p.m. with splittings of 12.2 and 9.8 Hz, respectively, due to the $^1J(^{103}Rh-^{13}C)$ coupling, as observed for complex (**1**).

With increasing temperature, other proton signals assigned to those of [{RhCl(cod)}$_2$] and of the ligand are observed besides the signals of the complex (Figure 4). This indicates a partial dissociation of the complex to [{RhCl(cod)}$_2$] and ligand.

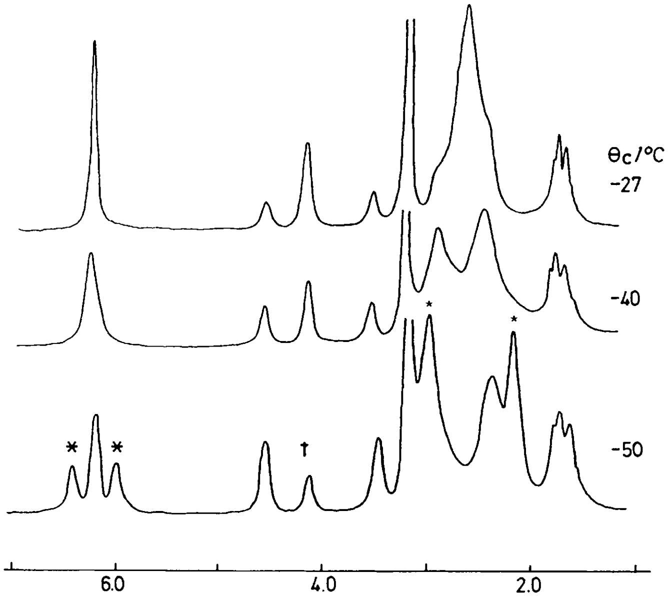
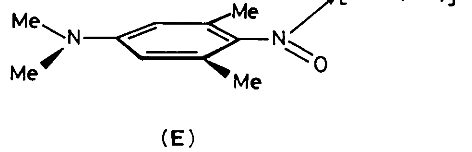


Figure 5. Proton n.m.r. spectra of a [$^2H_1$]chloroform solution containing [{RhCl(cod)}$_2$] (1.65×10^{-2} mol kg^{-1}) and 2,6-Me_2-4-$Me_2NC_6H_2NO$ (7.72×10^{-2} mol kg^{-1}): * signals of unco-ordinated ligand; † signal of [{RhCl(cod)}$_2$]



(**E**)

Since no complex of [RhCl(cod)] and 2,6-Me_2-4-$Me_2NC_6H_2NO$ has been isolated, ^1H n.m.r. spectra of the ligand in [$^2H_1$]chloroform containing an excess of [{RhCl(cod)}$_2$] have been measured (Figure 5). At −50 °C the cod-olefin proton signals which are reasonably ascribed to the complex [RhCl(cod)(2,6-Me_2-4-$Me_2NC_6H_2NO$)] appear at δ 3.54 and 4.62, while the cod olefin-proton signals due to [{RhCl(cod)}$_2$] are observed at δ 4.20. The signal due to H^3 and H^5 of the complexed ligand appears at δ 6.26, while the free ligand exhibits two signals at δ 6.02 and 6.50 for these protons owing to the hindered rotation of the nitroso group around the C–NO bond. With increasing temperature, the intensities of the dissociated species increase and the ring proton signals due to both the complexed and free ligand coalesce. Thus, these findings may suggest that Rh–N ligation occurs in [RhCl(cod)(2,6-Me_2-4-$Me_2NC_6H_2NO$), the co-ordination bond being directed out of the plane of the six-membered ring of the ligand as in (**E**). This presumably arises from the steric hindrance of the 2,6-

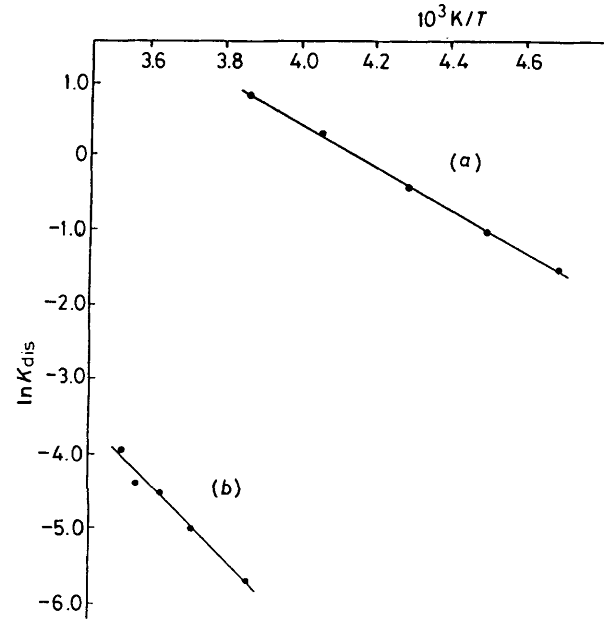


Figure 6. Plots of ln K_{dis} against 10^3 K/T (T = temperature) for [RhCl(cod)L] [L = 2-Me-4-$Me_2NC_6H_3NO$(*a*) and 2,6-Me_2-4-$Me_2NC_6H_2NO$(*b*)] in [$^2H_1$]chloroform

methyl groups toward the RhCl(cod) moiety. In accord with this, the signals due to 2- and 6-methyl protons seem to occur at δ 3.20 as a singlet, although this is obscured by the N-methyl signals. For the free ligand at low temperature, two signals at δ 2.25 and 3.06 occur.

The ^{13}C n.m.r. spectrum of a [$^2H_1$]chloroform solution containing ligand and [{RhCl(cod)}$_2$] measured at −50 °C shows signals due to [RhCl(cod)(2,6-Me_2-4-$Me_2NC_6H_2NO$)], one for C^2 and C^6 at δ 128.1 p.p.m. and one for the 2- and 6-methyl carbons at δ 23.9 p.p.m. This is in contrast to the appearance of two signals due to C^2 and C^6 at δ 126.0 and 151.6 p.p.m. and due to the 2- and 6-methyl carbons at δ 20.2 and 23.6 p.p.m. for the free molecule owing to restricted rotation around the C–NO bond,[15] supporting the above-mentioned Rh–N ligation in the present system. Moreover, the ^{13}C n.m.r. signals of the co-ordinated cod olefin carbons appear at δ 77.5 and 83.2 p.p.m. with $^1J(^{103}Rh-^{13}C)$ couplings of 13.2 and 7.0 Hz, respectively.

Thus, co-ordination of the nitroso nitrogen to the metal is favoured for the rhodium complexes, in great contrast to the nitroso oxygen bonding observed for [$SnMe_2Cl_2(4-Me_2NC_6H_4NO)_2$].[12]

By measuring intensities of the cod olefin-proton signals of [{RhCl(cod)}$_2$] and [RhCl(cod)L]) (L = 2-Me-4-$Me_2NC_6H_3NO$ or 2,6-Me_2-4-$Me_2NC_6H_2NO$) at various temperatures the dissociation constants (K_{dis}) of [RhCl(cod)L] [equation (1)]

$$[\mathrm{RhCl(cod)L}] \xrightarrow{K_{dis}} \tfrac{1}{2}[\{\mathrm{RhCl(cod)}\}_2] + \mathrm{L} \qquad (1)$$

have been determined. Moreover, from the Arrhenius plot of ln K_{dis} against 1/T (T = temperature) (Figure 6), the thermodynamic parameters at 259 K have been determined: [RhCl(cod)(2-Me-4-$Me_2NC_6H_3NO$)] (**2**), $K_{dis}(259) = (3.03 \pm 0.15) \times 10^{-3}$ mol$^{\frac{1}{2}}$ kg$^{-\frac{1}{2}}$, $\Delta H = 41.5 \pm 1.0$ kJ mol^{-1}, and $\Delta S(259) = 145 \pm 8$ J K^{-1} mol^{-1}; [RhCl(cod)(2,6-Me_2-4-$Me_2NC_6H_2NO$)], $K_{dis}(259) = 2.27 \pm 0.10$ mol$^{\frac{1}{2}}$ kg$^{-\frac{1}{2}}$, $\Delta H = 24.5 \pm 0.6$ kJ mol^{-1}, $\Delta S(259) = 102 \pm 2$ J K^{-1} mol^{-1}. Complex (**1**) is too stable to determine the dissociation constant by ^1H n.m.r. spectroscopy, while the methyl groups introduced at positions 2 and 6 of the benzene ring greatly accelerate the dissociation of the Rh–N bond owing to steric hindrance from these groups.

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