corresponding resonance in the free ligand. In the cationic, fully chelated complex **15**, the ^{13}C NMR pattern of the ligand is seen as another simple nine-line pattern, as is required by either the C_3 or C_{3v} symmetry of this complex.

The synthesis and characterization of complexes **13** and **15** demonstrate the ability of TriCN to act as a facially coordinating tridentate ligand. Other TriCN-type ligands, such as those with isocyano rather than cyano donor groups, would also be expected to form stable metal complexes. Such octahedral complexes with two TriCN-type ligands would have especially interesting geometries.

Acknowledgement is made to the National Science Foundation (Grant No. CHE78-07913) for support of this research. We also thank Margaret A. McMichael for her help in preparing some of the ligands.

Registry No. **2**, 87226-86-6; **3**, 87226-87-7; **4**, 87226-88-8; **5**, 87226-89-9; **6**, 87226-90-2; (*E*)-**7**, 87226-91-3; (*Z*)-**7**, 87226-93-5; **8**, 87226-92-4; **9**, 74252-09-8; **10**, 87249-28-3; **11**, 87249-29-4; **12**, 87261-29-8; **13**, 87249-31-8; **14**, 87249-32-9; **15**, 87249-34-1; Mn(CO)$_5$Br, 14516-54-2; Re(CO)$_5$Br, 14220-21-4; Mn$_2$(CO)$_6$(CH$_3$CN)$_2$(μ-Br)$_2$, 38433-31-7; 2-cyanophenol, 611-20-1; 1,3-dibromopropane, 109-64-8; 1,4-bromobutane, 110-52-1.

Contribution from the Inorganic Chemistry Laboratory, University of Oxford, Oxford OX1 3QR, England,
and the Department of Chemistry, The Open University, Milton Keynes MK7 6AA, England

^{15}N NMR Studies of Nitrosyl (Bent and Linear), Nitro, and Nitrito Ligands in 4-, 5-, and 6-Coordinate Complexes of the Platinum Metals

LINDA K. BELL,[†] JOAN MASON,*[‡] D. MICHAEL P. MINGOS,*[†] and DAVID G. TEW[†]

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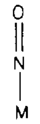
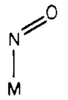
High-field NMR spectroscopy of highly ^{15}N-enriched nitrosyl complexes has shown that nitrogen is deshielded by up to 450 ppm in bent as compared with linear nitrosyl ligands. As in related (e.g., diazenido) groups, the deshielding correlates with the presence of low-energy $n_N \rightarrow \pi^*$ electronic circulations in the magnetic field and so is diagnostic of the bent geometry. Nitrogens in adjacent linear nitrosyl groups are deshielded by 100–150 ppm compared with corresponding mononitrosyl complexes, which may imply substantial overlap of the π HOMOs in the dinitrosyls. There are indications also of some deshielding when nitro and bent nitrosyl groups are adjacent. The 5-coordinate ruthenium dinitrosyl complex [RuCl(^{15}NO)(NO)(PPh$_3$)$_2$]$^+$ has been shown by ^{15}N and ^{31}P NMR spectroscopy to have a constitution in solution different from that of the solid. Earlier X-ray crystallographic work gave the structure as square pyramidal with a bent apical nitrosyl ligand and a linear equatorial nitrosyl ligand. The solution contains isomeric structures in equilibrium. However, 5-coordinate rhodium complexes with only one nitrosyl group and no other "ambiguous" ligand, namely [RhCl(CO)(^{15}NO)(P-*i*-Pr$_3$)$_2$]$^+$ and [RhCl(^{15}NO)(^{15}NO$_2$)(PR$_3$)$_2$] with R = *i*-Pr, Cy, or Ph, have the square-pyramidal geometry with bent apical nitrosyl in solution as in the solid state. The nitro ligand resonances are found at medium field, between those of nitrite ion and nitroalkanes, as also are those of linear nitrosyls, close to that of free NO$^+$. Bent nitrosyls, however, resonate at very low field, in the same region as nitrosoalkanes, in which nitrogen carries a lone pair. Nitrogen NMR spectroscopy is thus a useful probe of geometry of nitrosyl ligands and of complexes in solution when alternative structures are available, as through an intramolecular redox process.

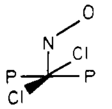
The ability of nitric oxide to coordinate to transition metals in linear (**1**) or bent (**2**) fashion was first established unambiguously as a result of X-ray crystallographic studies in the solid state, particularly by Ibers and co-workers.[1] These studies also suggested that for five-coordinate nitrosyl complexes the potential energy surface connecting alternative linear and bent nitrosyl conformations might be soft, since even for isoelectronic molecules the three limiting geometries illustrated in **3**–**5** were observed in the solid state.[2-5] (In order to limit the confusion that can arise from the NO$^+$–NO$^-$ formalism, we follow Enemark and Feltham's suggested notation {M(NO)}^{x} to designate nitrosyl complexes.[6]) Further, MNO angles between 120 and 180° are well documented (though less common), notably in complexes with two cis nitrosyl groups.[6] The occurrence of such a soft potential energy surface has been used to account for differences in the substitution and catalytic reactions of metal nitrosyl complexes compared to carbonyl complexes.[7] In addition, the theoretical aspects of nitrosyl binding have been discussed by several workers.[8]



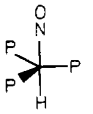
(M-N-O ~ 180°)
1



(M-N-O ~ 120°)
2



[IrCl$_2$(NO)(PPh$_3$)$_2$]
{M(NO)}^{8}
3



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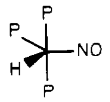
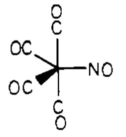


[IrH(NO)(PPh$_3$)$_3$]$^+$
{M(NO)}^{8}
4a 4b



[Mn(CO)$_4$(NO)]
{M(NO)}^{8}
5

In this paper we report the first observations in ^{15}N nuclear magnetic resonance of bent as well as linear nitrosyl ligands in transition-metal complexes, the large difference in nitrogen shifts in the bent compared to the linear ligand showing the value of nitrogen NMR in the structural characterization of nitrosyl complexes in solution. In addition, we have identified ranges of ^{15}N resonances for nitro and hyponitrito ligands

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[‡] The Open University.

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coordinated to transition metals, which should facilitate the study of the reactions of nitrosyl complexes involving these species as intermediates. Although infrared spectroscopy may also be used to study the structures and reactions of nitrosyl complexes in solution, the overlap in the ν(NO) range characteristic of linear and bent nitrosyl ligands, viz. 2000–1600 cm^{-1} (linear) and 1725–1525 cm^{-1} (bent), has limited the usefulness of this technique as a structural probe.[1]

Nitrogen NMR spectroscopy appeared to be particularly suitable for distinguishing between bent and linear M–N–O conformations because of the large downfield shift (by hundreds of ppm) that was expected for the bent as compared with the linear nitrosyl ligand.[9] This has been observed previously for the analogous diazenido ("iminonitrosyl") ligand $-N_\alpha{=}NR$, which can be either linear or bent at the ligating atom N_α.[10] Studies on ^{15}N-enriched diazenido complexes have shown that rhodium complexes with a bent Rh–N–N group have $^{15}N_\alpha$ resonances approximately 350 ppm downfield of those characteristic of complexes of molybdenum, tungsten, rhenium, and ruthenium with linear M–N–N groups. This deshielding can be attributed[9] to low-energy $n_N \rightarrow \pi^*$ electronic circulations in the magnetic field, when conjugated nitrogen atoms carry a lone pair, and therefore is an intrinsic property of the bent geometry.

The limited nitrogen NMR studies on transition metal nitrosyl complexes that have been reported can be related to the lability of the nitrosyl ligand and technical difficulties of ^{14}N and ^{15}N NMR spectroscopy.[9] Both nuclei have relatively low sensitivities to NMR detection because of their low gyromagnetic ratios. ^{14}N, although abundant, is quadrupolar, the line width increasing with molecular size and with the local electronic asymmetry, so that linear nitrosyls give rather broad lines ($W_{1/2} \simeq 500$ Hz),[11-15] and no ^{14}N resonances have been identified for bent nitrosyl complexes. ^{15}N has a nuclear spin of $^1/_2$ but low natural abundance (0.365%) and slow relaxation particularly when there are no protons attached to nitrogen.[9] To date only one ^{15}N NMR study of metal nitrosyl complexes has been reported, by Legzdins, Roberts, and co-workers.[16]

Experimental Section

To maximize sensitivity, the ^{15}N NMR spectra were measured on samples with 99–95%-enriched ^{15}N, and the spectra were run on a Bruker WH-400 spectrometer operating at 40.55 MHz. For several of the compounds, [Cr(acac)$_3$] was added to promote relaxation but not in sufficient amount to require a susceptibility correction. The reference standard was $CD_3{}^{15}NO_2$. The $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker WH-400 or WH-90 spectrometer, with 85% aqueous H_3PO_4 as external standard. Infrared spectra were recorded on Perkin-Elmer 457 and Pye Unicam SP200 infrared spectrometers, either as Nujol mulls between KBr plates or in solution in a 0.25-mm CaF_2 cell. The frequencies were assigned relative to a polystyrene standard.

$Na^{15}NO_2$ (95% enriched) and ^{15}NO gas (99% enriched) were purchased from Goss Scientific Instruments Ltd.

Bis(dimethylphenylphosphine)[(^{15}N)nitrosyl]trichlororuthenium, [RuCl$_3$(^{15}NO)(PMePh$_2$)$_2$] (6). [RuCl$_3$(^{15}NO)$\cdot x$H$_2$O] was prepared from [RuCl$_3\cdot x$H$_2$O], HCl(aq), and Na^{15}NO$_2$ (96% labeled) by the method of Fletcher et al.[17] and converted into [RuCl$_3$(^{15}NO)(PMePh$_2$)$_2$] by the method of Chatt and Shaw.[18] [RuCl$_3$(^{15}NO)$\cdot x$H$_2$O] was dissolved in ethanol (15 mL), and 3 mol equiv of PMePh$_2$ in ethanol (5 mL) was added. The solution was refluxed for 10 min and after being reduced to ca. 10 mL was cooled to 0 °C. The golden yellow solid that separated from the solution was filtered and washed with cold ethanol (2 × 10 mL) and diethyl ether (2 × 10 mL). The solid was dried in vacuo and identified as [RuCl$_3$(^{15}NO)(PMePh$_2$)$_2$] on the basis of infrared evidence: ν(^{15}NO) 1845 cm^{-1} (cf. [RuCl$_3$(NO)(PMePh$_2$)$_2$] ν(NO) 1876 cm^{-1}). Anal. Calcd for $RuC_{26}H_{26}NOCl_3P_2$: C, 49.0; H, 4.7; N, 2.2. Found: C, 49.0; H, 4.7; N, 2.2. The yield was 80% based on RuCl$_3\cdot x$H$_2$O.

Bis(triphenylphosphine)[(^{15}N)nitrosyl]nitrosylchlororuthenium(1+) Tetrafluoroborate, [RuCl(^{15}NO)(NO)(PPh$_3$)$_2$]BF$_4$ (12). [RuCl$_3$(^{15}NO)(PPh$_3$)$_2$] was obtained as a yellow crystalline solid by a procedure analogous to that used for [RuCl$_3$(^{15}NO)(PMePh$_2$)$_2$]. [RuCl$_3$(^{15}NO)(PPh$_3$)$_2$] (0.15 g) was refluxed in benzene (20 mL) with an excess of a Zn–Cu couple for 1 h to give a deep emerald green solution of [RuCl(^{15}NO)(PPh$_3$)$_2$]. This solution was filtered into a suspension of 1 mol equiv of NOBF$_4$ in benzene (20 mL) containing ethanol (~1 mL). The solution rapidly changed from green to orange, and when it was reduced in volume and cooled to 0 °C, an orange precipitate of [RuCl(NO)(^{15}NO)(PPh$_3$)$_2$]BF$_4$ separated. The compound was identified on the basis of its infrared spectrum and analytical data. Infrared: ν(NO) 1865, 1686 cm^{-1}; ν(^{15}NO) 1823, 1658 cm^{-1} (Nujol).[19]

Bis(triisopropylphosphine)(sulfur dioxide)chlororhodium, [RhCl(SO$_2$)(P-*i*-Pr$_3$)$_2$], was prepared in a manner similar to that reported for [RhCl(SO$_2$)(PCy$_3$)$_2$].[20] [Rh(C$_8$H$_{12}$)Cl]$_2$ (0.15 g) and P-*i*-Pr$_3$ (0.2 g) were stirred in benzene (10 mL) for 10 min, and then a stream of sulfur dioxide gas was passed through this solution for a further 10 min. During this time the solution changed color from yellow to deep red-brown. Reduction of the volume of this solution and the addition of ethanol resulted in the precipitation of [RhCl(SO$_2$)(P-*i*-Pr$_3$)$_2$] as a dark red crystalline solid, which was recrystallized from dichloromethane and ethanol (yield 83%).

Anal. Calcd for $RhC_{18}H_{42}P_2O_2SCl$: C, 41.8; H, 8.0; Cl, 6.8; S, 6.1. Found: C, 41.3; H, 8.0; Cl, 6.6; S, 6.2. Infrared: ν(SO$_2$) 1262, 1118, 567 cm^{-1} (Nujol). ^{1}H NMR (CDCl$_3$): δ 1.36 (d of t, $^1/_2(J_{HP} + J_{HP'}) = 3.5$ Hz, $^3J_{CH-CH_3} = 7.2$ Hz, 36 H), 2.75 (septet of t, $^3J_{CH-CH_3} = 7.2$ Hz, $^1/_2(J_{HP} + J_{HP'}) = 2$ Hz, 6 H). The spectra show "virtual" coupling effects characteristic of equivalent phosphorus nuclei P and P′. $^{31}P\{^1H\}$ NMR: δ 40.2 (d, $^1J_{RhP} = 107.4$ Hz).

Bis(triisopropylphosphine)[(^{15}N)nitrosyl]chlororhodium(1+) Perchlorate, [RhCl(^{15}NO)(P-*i*-Pr$_3$)$_2$]ClO$_4$ (8a). A methanolic solution of HClO$_4$ (0.24 M, 2.0 mL) was added to a suspension of [RhCl(^{15}NO)(^{15}NO$_2$)(P-*i*-Pr$_3$)$_2$] (0.1 g) in methanol (15 mL) and the solution stirred at room temperature for 24 h. The volume of the solution was reduced, and when it was cooled to −30 °C, a dark red crystalline solid separated, which was recystallized from methanol (yield 85%) and identified as [RhCl(^{15}NO)(P-*i*-Pr$_3$)$_2$]ClO$_4$. Anal. Calcd for $RhC_{18}H_{42}O_5P_2Cl_2N$: C, 36.7; H, 7.1; N, 2.4; Cl, 12.1. Found: C, 36.6; H, 7.3; N, 2.3; Cl, 12.2. Infrared: ν(^{15}NO) 1842 cm^{-1} (Nujol) (cf. ν(NO) 1880 cm^{-1} (Nujol)), 1878 cm^{-1} (CHCl$_3$ solution). Molar conductivity $\Lambda_M = 83\ \Omega^{-1}$ L mol^{-1} (~10^{-3} M solution). ^{1}H NMR (CD$_3$OD): δ 1.51 (d of t, $^1/_2\ (J_{HP} + J_{HP'}) = 4$ Hz, $^3J_{CH-CH_3} = 6.9$ Hz, 36 H), 3.05 (septet of t, $^1/_2\ (J_{HP} + J_{HP'}) = 2$ Hz, $^3J_{CH-CH_3} = 6.9$ Hz, 6 H). $^{31}P\{^1H\}$ NMR: δ 58.1 (d, $J_{RhP} = 91.2$ Hz).

Bis(triisopropylphosphine)[(^{15}N)nitrosyl]chlororhodium(1+) Tetrafluoroborate, [RhCl(^{15}NO)(P-*i*-Pr$_3$)$_2$]BF$_4$ (8b). RhCl (P-*i*-Pr$_3$)$_2$(SO$_2$) (0.1 g) was dissolved in benzene (10 mL), and a solution of NOBF$_4$ (0.025 g) in THF (10 mL) was rapidly added. There was little change in the color of the solution after stirring for 10 min at room temperature, but when it was cooled to 0 °C, a dark red solid separated and was identified as [RhCl(^{15}NO)(P-*i*-Pr$_3$)$_2$]BF$_4$, yield 40% based on [RhCl(P-*i*-Pr$_3$)$_2$(SO$_2$)]. Anal. Calcd for $RhC_{18}H_{42}F_4P_2ClNO$: C, 37.5; H, 7.3, N, 2.4, Cl, 6.2. Found: C, 37.2; H, 6.7; N, 2.3; Cl, 5.9. Infrared: ν(^{15}NO) 1843 cm^{-1}; ν(NO) 1885 cm^{-1} (Nujol).

Bis(triisopropylphosphine)(carbonyl)[(^{15}N)nitrosyl]chlororhodium(1+) Perchlorate, [RhCl(CO)(^{15}NO)(P-*i*-Pr$_3$)$_2$]ClO$_4$ (9). RhCl(^{15}NO)(P-*i*-Pr$_3$)$_2$]ClO$_4$ (0.1 g) was dissolved in methanol (15 mL),

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and carbon monoxide was passed through the solution for 20 min, after which time an orange precipitate had separated from the solution and was identified as [RhCl(CO)(^{15}NO)(P-*i*-Pr$_3$)$_2$]ClO$_4$ (yield 80%). Infrared: ν(CO) 2045 cm^{-1} (Nujol); ν(^{15}NO) 1687 cm^{-1}; ν(NO) 1712 cm^{-1} (Nujol). The related BF$_4^-$ salt was prepared by addition of a THF solution of NOBF$_4$ to a benzene solution of [RhCl(CO)(P-*i*-Pr$_3$)$_2$], with stirring for 10 min. The orange precipitate was recrystallized from CH$_2$Cl$_2$/ethanol (yield 73%). Infrared ν(CO) 2060 cm^{-1}; ν(NO) 1720 cm^{-1} (Nujol). Anal. Calcd for RhC$_{19}$H$_{42}$F$_4$P$_2$O$_2$BN: C, 37.8; H, 7.6; N, 2.3; Cl, 5.9. Found: C, 37.9; H, 7.1; N, 2.1; Cl, 6.2.

Bis(triisopropylphosphine)chloro[(^{15}N)nitro][(^{15}N)nitrosyl]rhodium, [RhCl(^{15}NO$_2$)(^{15}NO)(P-*i*-Pr$_3$)$_2$] (10a). [RhCl(P-*i*-Pr$_3$)$_2$(SO$_2$)] (0.2 g) was suspended in hexane (15 mL) and stirred under an atmosphere of nitric oxide (99% enriched ^{15}NO) for 2 h. A green solid separated from the suspension and was recrystallized from dichloromethane–ethanol to give green crystals of [RhCl(^{15}NO$_2$)(^{15}NO)(P-*i*-Pr$_3$)$_2$] (**10a**) (yield 85%). Anal. Calcd for RhC$_{18}$H$_{42}$P$_2$N$_2$O$_3$Cl: C, 40.4; H, 7.9; N, 5.2; Cl, 6.6. Found: C, 40.3; H, 8.7; N, 4.4; Cl, 6.2. Infrared: ν(^{15}NO) 1654, 1630 cm^{-1} (cf. ν(NO) 1684, 1657 cm^{-1} (Nujol); 1692 cm^{-1} (CHCl$_3$)).

Bis(tricyclohexylphosphine)chloro[(^{15}N)nitro][(^{15}N)nitrosyl]rhodium (10b), [RhCl(^{15}NO$_2$)(^{15}NO)(PCy$_3$)$_2$], was prepared in a similar fashion. Infrared: ν(^{15}NO) 1652, 1626 cm^{-1}.

Bis(triphenylphosphine)chloro[(^{15}N)nitro][(^{15}N)nitrosyl]rhodium (10c), [RhCl(^{15}NO$_2$)(^{15}NO)(PPh$_3$)$_2$], was prepared in a similar fashion from [RhCl(PPh$_3$)$_3$] as described by Hughes.[21] Infrared: ν(^{15}NO) 1630, 1595 cm^{-1}; ν(^{15}NO$_2$) 1388, 1295 cm^{-1}.

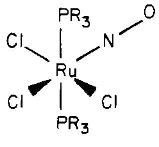
Bis(triphenylphosphine)((^{15}N)hyponitrito-*O*,*O*′)platinum(II) (11), [Pt(^{15}N$_2$O$_2$) (PPh$_3$)$_2$], was synthesized from Pt(PPh$_3$)$_3$ and ^{15}NO gas (99% enriched) according to the method suggested by Robinson.[22] Infrared: ν(^{15}N$_2$O$_2$) 1261, 1216, 1041 cm^{-1} (Nujol).

X-ray Crystallographic Analysis of [RhCl(NO$_2$)(NO)(PCy$_3$)$_2$]. The crystallographic analysis of [RhCl(NO$_2$)(NO)(PCy$_3$)$_2$] was hampered by crystallographic disorder of the NO$_2$ and Cl ligands and the bent nitrosyl ligand. Attempts to resolve the disorder by collecting data at low temperatures (200 K) failed to improve the situation markedly. The full details of the crystallographic analysis will be published elsewhere.[23] The relevant crystal data are summarized briefly below.

A single crystal of [RhCl(NO$_2$)(NO)(PCy$_3$)$_2$] of dimensions 0.1 × 0.2 × 0.05 mm was used: triclinic, space group $P1$-$C_i^{\prime}$ (No. 2), $a = 10.386$ (6) Å, $b = 10.710$ (9) Å, $c = 18.093$ (13) Å, $\alpha = 100.71$ (6)°, $\beta = 98.61$ (5)°, $\gamma = 96.17$ (6)°, $V = 1935$ (2) Å^3. Data were collected at 200 K; 7442 reflections having $3 \geq 2\theta \geq 55°$ were collected on a computer-controlled four-circle Nicolet diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) and 1.10° wide ω scans. The structure was solved by heavy-atom techniques, and the resulting non-hydrogen atom positions were refined anisotropically to convergence ($R = 0.060$ and $R_w = 0.067$) for 4204 independent reflections having $I > 3\sigma(I)$. The structure has a square-pyramidal coordination about the rhodium atom similar to that reported for [RhCl$_2$(NO)(PPh$_3$)$_2$], but the severe disorder of the bent apical NO ligand and between the axial NO$_2$ and Cl ligands limited the usefulness and reliability of the structure.

Results and Discussion

Linear Nitrosyl Ligands. Table I gives our ^{15}N measurements for linear nitrosyl ligands in complexes of ruthenium and rhodium, with ^{14}N and ^{15}N literature values, and NO stretching frequencies for comparison. The ^{15}N shift of −30.9 ppm (relative to neat liquid nitromethane, positive downfield) observed for [RuCl$_3$(NO)(PMePh$_2$)$_2$] (**6**) closely resembles those observed in ^{14}N resonance for other {M(NO)}^{6} octahedral ruthenium complexes.[11-13,15] The ^{15}N resonance is a triplet with $^2J_{\mathrm{P}^{15}\mathrm{N}} = 3.8$ Hz, of a magnitude appropriate to cis-nitrosyl–phosphine coupling,[24] supporting the structure that was considered likely,[25] with the nitrosyl trans to a chloro ligand.



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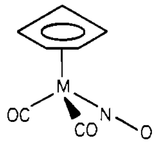

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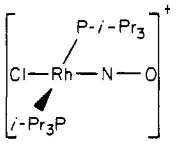

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No nitrogen shifts have hitherto been reported for rhodium nitrosyl complexes. The ^{14}N shifts of linear nitrosyl ligands in tetrahedral and octahedral complexes of iron, cobalt, ruthenium, and osmium fall in the range −75 to +60 ppm,[11-15] as do the ^{15}N shifts of linear nitrosyl in mononitrosyl "piano-stool" derivatives of chromium, molybdenum, and tungsten (**7**) (for which the ^{1}H, ^{13}C, and ^{15}N NMR spectra showed the structure in solution to be the same as in the crystal).[16] Also within this range is the ^{15}N resonance of the planar complex ion [RhCl(NO)(P-*i*-Pr$_3$)$_2$]$^+$ (**8**) (Table I). The putative free ligand NO$^+$ resonates near −5 ppm,[26] so the coordination shifts of the linear nitrosyls amount to a few tens of ppm. These are comparable with coordination shifts observed for metal carbonyls in ^{13}C resonance, given that ranges of nitrogen shifts are normally larger than (often double) those of carbon shifts in isoelectronic groups.[9] The coupling constant $^1J_{\mathrm{Rh}^{15}\mathrm{N}} = 58$ Hz is larger than expected from the comparison with $^1J_{\mathrm{Rh}^{13}\mathrm{C}}$ values (ca. 70 Hz) for comparable carbonyl compounds,[26] if we allow for the ratio (0.4) of the magnetogyric ratios of ^{15}N and ^{13}C.

Table I shows also that nitrogen in dinitrosyl piano-stool complexes [M(η^5-C$_5$H$_5$)Cl(NO)$_2$] of chromium, molybdenum, or tungsten is deshielded by 135–160 ppm as compared with that in the mononitrosyls (**7**). This deshielding finds no parallel in the ^{13}C resonance of the carbonyl ligand: thus, ^{13}CO in the dicarbonyl nitrosyl complex [Mo(η^5-C$_5$H$_5$)(CO)$_2$(NO)] is more shielded (by 18 ppm) than in the monocarbonyl complex [Mo(η^5-C$_5$H$_5$)(CO)(NO)(PPh$_3$)],[16] and ^{13}CO in [Mo(CO)$_6$] is more shielded still (by 25 ppm),[27] with trans influences coming into play. The magnitude of the ^{15}N deshielding suggests electronic interaction between the adjacent linear nitrosyls. The deshielding of nitrogen in the dinitrosyls suggests that there is orbital interaction between adjacent linear nitrosyl groups, which reduces the HOMO–LUMO gap for the circulation of charge close to nitrogen in the magnetic field.[9] The presence of a stable LUMO in dinitrosyls was recently shown by the synthesis of the 19-electron complexes [W(η^5-C$_5$H$_5$)(NO)$_2$(PR$_3$)][28a] and suggested also by the PE spectra of [M(η^5-C$_5$H$_5$)(NO)$_2$X] compounds. Theoretical and structural studies on dinitrosyl complexes have confirmed that the interaction between adjacent nitrosyl ligands is larger than that between adjacent carbonyls and is often accompanied by deviations from linearity.

Bent Nitrosyl Ligands. Table II gives ^{15}N NMR spectroscopic results (and IR stretching frequencies for comparison) for four rhodium complexes that have square-pyramidal coordination in the solid state with a bent apical nitrosyl ligand and trans phosphine ligands in the plane. The [RhCl(CO)(^{15}NO)(P-*i*-Pr$_3$)$_2$]$^+$ cation (**9**) was synthesized by the following independent synthetic routes:

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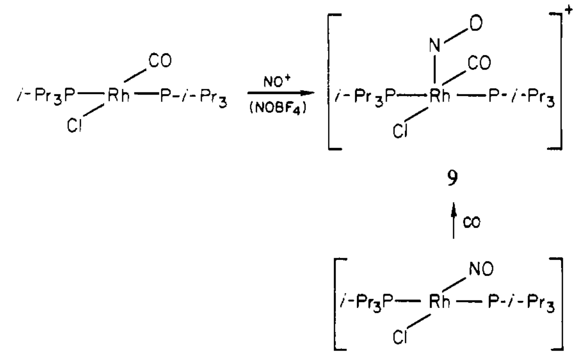
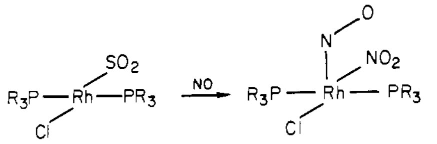


The structure of **9** is supported by the analogy with $[IrCl(CO)(NO)(PPh_3)_2]^+$,[1] and the close similarity in NO stretching frequencies; $\nu(NO) = 1687\ cm^{-1}$ in the rhodium and $1680\ cm^{-1}$ in the iridium complex. The triisopropylphosphine complexes were chosen for the ^{15}N NMR study because of their higher solubilities in organic solvents.

The ^{15}N NMR spectrum of **9** shows only a single, rather low-field resonance at 368.2 ppm, clearly assignable to the bent nitrosyl ligand. It is a doublet with a rather small coupling constant $J_{Rh^{15}N} = 4.6$ Hz, in accord with the general observation that coupling constants to nitrogen carrying a lone pair may be small, since the contributions to the Fermi contact term (which dominates the coupling constant) from the bonding and the nonbonding electrons are opposite in sign and partially cancel.[30] The spectrum of **9** and those of the compounds discussed below were run at low temperatures (−65 to −70 °C) but showed little changes from the spectra observed at room temperatures.

For the bent nitrosyl ligand, one can take the nitrogen shift in nitrosoalkanes RNO as a measure of the "free-ligand" resonance since the geometry at nitrogen is similar and the electronic interaction of the ligand and the alkyl group is small. Nitrosoalkanes such as *t*-BuNO have nitrogen resonances in the 560–600 ppm region[26] (cf. also 530 ppm for PhNO); thus, the coordination shifts are of the magnitude expected, since they tend to increase the more deshielded the ligating atom.

The related complexes $[RhCl(NO_2)(NO)(PR_3)_2]$ (PR_3 = PCy_3 or P-*i*-Pr_3) (**10**) were synthesized from the corresponding square-planar SO_2 complexes $[RhCl(SO_2)(PR_3)_2]$ and NO in the following manner:



10a, R = *i*-Pr
b, R = Cy

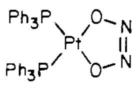
These complexes show two ν(NO) stretching vibrations at ca. 1683 and 1657 cm^{-1} in the solid state (a single broad band at ca. 1692 cm^{-1} in $CHCl_3$ solution) and no bands that could be unambiguously assigned to the nitro ligands, although the related complex $[RhCl(NO_2)(NO)(PPh_3)_2]$ has bands at 1657 and 1629 cm^{-1} (ν(NO)) and 1413 and 1312 cm^{-1} ($\nu(NO_2)$). Therefore, on the basis of the IR and analytical data it was difficult to distinguish the structre shown in **10** from the dinitrosyl structure $[RhCl(NO)_2(PR_3)_2]$ (R = Cy or *i*-Pr).

Single-crystal X-ray structural determinations of $[RhCl(NO_2)(NO)(PCy_3)_2]$ and $[RhCl(NO_2)(NO)(P\text{-}n\text{-}Bu_3)_2]$[23] have established that the complexes **10** do indeed have a square-pyramidal geometry about the metal atom, but severe crystallographic disorder of the NO and NO_2 groups hindered an unambiguous delineation of the structures of the complexes. The equatorial chloro and nitro ligands are disordered, and least-squares refinements failed to distinguish this possibility from a 4-fold disorder of an equatorial bent nitrosyl. In addition, the apical nitrosyl shows a 2-fold disorder similar to that observed previously for $[IrCl_2(NO)(PPh_3)_2]$[2] and $[Ir(NO)MeI(PPh_3)_2]$.[31]

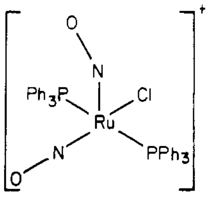
The ^{15}N NMR spectra of the compounds $[RhCl(NO)(NO_2)(PR_3)_2]$ (Table II) clearly demonstrate that the complexes are indeed nitrosyl–nitro complexes since they show a low-field resonance (453–516 ppm) that is assigned to the bent apical nitrosyl (see Table II), and no coupling was resolved (with the digital resolution 1.8 Hz). In addition, the compounds show a resonance in the range 44–78 ppm (doublets with $^1J_{Rh^{15}N}$ = 27 or 28 Hz) that can be attributed to the coordinated nitro ligand. The nitrogen shifts in the nitrite ion (230 ppm), or nitroalkanes such as nitromethane (with zero chemical shift), indicate the expected region for nitro ligands, in which our nitro ligand resonances are seen to fall (Table II). (A chemical shift has been reported for a nitro ligand, but the resonance was later found to be due to the nitrate anion.[32])

In view of our earlier discussion of a downfield shift of ca. 150 ppm in the nitrosyl resonance when there are two adjacent nitrosyls, it is interesting to note that the nitrogen in an apical nitrosyl group is deshielded by 100 ppm when there is an adjacent nitro group, as in the nitro–nitrosyl complexes of rhodium compared with *trans*-$[RhCl(CO)(^{15}NO)(P\text{-}i\text{-}Pr_3)_2]^+$ (Table II).

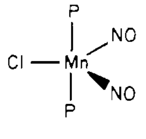
The Hyponitrito Ligand. The reaction of nitric oxide with $[Pt(PPh_3)_3]$ leads to the platinum(II) hyponitrito complex **11**,



11



12



$[MnCl(NO)_2\{P(OMe)_2Ph\}]$
13

which has a five-membered chelate ring.[33] The ^{15}N NMR spectrum of **11** shows a singlet with δ 34.9, which lies in the expected region, by comparison with that of the free hyponitrite ligand that has a nitrogen shift of ca. 83 ppm in aqueous alkaline solution.[34]

The observation of characteristic ^{15}N resonances and coupling constants for linear and bent nitrosyl ligands and nitrito and hyponitrito ligands suggests interesting possibilities for studying transformations of nitrosyl complexes, and such investigations are currently being pursued in our laboratories.

$[RuCl(NO)_2(PPh_3)_2]BF_4$. $[RuCl(NO)_2(PPh_3)_2]BF_4$ (**12**) represented the first example of an $[M(NO)_2]^8$ complex to be characterized in the solid state with both a linear and a bent nitrosyl ligand.[35] Quite fast interchange of the nitrosyl ligand positions by an intramolecular redox process was proposed by Collman[36] to account for the IR spectral properties of $[RuCl(^{15}NO)(NO)(PPh_3)_2]PF_6$. When $[RuCl(^{15}NO)(NO)(PPh_3)_2]PF_6$ was synthesized by adding a methanol solution of $NOPF_6$ to a solution of $[RuCl(^{15}NO)(PPh_3)_2]$, it was

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Table I. NMR and IR Measurements of Transition-Metal Complexes with Linear Nitrosyl Ligands

	solvent	$\delta(^{15}N)^{a,b}$	$\nu(^{14}NO)/cm^{-1}$	ref
nitrosonium ion				
$NO^+AsF_6^-$	anhyd HF	−7.5		*c*
$NO^+BF_4^-$	SO_2	−3.2		27
mononitrosyls				
six-coordinate $\{M(NO)\}^6$, octahedral				
$[RuCl_3(^{15}NO)(PPh_3)_2]$	CD_2Cl_2	−36.7		
$[RuCl_3(^{15}NO)(PMePh_2)_2]$ (6)	CD_2Cl_2	-30.9^d	1876^j	
$[RuCl_5(NO)]^{2-}$	aq	−48	1910^j	13
		−46		15
$[Ru(H_2O)_2(NO)(NO_3)]$	tbp	−48 $\delta(^{14}N)^e$		11
$[RuCl_3(H_2O)_2(NO)]$	aq	−41	1895, 1800^j	11
$[Ru(NH_3)_5(NO)]Cl_3$	aq	−29	1913^j	15
		−27		
four-coordinate $\{M(NO)\}^8$, square planar				
trans-$[RhCl(^{15}NO)(P\text{-}i\text{-}Pr_3)_2](ClO_4)$ (8)	CD_2Cl_2	24.0^f	1880^j	
piano-stool $\{M(NO)\}^6$				
$[Cr(\eta^5\text{-}C_5H_5)(CO)_2(NO)]$ (7a)	$CHCl_3$	49.0	1680^k	16
$[Mo(\eta^5\text{-}C_5H_5)(CO)_2(NO)]$	$CHCl_3$	37.6	1663^k	16
$[Mo(\eta^5\text{-}C_5H_5)(CO)(PPh_3)(NO)]$	$CHCl_3$	35.4	1607^k	16
$[W(\eta^5\text{-}C_5H_5)(CO)_2(NO)]$	$CHCl_3$	16.5	1655^k	16
dinitrosyl, $\{M(NO)_2\}^8$				
$[RuCl(^{15}NO)_2(PPh_3)_2](BF_4)$ (12)	$(CD_3)_2CO$	$131.5^{g,h}$	1845, 1687;^{j} 1828 vs, 1778 s, 1739 sh, 1722 s ^{l}	
		134.9^i		
	CD_3OD	128.9^m		
piano-stool $\{M(NO)\}^6$				
$[Cr(\eta^5\text{-}C_5H_5)Cl(NO)_2]$	$CHCl_3$	184.6	1816, 1711^k	16
$[Mo(\eta^5\text{-}C_5H_5)Cl(NO)_2]$	$CHCl_3$	185.4	1759, 1655^k	16
$[W(\eta^5\text{-}C_5H_5)Cl(NO)_2]$	$CHCl_3$	172.9	1733, 1650^k	16

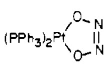
[a] In ppm relative to neat liquid nitromethane; low-field positive; measured at 25 °C unless otherwise specified. [b] $\delta(^{31}P)$ values relative to 85% H_3PO_4(aq). [c] Mason, J.; Christe, K. O. *Inorg. Chem.* **1983**, *22*, 1849. [d] Triplet with $^2J_{P^{15}N} = 3.8\ (1.5)$ Hz; $\delta(^{31}P)^b$ 7.3. [e] Relative to neat liquid nitromethane; low-field positive. The uncertainty of the ^{14}N measurements in the metal complexes[11-15] is ca. 10 ppm, because of the breadth of the lines (typically 500 Hz at half-height) and referencing uncertainties. [f] Doublet, $J_{Rh^{15}N} = 52\ (2)$ Hz; $\delta(^{31}P)^b$ 58.1. [g] Measured at 30 °C. [h] $\delta(^{31}P)^b$ 31.5; $W_{1/2} = 35$ Hz. [i] Measured at −90 °C; $\delta(^{31}P)^b$ 27.6. [j] Solid, Nujol mull. [k] CH_2Cl_2 solution. [l] Methanol solution. [m] Measured at −50 °C.

Table II. ^{15}N NMR Measurements of Bent Nitrosyl Ligands and Nitro and Hyponitrito Ligands in Complexes of Rhodium and Platinum in CD_2Cl_2 Solution

Square-Pyramidal $\{M(NO)\}^8$

	NO		NO$_2$		
	$\delta(^{15}N)^b$	$^1J_{Rh^{15}N}$/Hz	$\delta(^{15}N)^b$	$^1J_{Rh^{15}N}$/Hz	$\nu(^{14}NO)^a/cm^{-1}$
trans-$[RhCl(CO)(^{15}NO)(P\text{-}i\text{-}Pr_3)_2]ClO_4$ (9)	368.2	4.6 (0.8)	...	...	1712
trans-$[RhCl(^{15}NO)(^{15}NO_2)(PCy_3)_2]$ (10b)	466.1		45.8	28	1684, 1654
	452.7^c		47.1^c	27	
trans-$[RhCl(^{15}NO)(^{15}NO_2)(P\text{-}i\text{-}Pr_3)_2]$ (10a)	467.6		43.6	27	1684, 1657
	454.6^d		45.6^d	27	
trans-$[RhCl(^{15}NO)(^{15}NO_2)(PPh_3)_2]$ (10c)	481.5		43.6	29	1657, 1629
cf. $Na^{15}NO_2$(aq)	...		230	...	

Square-Planar Hyponitrito

	M(O$_2$N$_2$)		
	$\delta(^{15}N)^b$	$^1J_{Pt^{15}N}$/Hz	$\nu(^{14}NO)^a/cm^{-1}$
 (11)	34.9	36.2	1289, 1240, 1216, 1065
cf. $^-ONNO^-,2Na^+$(aq)	83		

[a] Nujol mull. [b] Relative to neat liquid nitromethane; low-field positive; normally measured at 25 °C. [c] Measured at −70 °C. [d] Measured at −60 °C.

found that "during the 15 min required for isolation from methanol, four bands appear...indicating equilibration of the two forms in solution". A Berry pseudorotation process involving a triagonal-bipyramidal intermediate was proposed by Collman et al.[36] and also by Pierpont and Eisenberg[35] to account for the equal distribution of ^{15}NO between apical and equatorial sites in **12**. A five-coordinate trigonal-bipyramidal $\{M(NO)_2\}^8$ structure (**13**) with approximately linear (M–N–O ~ 164°) nitrosyls was subsequently established for the complex $[MnCl(NO)_2\{P(OMe)_2Ph\}_2]$.[37]

If structure **12** were maintained in solution, the ^{15}N spectrum of $[RuCl(^{15}NO)_2(PPh_3)_2]^+$ would be expected to give a resonance in the neighborhood of ±50 ppm for the linear

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[37] Laing, M.; Reimann, R. H.; Singleton, E. *Inorg. Chem.* **1979**, *18*, 1648.

nitrosyl and a resonance at low field in the region of 400–500 ppm as observed for the square-pyramidal complexes of rhodium with bent apical nitrosyl ligands. Instead, the ^{15}N NMR spectrum of **12** in $(CD_3)_2CO$ shows a single resonance at 131.5 ppm at 303 K and 134.9 ppm at 183 K. The line width at half-height shows little broadening as the temperature is lowered and is 8.1 Hz at 303 K and 9.3 Hz at 183 K. The $^{31}P\{^1H\}$ NMR spectrum shows only a slightly broadened singlet in the temperature range 303–183 K (Table I). The complex does not exchange with free NO^+ at the lower temperatures but does at room temperature.

To throw further light on the structure, we measured the infrared spectra of the unenriched complex in methanolic solution. The solid gives two ^{14}NO bands in Nujol at 1860 and 1685 cm^{-1}, consistent with the presence of one linear and one bent nitrosyl ligand, as shown by X-ray crystallography. In methanolic solution, however, the nitrosyl bands show major frequency shifts and increase in number: strong absorptions are observed at 1828, 1778, and 1722 cm^{-1}, with a shoulder at 1739 cm^{-1}. After evaporation of the solvent in vacuo, the solid gave the same IR spectrum in Nujol as before, showing that no major decomposition had occurred in solution. Corresponding results were obtained with the ^{15}N-semienriched compound.

Thus, the vibrational spectra suggest the formation of two isomeric structures in solution, and it is probable that one has a trigonal-bipyramidal geometry with equivalent nitrosyl ligands similar to that reported for $[MnCl(NO)_2\{P(OMe)_2Ph\}_2]$[37] and the second a square-pyramidal structure (**12**) as in the solid[35] (possibly with coordination of the solvent). The evidence suggests that these isomers interconvert rapidly on the NMR time scale by an intramolecular process, to give a single ^{15}N resonance. Further evidence for this proposal has been obtained by studies on a 50% ^{15}N-enriched sample of $[RuCl(NO)_2(PPh_3)_2]BF_4$ for which an equlibrium isotope effect has been observed. The ^{15}N NMR spectrum of the complex is being studied in the solid state, and these results will be discussed in detail in a later paper.[38]

Acknowledgment. We thank the Science and Engineering Research Council for the provision of high-field NMR facilities, Drs. Oliver Howarth and Eirian Curzon for their help with the 400-MHz spectra run at Warwick University, and Dr. John Jeffrey of Bristol University for running the FT IR spectra.

Registry No. **6** (PR_3 = $PMePh_2$), 86501-86-2; **6** (PR_3 = PPh_3), 86501-87-3; **8a**, 86501-85-1; **8b**, 87306-13-6; **9**, 86501-83-9; **10a**, 86501-80-6; **10b**, 86501-81-7; **10c**, 86501-79-3; **11**, 87306-14-7; **12**, 87306-12-5; $[RhCl(SO_2)(P\text{-}i\text{-}Pr_3)_2]$, 87318-56-7.

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(38) A preliminary communication of this work has now appeared: Bell, L. K.; Mingos, D. M. P.; Tew, D. G.; Larkworthy, L. C.; Sandell, B.; Povey, D. C.; Mason, J. *J. Chem. Soc., Chem. Commun.* **1983**, 125.

Contribution from the Department of Chemistry,
North Dakota State University, Fargo, North Dakota 58105

Mass Spectra of Rhenium(III) and Ruthenium(III) Complexes of 2,4-Pentanedione, 1,1,1-Trifluoro-2,4-pentanedione, and 1,1,1,5,5,5-Hexafluoro-2,4-pentanedione

MELVIN L. MORRIS and R. D. KOOB*

Received December 15, 1982

The mass spectra of the title compounds have been obtained, and the results are interpreted in terms of formalisms developed from investigations of other 2,4-pentanedionato–metal complexes. The chelates of Ru(III) and Rh(III) show some unusual properties. The mass spectra of the complexes of all three ligands with ruthenium show little tendency for internal redox reactions, resulting in oxidation states for the metal other than +3. Rhodium, on the other hand, when complexed with hfa, exhibits a number of peaks that can be assigned to lower oxidation states, +2 and +1, of the metal including a peak corresponding to the $Rh(I)^+$ ion. Complexes of rhodium with tfa and acac are more similar to their ruthenium counterparts and demonstrate considerably less tendency toward reduced oxidation states. For both metals, loss of internal portions of the ligand, e.g. CO and CO_2, is observed. Apparently, migration of end groups such as methyl to the metal plays a role by forming either intermediates or transition states in these reactions. Bonds between small ligand fragments and Rh appear to be considerably more labile than comparable bonds to Ru.

Introduction

While the mass spectra of numerous complexes of transition metals with β-diketones have been published,[1] rhodium and ruthenium have been overlooked. Appearance potential data[2] and chemical ionization mass spectra[3] have been presented, but not a discussion of the ion dissociation reactions of the molecular ions. This is somewhat surprising in view of the tremendous interest in these metals as catalysts.[4] Investigations of other metal complexes have demonstrated that the mass spectrometer is a convenient apparatus to use in the examination of a number of properties of metal complexes. Gas-phase ion chemistry of these compounds has remarkable similarities with solution chemistry. Parallels have been shown with respect to redox reactions,[1] hard–soft acid–base considerations,[5] and most recently, olefin complex-forming reactions.[6] We have examined the mass spectra of the title compounds and present our findings here.

Experimental Section

Mass spectra were obtained on a Varian MAT CH-5DF reversed-geometry double-focusing mass spectrometer. An electron-impact source was operated at 70-eV ionizing voltage and maintained at 250 °C. Pressure in the source never ex-

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