Synthesis and Reactivity of the Tetrakis(acetonitrile)nitrosylrhodium Dication

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The salts [NO][X] (X = BF_4 or PF_6) react with [Rh(1,5-C_8H_{12})(NCMe)$_2$][X] or [Rh(1,5-C_8H_{12})$_2$][X] in acetonitrile to give [Rh(NCMe)$_4$(NO)][X]$_2$ (1), and with [{Rh(1,5-C_8H_{12})Cl}$_2$] or [{Rh(CO)$_2$Cl}$_2$] to give [RhCl(NCMe)$_3$(NO)][X] (2). Complexes (1), with L, $Ph_2PCH_2CH_2PPh_2$ (dppe), Na[S_2CNMe_2]·$2H_2O$, and CO afford [Rh(NCMe)$_2$(NO)L$_2$][X]$_2$ [L = PPh_3 (3) or $AsPh_3$ (4)], [Rh(NO)(dppe)$_2$][X]$_2$ (5), [Rh(NO)(S_2CNMe_2)$_3$][X] (6), and [Rh(CO)$_2$(NCMe)$_2$][X] (7) respectively. Complexes (2) react with PPh_3 to give [RhCl(NCMe)(NO)(PPh$_3$)$_2$][X] (8) which may also be prepared from (3) and Cl^-. Excess of halide ion with (3), however, yields [RhY$_2$(NO)(PPh$_3$)$_2$] (Y = Cl or I), whereas Na[S_2CNR_2]·nH_2O give [Rh(PPh$_3$)$_2$(S_2CNR_2)$_2$][X] (R = Me or Et) with loss of the co-ordinated nitrosyl ligand. In the presence of PPh_3, (3) reacts with N_2H_4 to give [Rh(NO)(PPh$_3$)$_3$] (9).

The analogous ^{15}NO species have also been prepared and attempts have been made to assign the 'bent' or 'linear' modes of bonding to the metal-nitrosyl groups on the basis of i.r. and ^{15}N n.m.r. spectroscopy.

THE recent renewal of interest in metal nitrosyl complexes has, in the main, stemmed from the observation that nitrogen monoxide may bond to a transition metal in either a 'bent' (formally as $[NO]^-$) or 'linear' (formally as $[NO]^+$) fashion, and that the interconversion of 'bent' and 'linear' nitrosyls can occur *via* intramolecular isomerisation. Such an interconversion, which formally leads to a change in metal oxidation state, *viz.* $M^{n+}(NO)^+ \rightleftharpoons M^{(n+2)+}(NO)^-$, and also to a change in co-ordination geometry, may form the basis for catalytic reactions. In addition, the reactions of co-ordinated NO with molecules such as carbon monoxide (to give CO_2 and N_2O) [1] has stimulated interest in the use of metal nitrosyls in, for example, atmospheric pollution control.

In the case of rhodium and iridium complexes, where catalytic † reactions might be expected, relatively little is known. We therefore report details [2] of our studies on the preparation and reactivity of a series of rhodium nitrosyl complexes, which should enable a study to be made of the effects of varying the donor–acceptor properties of other ligands present on the mode of bonding of the nitrosyl ligand. We also describe the preparation of ^{15}N-labelled complexes, using [^{15}NO][BF_4], and their use in i.r. and ^{15}N n.m.r. studies of the bending and straightening of the metal–nitrosyl linkage.

RESULTS

The addition of [NO][X] (X = BF_4 or PF_6) to either [Rh(1,5-C_8H_{12})(NCMe)$_2$][X] or [Rh(1,5-C_8H_{12})$_2$][BF_4] in acetonitrile resulted in the immediate formation of deep green solutions from which [Rh(NCMe)$_4$(NO)][X]$_2$ (1) were isolated as emerald-green crystals. The complexes were characterised by elemental analysis and conductivity measurements (Table 1) and by their i.r. spectra in Nujol which showed strong bands at 1 758 cm^{-1} [ν(NO)] and at 2 310 and 2 345 cm^{-1} [ν(CN)]. The ^1H n.m.r. spectra of (1) in CD_3NO_2 showed one singlet at τ 7.40, due to co-ordinated acetonitrile, which rapidly decreased in intensity while a new singlet at τ 7.87, due to the free nitrile (τ 8.00 in CD_3NO_2), appeared. Whether decomposition, or exchange between co-ordinated nitrile and CD_3NO_2, occurs is not clear, although a slight shift of the 'free' nitrile peak from the τ value found for MeCN in CD_3NO_2 and a slight broadening of the peak suggest exchange. The ^1H n.m.r. spectra of (1) in CD_3CN also showed decay of the signal due to co-ordinated nitrile and growth of the signal due to free nitrile; when diethyl ether was added to the mixture, after 10—15 min [Rh(NCCD$_3$)$_4$(NO)][X]$_2$ could be isolated. Similar replacement could be carried out by dissolving (1) in Bu^{t}CN and, after several minutes, isolating [Rh(NCBu^t)$_4$(NO)][X]$_2$ by diethyl ether precipitation. The t-butyl complex was also prepared directly from [Rh(1,5-C_8H_{12})$_2$][X] and [NO][X] in Bu^{t}CN, and was fully characterised (Tables 1 and 2). The ^1H n.m.r. spectrum of this complex in CD_3NO_2 showed one singlet at τ 8.41 which again decayed while growth of the singlet (τ 8.63) due to free nitrile (τ 8.67 in CD_3NO_2) occurred.

The chloro-bridged dimers [{Rh(1,5-C_8H_{12})Cl}$_2$] and [{Rh(CO)$_2$Cl}$_2$] also reacted with [NO][PF_6] in MeCN to give [RhCl(NCMe)$_3$(NO)][PF_6] (2) as a brown-green solid. The reaction between the cyclo-octadienerhodium complex and [NO][PF_6] contrasts with that of NOCl in solvents such as $CHCl_3$ which affords the air-sensitive brown polymer [{RhCl$_2$(NO)}$_n$], and with that between [{Ir(1,5-C_8H_{12})Cl}$_2$] and NOCl which gives green [Ir(1,5-C_8H_{12})Cl$_2$(NO)].[3]

The lability of the nitrile ligands in (1), suggested by the

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† A solution of [Rh(NCMe)$_4$(NO)][X]$_2$ (X = BF_4 or PF_6) in $MeNO_2$ is an effective catalyst (room temperature) for the di-, tri-, and tetra-merisation of isobutylene (N. G. Connelly, P. T. Draggett, and M. Green, unpublished work).

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[2] N. G. Connelly, M. Green, and T. A. Kuc, *J.C.S. Chem. Comm.*, 1974, 542.

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TABLE 1

Analytical and conductance data for rhodium nitrosyl complexes

Complex	Colour	Yield (%)	Λ [a] S cm^2 mol^{-1}	Analyses [b] (%) C	H	N
$[Rh(NCMe)_4(NO)][BF_4]_2$ (1)	Emerald green	93		20.4 (20.3)	2.7 (2.4)	14.5 (14.8)
$[Rh(NCMe)_4(NO)][PF_6]_2$	Emerald green	92	153	16.6 (16.4)	2.4 (2.1)	11.4 (11.9)
$[Rh(NCBu^t)_4(NO)][PF_6]_2$	Green	90	155	31.3 (31.8)	4.8 (4.8)	9.3 (9.3)
$[RhCl(NCMe)_3(NO)][PF_6]$ (2)	Green-brown	86	76	17.4 (16.5)	2.2 (2.1)	12.6 (12.8) [c]
$[Rh(NCMe)_2(NO)(PPh_3)_2][PF_6]_2$	Olive green	93	152	47.1 (46.7)	3.6 (3.5)	4.5 (4.1)
$[Rh(NCMe)_2(NO)(PPh_3)_2][BF_4]_2$ (3)	Olive green	91		52.6 (52.6)	4.0 (4.0)	4.2 (4.6)
$[Rh(AsPh_3)_2(NCMe)_2(NO)][BF_4]_2$ (4)	Olive green	94		47.7 (48.0)	3.6 (3.6)	4.2 (4.2)
$[RhCl(NCMe)(NO)(PPh_3)_2][PF_6]$ (8)	Yellow-green	66	81	52.2 (51.9)	4.3 (3.8)	2.7 (3.2) [d]
$[Rh(NO)(dppe)_2][BF_4]_2$ (5)	Green	83		56.3 (56.6)	4.3 (4.4)	1.4 (1.3)
$[Rh(NO)(dppe)_2][PF_6]_2$	Green	86		51.3 (51.2)	4.2 (4.0)	1.2 (1.1)
$[Rh(NO)(S_2CNMe_2)_3][BF_4]$ (6)	Brown	54		18.4 (18.6)	3.1 (3.1)	9.5 (9.6)
$[Rh(NO)(S_2CNMe_2)_3][PF_6]$	Brown	31	41	17.1 (16.9)	3.0 (2.8)	8.9 (8.8

[a] 10^{-4} mol dm^{-3} in CH_3NO_2. [b] Calculated values are given in parentheses. [c] P 6.9 (7.1%); Cl, 7.8 (8.1%). [d] P 10.4 (10.6%); Cl 3.4 (4.0%).

appearance of the ^1H n.m.r. spectra, and (2) is confirmed by their reactions with a number of other ligands. Addition of excess of PPh_3 or $AsPh_3$ to acetonitrile solutions of (1), or to suspensions of (1) or (2) in CH_2Cl_2, afforded green solutions from which $[Rh(NCMe)_2(NO)(PPh_3)_2][X]_2$ (3) [^1H n.m.r. (in CD_2Cl_2): τ 2.33 (br. m, 30 H, PPh_3) and 8.11 (s, 6 H, CH_3CN)], $[Rh(AsPh_3)_2(NCMe)_2(NO)][X]_2$ (4) [^1H n.m.r. (in CD_2Cl_2): τ 2.45 (br. m, 30, H, PPh_3), and 8.00 (s, 6 H, CH_3CN)], and $[RhCl(NCMe)(NO)(PPh_3)_2][PF_6]$ (8) [^1H n.m.r. (in CD_2Cl_2): τ 2.46 (br. m, 30 H, PPh_3) and 8.52 (s, 3 H, CH_3CN)] were isolated as green crystalline solids. Complex (8) was also prepared by the addition of stoicheiometric amounts of $[N(PPh_3)_2]Cl$ to (2) in CH_2Cl_2. Excess of halide in MeCN, however, afforded the known neutral species $[RhY_2(NO)(PPh_3)_2]$ (Y = Cl or I) in virtually quantitative yields.

TABLE 2

Infrared data (cm^{-1}) [a] for rhodium nitrosyl complexes

Complex	$\tilde{\nu}$(CN)	$\tilde{\nu}(^{14}NO)$	$\tilde{\nu}(^{15}NO)$	$\tilde{\nu}(^{14}NO)$ (corrected) [b]	$\tilde{\nu}(^{15}NO)$ (calc.) [c]
$[Rh(NCMe)_4(NO)][BF_4]_2$ (1)	2 345, 2 325	1 758	1 727	1 588	1 726
$[Rh(NCBu^t)_4(NO)][PF_6]_2$	2 310	1 765		1 595	
$[RhCl(NCMe)_3(NO)][PF_6]$ (2)	2 335, 2 310	1 700		1 590	
$[Rh(NCMe)_2(NO)(PPh_3)_2][BF_4]_2$ (3)	2 320, 2 350	1 734	1 705	1 564	1 703
		1 703 [d]			
$[Rh(AsPh_3)_2(NCMe)_2(NO)][BF_4]_2$ (4)	2 320, 2 300	1 720		1 550	
$[Rh(NO)(dppe)_2][BF_4]_2$ (5)		1 730	1 700	1 630	1 699
		1 718 [d]			
$[RhCl(NCMe)(NO)(PPh_3)_2][PF_6]$ (8)		1 698 [e]		1 588	
$[Rh(NO)(S_2CNMe_2)_3][BF_4]$ (6)		1 545	1 530	1 435	1 517
$[RhCl_2(NO)(PPh_3)_2]$		1 632	1 605	1 602	1 602
$[RhI_2(NO)(PPh_3)_2]$		1 626	1 598	1 596	1 597
$[Rh(NO)(PPh_3)_3]$		1 610	1 578	1 600	1 582

[a] In Nujol unless otherwise stated. [b] By application of Ibers' rules.[5] [c] From $\tilde{\nu}(^{15}NO) = 0.982\ \tilde{\nu}(^{14}NO)$. [d] In CH_2Cl_2. [e] In $CHCl_3$.

Displacement of four acetonitrile ligands from (1) occurred with $Ph_2PCH_2CH_2PPh_2$ (dppe) and with $[S_2CNMe_2]^-$. In acetonitrile or CH_2Cl_2, dppe gave green $[Rh(NO)(dppe)_2][X]_2$ (5), whereas $[S_2CNMe_2]^-$ yielded a brown complex formulated on the basis of analytical data (C, H, and N) on both the $[BF_4]^-$ and $[PF_6]^-$ salts as $[Rh(NO)(S_2CNMe_2)_3][X]$ (6). The nature of (6) has not been conclusively established. The molar conductivity in $MeNO_2$ (10^{-4} mol dm^{-3} solution, 41 S cm^2 mol^{-1}) is low for a 1 : 1 electrolyte (usually $\approx$75—80 S cm^2 mol^{-1}), but this is possibly due to incomplete dissociation. The ^1H n.m.r. spectrum in $(CD_3)_2CO$ is of no help as only one broad peak centred at *ca.* τ 6.5 was observed; no sharpening of the spectrum was seen between −95 and 55 °C. The i.r. spectrum confirms the presence of the anion, X, and also showed an intense band at 1 545 cm^{-1} assigned [2] to ν(NO). Although co-ordinated dithiocarbamate ligands absorb in the 1 510—1 560 cm^{-1} region [ν(CN)], thus making the assignment of ν(NO) and ν(CN) difficult, labelling of the complex with ^{15}NO appears to bring about a shift in the position of the band at 1 545 cm^{-1}. The calculated value for $\nu(^{15}NO)$, based on a value of 1 545 cm^{-1} for $\nu(^{14}NO)$, is 1 517 cm^{-1}, somewhat lower than the band observed for $[Rh(^{15}NO)(S_2CNMe_2)_3][BF_4]$ (ν at $\approx$1 525—1 530 cm^{-1}). It therefore appears that the nature of (6) will only be determined by an *X*-ray structural analysis.

Complexes (3) reacted with $Na[S_2CNR_2]\cdot nH_2O$, to give yellow crystals of $[Rh(PPh_3)_2(S_2CNR_2)_2][X]$ (R = Me or Et) {earlier [2] incorrectly formulated as $[Rh(NO)(PPh_3)_2(S_2CNR_2)][X]$} with loss of co-ordinated NO. Although such nitrosyl loss is uncommon, it also occurs in the reaction between (1) and CO under pressure (3 atm),* giving $[Rh(CO)_2(NCMe)_2][X]$ (7). Finally, the reaction of (3) with hydrazine in the presence of excess of triphenylphosphine gave good yields of $[Rh(NO)(PPh_3)_3]$ (9); regeneration of (3) occurred by the reaction of (9) with [NO][X] in acetonitrile.

DISCUSSION

The unequivocal assignment of 'bent' or 'linear' co-ordination to the metal–nitrosyl group on the basis of any method other than *X*-ray crystallography is diffi-

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* Throughout this paper: 1 atm = 101 325 Pa.

cult,[4] and to date * attempts to obtain suitable crystals of the rhodium cations have not been successful. We have therefore used i.r. studies on the ^{14}NO and corresponding ^{15}NO complexes combined with ^{15}N n.m.r. measurements to make a preliminary assignment of structures.

Haymore and Ibers[5] suggested that ν(NO) can be used to assign the geometry of nitrosyls if corrections are made for the charge on the complex, for the nature of the other ligands present, and for the position of the central transition metal in the Periodic Table. Listed in Table 2 are the ' corrected ' values for ν(NO) which are, for (1), (3), and (5) respectively, 1 588, 1 564, and 1 630 cm^{-1}. The complexes $[Rh(NO)(PPh_3)_3]$ {by analogy with $[Ir(NO)(PPh_3)_3]$}[6] and $[RhCl_2(NO)(PPh_3)_2]$[7] have been shown to contain linear and bent nitrosyl groups respectively, and have ' corrected ' ν(NO) values of 1 620 and 1 602 cm^{-1}, which suggests that (1) and (3) may contain $[NO]^-$ ligands whereas (5) may contain a linear metal–nitrosyl arrangement. The latter conclusion seems likely in that $[Ru(NO)(dppe)_2][PF_6]$ (10) has[8] a trigonal-bipyramidal structure with a linear $[NO]^+$ group. The real ν(NO) values for (5) and (10) are 1 734 and 1 673 cm^{-1}, the former being higher because of the increased positive charge causing decreased back donation to the π*(NO) orbitals, which on correction are 1 630 and 1 633 cm^{-1}. On the basis of their ' corrected ' ν(NO) values, both (1) and (3), as well as (2) and (8), are likely to be square planar with bent, axial, $[NO]^-$ groups, although insufficient corroborative data are available.

Attempts have recently been made[9] to assign bent or linear M–N–O structures on the basis of Δ, the difference between ν(^{15}NO) and ν(^{14}NO). It has been noted that, for a series of rhodium nitrosyl complexes, those containing ' linear ' nitrosyls have values of Δ between 36 and 44 cm^{-1} whereas those containing ' bent ' nitrosyls have Δ = 25—28 cm^{-1}. The values for (1), (3), (5), $[Rh(NO)(PPh_3)_3]$, and $[RhCl_2(NO)(PPh_3)_2]$ are 31, 29, 30, 32, and 27 cm^{-1}. While the last complex contains a ' bent ' nitrosyl, and has a Δ value in accord with this, the Δ values for (1), (3), (5), and $[Rh(NO)(PPh_3)_3]$ are very similar and also between the two ranges given. For the new complexes reported here, then, measurement of Δ does not appear to be useful.

As noted earlier, labelling (6) with ^{15}N seems to suggest that ν(NO) occurs, for the unlabelled complex, at 1 545 cm^{-1}. If this is correct then such a low value for ν(NO) must suggest the presence of a bent metal–nitrosyl group. The isoelectronic species $[Ru(NO)(S_2CNEt_2)_3]$ is octahedral[10] with a linear $[NO]^+$ group *trans* to the sulphur atom of a unidentate dithiocarbamate ligand and has ν(NO) at 1 803 cm^{-1}. Complexes (6) must therefore either have a similar octahedral structure with a bent $[NO]^-$ ligand, or a seven-co-ordinate structure with three chelating sulphur ligands as well as the bent nitrosyl group.

With ^{103}Rh having a nuclear spin of $I = \frac{1}{2}$ the possibility occurs that for ^{15}N-labelled nitrosylrhodium complexes one can not only measure ^{15}N chemical shifts by n.m.r. methods but also $J(^{103}Rh-^{15}N)$ which may be expected to show a large dependence on the hybridisation of the nitrosyl nitrogen atom. For $[NO]^+$ complexes, with *sp*-hybridised nitrogen, $J(^{103}Rh-^{15}N)$ should differ considerably from those of $[NO]^-$ complexes in which the nitrogen atom is sp^2 hydridised. We therefore attempted to record ^{15}N n.m.r. spectra of the nitrosyl species reported herein. Although difficulty was found with the actual spectral measurements, (1) showed only one singlet at δ 964.0 p.p.m. (relative to $[^{15}NH_4]^+$). Whether the absence of $^{103}Rh-^{15}N$ coupling is due to the nitrosyl group occurring as $[NO]^-$ and that $[NO]^+$ complexes will show such coupling is for speculation only. We hope to be able to report our findings at a later date.

EXPERIMENTAL

The preparation and purification of the complexes described were carried out under an atmosphere of dry nitrogen; $[\{Rh(CO)_2Cl\}_2]$,[11] $[\{Rh(1,5\text{-}C_8H_{12})Cl\}_2]$,[12] and $[Rh(1,5\text{-}C_8H_{12})(NCMe)_2][BF_4]$[13] were prepared by published procedures. The salts $[NO][PF_6]$ and $[NO][BF_4]$ were purchased from Ozark Mahoning Co., Tulsa, Oklahoma, and $[^{15}NO][BF_4]$ was prepared from $Na[^{15}NO_2]$ purchased from the British Oxygen Co. Ltd. ^{15}NO-Labelled nitrosyl complexes were prepared by exactly the same methods detailed below for the ^{14}NO species. All the solvents were dried by standard methods and deoxygenated before use.

Infrared spectra were recorded on Perkin-Elmer PE 257 or PE 457 spectrophotometers and calibrated against the band at 1 601 cm^{-1} of polystyrene. Hydrogen-1 n.m.r. spectra were obtained on a Varian Associates HA 100 spectrometer at 100 MHz and ^{31}P n.m.r. spectra on the Jeol PFT 100 spectrometer at 40.48 MHz. Microanalyses were by the staff of the Microanalytical Service of the School of Chemistry, University of Bristol.

$[^{15}N]$*Nitrosyl Tetrafluoroborate*, $[^{15}NO][BF_4]$.—To a stirred mixture of water (0.25 cm^3), sulphuric acid (0.35 cm^3), and n-pentanol (1.5 cm^3, 13.9 mmol) cooled to −10 °C was added dropwise a cooled (0 °C) solution of $Na[^{15}NO_2]$ (0.95 g, 13.8 mmol) in water (4 cm^3). After stirring for 90 min at room temperature the resulting solution was decanted from precipitated $Na_2[SO_4]$. The upper pale-yellow layer of crude amyl nitrite was separated and dried over anhydrous

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* This difficulty is underlined by the observation that crystals, which were considered to be (3), were shown by *X*-ray crystallography to be in fact $[Rh(NCMe)_3(NO)(PPh_3)_2]^{2+}$, *i.e.* an O_h complex with bent nitrosyl; the additional mol of MeCN is lost only on pumping (N. G. Connelly, P. T. Draggett, M. Green, B. A. Kelly, and A. J. Welch, unpublished work).

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$Mg[SO_4]$ for 1 h. The crude amyl nitrite was then added dropwise over 20 min to a stirred mixture of 40% aqueous HBF_4 (3.0 cm^3, 13.6 mmol) and propionic anhydride (18 cm^3) previously cooled to −15 °C; the reaction temperature was maintained below −10 °C. After stirring for 10 min at −10 °C the white precipitate of $[^{15}NO][BF_4]$ was filtered off, washed with propionic anhydride at −10 °C, and dried *in vacuo* at room temperature, yield 0.97 g (60%).

Tetrakis(acetonitrile)nitrosylrhodium Bis(tetrafluoroborate), $[Rh(NCMe)_4(NO)][BF_4]_2$ (1).—To a rapidly stirred solution of $[Rh(1,5\text{-}C_8H_{12})(NCMe)_2][BF_4]$ (304 mg, 0.8 mmol) in acetonitrile (1 cm^3) at 0 °C was added $[NO][BF_4]$ (94 mg, 0.8 mmol) in small portions over a period of 20 min. After stirring at room temperature for another 20 min, diethyl ether (20 cm^3) was slowly added to the deep emerald-green solution. Immediate precipitation of the product as either an emerald-green crystalline solid or as an oil which rapidly solidified on stirring occurred. The solid was washed with diethyl ether (2 × 10 cm^3), CH_2Cl_2 (2 × 10 cm^3), and diethyl ether (2 × 10 cm^3), recrystallised from acetonitrile–diethyl ether, and dried *in vacuo* to yield the *product* as a dark green crystalline solid, yield 350 mg (93%). The complex is stable in dry air but in the presence of moisture slowly becomes brown. It is soluble in MeCN and $MeNO_2$ to give stable green solutions under nitrogen, but reacts with other polar solvents such as acetone and methanol to give brown solutions. The Bu^tCN analogue was prepared, in 90% yield, from $[Rh(1,5\text{-}C_8H_{12})_2][X]$ in Bu^tCN, as a green crystalline solid with similar properties.

Tris(acetonitrile)chloronitrosylrhodium Hexafluorophosphate, $[RhCl(NCMe)_3(NO)][PF_6]$ (2).— To $[\{Rh(1,5\text{-}C_8H_{12})Cl\}_2]$ (0.5 g, 1.0 mmol) in MeCN (50 cm^3) was added $[NO][PF_6]$ (0.18 g, 1.0 mmol) with rapid stirring. Addition of diethyl ether to the resulting green-brown solution gave a green-brown oil which slowly solidified on stirring. Recrystallisation twice from acetonitrile-diethyl ether gave the *product* as a green-brown solid, yield 0.75 g (86%). The complex may also be prepared from $[\{Rh(CO)_2Cl\}_2]$ in a similar fashion. It is soluble in acetonitrile to give brown-green solutions stable under nitrogen, but reacts with acetone and methanol to give brown solutions.

Bis(acetonitrile)nitrosylbis(triphenylphosphine)rhodium Bis(tetrafluoroborate), $[Rh(NCMe)_2(NO)(PPh_3)_2][BF_4]_2$ (3).— To a stirred solution of PPh_3 (80 mg, 0.3 mmol) in MeCN (1 cm^3) was added $[Rh(NCMe)_4(NO)][BF_4]_2$ (65 mg, 0.14 mmol). Slow dropwise addition of diethyl ether (12 cm^3) to the resulting green solution gave the *product* as a green crystalline solid which was recrystallised from acetonitrile–diethyl ether and dried *in vacuo*, yield 115 mg (91%). The complex is soluble in MeCN, CH_2Cl_2, and acetone to give stable green solutions in the absence of water. The solid complex is stable in air. The complex $[Rh(AsPh_3)_2(NCMe)_2(NO)][BF_4]_2$ (4) may be made in a similar fashion in 94% yield.

Acetonitrilechloronitrosylbis(triphenylphosphine)rhodium Hexafluorophosphate, $[RhCl(NCMe)(NO)(PPh_3)_2][PF_6]$ (8).— *Method* (*a*). To a vigorously stirred suspension of $[RhCl(NCMe)_3(NO)][PF_6]$ (0.11 g, 0.25 mmol) in CH_2Cl_2 (40 cm^3) was added PPh_3 (200 mg, 0.76 mmol) in CH_2Cl_2 (10 cm^3). After 30 min the brown solution was filtered and hexane (30 cm^3) was added. Slow evaporation afforded the *product* as yellow-green crystals which were recrystallised from dichloromethane–hexane, yield 145 mg (66%). The complex is stable in air, and dissolves in acetonitrile and CH_2Cl_2 to give yellow-green solutions stable under nitrogen.

Method (*b*). To a stirred solution of $[Rh(NCMe)_2(NO)(PPh_3)_2][PF_6]_2$ (200 mg, 0.19 mmol) in CH_2Cl_2 (25 cm^3) was added $[N(PPh_3)_2]Cl$ (110 mg, 0.19 mmol). The resulting yellow-green solution was filtered and hexane (50 cm^3) was added to afford pale green crystals which were recrystallised from dichloromethane–hexane, yield 180 mg (91%).

Dichloronitrosylbis(triphenylphosphine)rhodium, $[RhCl_2(NO)(PPh_3)_2]$.—To a stirred solution of $[Rh(NCMe)_2(NO)(PPh_3)_2][PF_6]_2$ (200 mg, 0.19 mmol) in MeCN (25 cm^3) was added $[N(PPh_3)_2]Cl$ (300 mg, 0.52 mmol). After 10 min filtration gave the complex as an orange-brown solid, yield 130 mg (92%). The complex $[RhI_2(NO)(PPh_3)_2]$ was prepared in a similar fashion from $[Rh(NCMe)_2(NO)(PPh_3)_2][BF_4]_2$ (250 mg, 0.265 mmol) and $[NMe_4]I$ (150 mg, 0.75 mmol). The chocolate-brown product was recrystallised twice from dichloromethane–hexane, yield 200 mg (88%).

Bis[1,2-bis(diphenylphosphino)ethane]nitrosylrhodium Bis(tetrafluoroborate), $[Rh(NO)(dppe)_2][BF_4]_2$ (5).—To dppe (250 mg, 0.63 mmol) in MeCN (3 cm^3) was added $[Rh(NCMe)_4(NO)][BF_4]_2$ (130 mg, 0.28 mmol). On stirring for 10 min and subsequent addition of diethyl ether the product was precipitated as olive-green crystals, yield 250 mg (83%). The air stable complex is soluble in CH_2Cl_2 and MeCN to give green solutions which are moderately stable in air.

Reactions of $[Rh(NCMe)_2(NO)(PPh_3)_2][BF_4]_2$.—*With* N_2H_4 *and* PPh_3. To a rapidly stirred suspension of PPh_3 (100 mg, 0.42 mmol) in MeCN (5 cm^3) and anhydrous hydrazine (0.15 cm^3) was added the complex (100 mg, 0.11 mmol) stepwise during a period of 20 min. An immediate precipitate of brick-red solid formed. After stirring for another 20 min, the product was filtered off, washed with MeCN (2 × 10 cm^3), and recrystallised from dichloromethane–hexane to give $[Rh(NO)(PPh_3)_3]$ (9) as brick-red crystals, yield 92 mg (90%).

With $Na[S_2CNMe_2]\cdot 2H_2O$. To a stirred suspension of $Na[S_2CNMe_2]\cdot 2H_2O$ (125 mg, 0.85 mmol) in CH_2Cl_2 (4 cm^3) was added the complex (100 mg, 0.11 mmol) to give a red-brown solution. After stirring for another 10 min, and filtration, the volume of the solution was reduced *in vacuo* to *ca.* 2 cm^3. Slow addition of diethyl ether (20 cm^3) yielded a yellow crystalline solid which was recrystallised twice from dichloromethane–diethyl ether as $[Rh(PPh_3)_2(S_2CNMe_2)_2][BF_4]$, yield 55 mg (56%).

Reactions of $[Rh(NCMe)_4(NO)][BF_4]_2$.—*With* $Na[S_2CNMe_2]\cdot 2H_2O$. To a stirred suspension of the complex (133 mg, 0.281 mmol) in CH_2Cl_2 (1.5 cm^3) was slowly added $Na[S_2CNMe_2]\cdot 2H_2O$ (151 mg, 0.843 mmol). The resulting red-brown solution was stirred for 60 min, filtered, and the residue washed with CH_2Cl_2 (2 × 3 cm^3). Addition of diethyl ether (20 cm^3) to the combined filtrate yielded a brown solid which was recrystallised twice from dichloromethane–diethyl ether to give $[Rh(NO)(S_2CNMe_2)_3][BF_4]$ (6) as brown microcrystals, yield 88 mg (54%).

With CO *under pressure*. A suspension of the complex (150 mg, 0.32 mmol) in CH_2Cl_2 (20 cm^3) was stirred for 48 h under CO (3 atm). The yellow solution was filtered, evaporated to *ca.* 10 cm^3, and excess of diethyl ether was added. The purple precipitate was recrystallised from dichloromethane–diethyl ether to give $[Rh(CO)_2(NCMe)_2][BF_4]$ (7) as purple-blue crystals, yield 65 mg (62%).

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