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The Preparation and Structure of Ruthenium and Osmium Nitrosyl Carbonyl Clusters Containing Double-Nitrosyl Bridges[1]

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The complexes $M_3(CO)_{10}(NO)_2$ (M = Ru, Os) have been prepared by the direct reaction of the carbonyls $M_3(CO)_{12}$ with nitric oxide. The crystal and molecular structure of di-μ-nitrosyl-decacarbonyltriruthenium has been determined using three-dimensional X-ray data collected by counter methods. The crystals have monoclinic symmetry, space group $P2_1/n$ with four molecules in a unit cell of dimensions $a = 7.639$, $b = 9.231$, $c = 26.293$ Å, and $\gamma = 108.45°$. Observed and calculated densities are 2.43 ± 0.01 g cm^{-3}. Least-squares refinement of the structure has led to a final value of the conventional R factor (on F) of 0.028 for 1237 reflections having $F^2 > 3\sigma_{F^2}$. The structure consists of well-separated monomeric units each containing three ruthenium atoms located at the vertices of an isosceles triangle. Two sides of the triangle are nearly equal in length (2.866 ± 0.005 Å) and represent normal Ru–Ru single bonds. The third side (3.15 Å) is lengthened by the presence of two bridging nitrosyl groups (N–O = 1.22 ± 0.02 Å). The structure has approximate C_{2v} symmetry and resembles that of $Fe_3(CO)_{12}$, with the double-nitrosyl bridge in place of the double-carbonyl bridge present in the latter compound. Infrared results show that both the ruthenium and osmium complexes have the same structure, in solution as well as in the solid state. Mass spectra are reported and discussed.

A large number of metal carbonyl cluster compounds have been prepared and their structures determined.[3] In addition to their intrinsic structural interest, they offer the possibility of multicenter catalysis. However, most clusters lack adequate substitutional lability except under drastic conditions where the integrity of the cluster is in doubt.[4] The observations that the mononuclear nitrosyl carbonyls isoelectronic with nickel carbonyl display a relative preference for an associative mechanism in exchange and substitution reactions[5] and that several mononuclear metal nitrosyls have been successfully employed as catalysts[6–8] suggested that the synthesis and investigation of nitrosyl carbonyl clusters would be desirable. Furthermore, the recent interest in the geometry of the coordinated nitrosyl ligand[9] prompted the extension of structural studies to multinuclear species.

The ready availability of $Ru_3(CO)_{12}$ and the well-known affinity of ruthenium for nitrosyl ligands made that metal an obvious synthetic choice. Earlier products reported from the reaction between $Ru_3(CO)_{12}$ and nitric oxide seem to have been largely the result of impurities in the nitric oxide.[1] $Ru_3(CO)_{10}(NO)_2$ is in fact readily formed from $Ru_3(CO)_{12}$ according to the reaction scheme

$$Ru_3(CO)_{12} \xrightarrow[C_6H_6]{\overset{NO}{80°}} \underset{\textbf{1}}{Ru_3(CO)_{10}(NO)_2} \xrightarrow[C_6H_6]{\overset{NO}{80°}} \underset{\textbf{2}}{[Ru(CO)_{1.3}(NO_2)_{1.6}]_n}$$

Reaction of **1** with nitric oxide under the conditions required for its formation leads to the production of **2**, a brown, insoluble, apparently polymeric material[10] which resisted all attempts (such as prolonged treatment with triphenylphosphine in boiling benzene) to cleave it into identifiable subunits. Hence the formation and destruction of $Ru_3(CO)_{10}(NO)_2$ are consecutive and competitive reactions, and maximum yields of **1** are obtained by stopping the reaction short of the disappearance of starting material and chromatographic separation of it from the product (see Experimental Section).

Chromatography of a large reaction mixture afforded a third product isolated in trace amounts (<0.5%) and characterized by elemental analysis and low-resolution mass spectrometry as $Ru_4C_{12}N_2O_{13}$ (**3**). From its empirical formula it seemed possible that the compound might be an N_2O complex: $Ru_4(CO)_{12}(N_2O)$. However, neither $Ru_3(CO)_{12}$ nor $Ru_3(CO)_{10}(NO)_2$ gave **3** on treatment with N_2O. Furthermore, the infrared band observed at 1510 cm^{-1} in the spectrum of **3** suggested a bridging nitrosyl ligand (see below) rather than a coordinated N_2O.[11]

Although **1** is only very slightly air sensitive and can be stored for many months at room temperature, it decomposes rapidly under nitrogen in boiling benzene. Thus it seemed desirable to prepare the analogous

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[1] Preliminary communication of part of this work: J. Norton, D. Valentine, Jr., and J. P. Collman, *J. Amer. Chem. Soc.*, **91**, 7537 (1969).

[2] (a) NSF predoctoral fellow, 1967–1971. (b) Stanford University. (c) On leave from Centro Chimica Composti Organometallici, CNR, Bologna, Italy. (d) University of Canterbury.

[3] For recent reviews see (a) P. Chini, *Inorg. Chim. Acta Rev.*, **2**, 31 (1968); (b) B. R. Penfold, *Perspect. Struct. Chem.*, **2**, 71 (1968).

[4] $Ru_3(CO)_{12}$ itself has been used as a catalyst recently by (a) F. L'Eplattenier, P. Matthys, and F. Calderazzo, *Inorg. Chem.*, **9**, 342 (1970), in the reduction of nitrobenzene to aniline, and by (b) P. Pino, G. Braca, F. Piacenti, G. Sbrana, M. Bianchi, and E. Benedetti, "First International Symposium: New Aspects of the Chemistry of Metal Carbonyls and Their Derivatives," Venice, 1968, p E2, to catalyze the hydroformylation of propylene and formation of hydroquinone from acetylenes. Both groups of workers employed temperatures of at least 150° and H_2 and CO pressures above 75 atm; the evidence presented suggests that under these conditions some monomeric species are present.

[5] (a) J. P. Day, D. Diamente, and F. Basolo, *Inorg. Chim. Acta*, **3**, 363 (1969); (b) F. Basolo, *Chem. Brit.*, **5**, 505 (1969). This preference may reveal itself in a decrease in the first-order rate constant as well as an increase in the second-order one.

[6] J. P. Candlin and W. H. Janes, *J. Chem. Soc. C*, 1856 (1968).

[7] E. A. Zuech, *Chem. Commun.*, 1182 (1968).

[8] J. P. Collman, N. W. Hoffman, and D. E. Morris, *J. Amer. Chem. Soc.*, **91**, 5659 (1969).

[9] See especially D. J. Hodgson and J. A. Ibers, *Inorg. Chem.*, **7**, 2345 (1968); D. A. Snyder and D. L. Weaver, *ibid.*, **9**, 2760 (1970).

[10] Although the elemental analysis and infrared spectrum are quite reproducible, no mononuclear monomeric unit with integral numbers of ligands is consistent with these analyses. The use of "NO_2" in the approximate empirical formula given is not meant to imply any particular mode of coordination; indeed, the infrared spectrum (see Experimental Section) suggests a complex mixture of various types of nitro ligands. A similar but cleaner reaction has been observed with nickel carbonyl: $Ni(CO)_4 + 4NO \rightarrow Ni(NO_2)(NO) + 4CO + N_2O$ (R. D. Feltham and J. T. Carriel, *Inorg. Chem.*, **3**, 121 (1964)).

[11] Coordinated N_2O has recently been reported to have infrared absorptions at 2110 and 1160 cm^{-1}: J. N. Armor and H. Taube, *Chem. Commun.*, 287 (1971). A referee has offered the plausible but not compelling suggestion that **3** might be $Ru_4(CO)_{11}(NO)(NCO)$ with the N-donor ligands bridging.

osmium compound in the hope of producing a nitrosyl carbonyl cluster of greater thermal stability.

$Os_3(CO)_{12}$ was prepared by reduction of $OsCl_3$ with CO and Zn in ethanol in preference to the known methods which employ OsO_4[12,13] on account of the convenience of the former reagent. The direct reaction of the carbonyl and nitric oxide was much slower than in the ruthenium case: the use of 60 psi of NO and 100° for 24 hr was necessary to effect a 13% conversion of $Os_3(CO)_{12}$ to $Os_3(CO)_{10}(NO)_2$ (**4**).

The compositions of both **1** and **4** were confirmed by low-resolution mass spectrometry. Their infrared spectra (see Experimental Section) contained nitrosyl bands around 1500 cm^{-1}, suggesting bridging nitrosyl ligands by the reasoning applied by King to several nitrosyl chromium and manganese compounds.[14] Although a badly disordered structure of one of these ($Cp_3Mn_3(NO)_4$) has been reported,[15] there has been no quantitative description of the geometry of a nitrosyl bridge.[15a] In order to discover the precise placement of the nitrosyl ligands as well as to provide such a quantitative description, we undertook an X-ray structural analysis of $Ru_3(CO)_{10}(NO)_2$.

Experimental Section

Infrared spectra were obtained on Perkin-Elmer Model 457 and 421 spectrophotometers. Mass spectra were recorded using Atlas CH4 and AEI MS9 spectrometers. Microanalyses were performed by the microanalytical laboratory of the Stanford Chemistry Department.

Materials.—$Ru_3(CO)_{12}$ was either purchased from Strem Chemicals Inc. or made by the method of Stone.[16] Commercial osmium trichloride (about 62% osmium) was purchased from both Englehard Industries and Matthey Bishop Inc. Nitric oxide (Matheson, 98.5%) was purified by passage over silica gel at −78° to remove nitrogen dioxide and nitrous oxide.[17] Benzene was distilled from sodium–potassium alloy under nitrogen.

Di-μ-nitrosyl-decacarbonyltriruthenium, $Ru_3(CO)_{10}(NO)_2$ (1).—$Ru_3(CO)_{12}$ (498 mg) was dissolved in 100 ml of boiling benzene with a flat glass frit slowly bubbling nitrogen through the solution. As soon as the system was thoroughly purged and all the carbonyl had gone into solution, the nitrogen flow was replaced by a stream of NO. Rapid NO flow (about 75 cm^3/min) was continued for 17 min, by which time the reaction mixture had become very dark. Nitrogen was then readmitted and the solution cooled. (After all NO has been removed from the system subsequent operations can be carried out in air as the solutions are fairly stable; however, nitrogen was admitted to refill evacuated vessels, the chromatography solvent was deaerated with nitrogen, the column was flushed with it before use, and filtration products were dried by blowing a stream of dry nitrogen through them.)

The brown polymeric by-product **2** was filtered off. *Anal.* Calcd for $Ru(CO)_{1.3}(NO_2)_{1.6}$: C, 7.40; N, 10.61. Found: C, 7.35; N, 10.64. Infrared spectrum (KBr) (cm^{-1}): 2080 (s), 2020 (s), 1870 (s), 1475 (w, vb), 1380 (m, sp), 1320 (w), 1270 (w), 1080 (w, vb), 825 (w). The filtrate was reduced in volume on a rotary evaporator (bath temperature not above 40°), heptane was added, and the mixture was placed in the freezer for crystallization. Filtration yielded 262 mg of combined product and starting material. The mixture was dissolved in 3:1 hexane–CCl_4 and chromatographed on silica gel; the green band containing the product (R_f about 0.20) was easily distinguished from the orange band containing $Ru_3(CO)_{12}$, which moved quite rapidly. After addition of heptane to the green solution, concentration, and cooling, 144 mg of $Ru_3(CO)_{10}(NO)_2$ (29% yield) crystallized. *Anal.* Calcd for $Ru_3C_{10}N_2O_{12}$: C, 18.67; H, 0.0; N, 4.35; mol wt 643. Found: C, 18.87; H, 0.0; N, 4.26; mol wt 630 (osmometric in benzene), 643 (mass spectrometric). Infrared spectra showed ν_{CO} (cyclohexane) at 2110 (w), 2077 (s), 2068 (s), 2061 (sh), 2038 (s), 2030 (s), 2026 (sh), 2015 (w), and 2000 (m) cm^{-1}, ν_{NO} (KBr) at 1517 (m) and 1500 (s) cm^{-1}, and a strong band (KBr) at 723 cm^{-1}.

$Ru_4C_{12}N_2O_{13}$ (3).—During chromatography of a portion of the material resulting from running the preceding reaction on a 2-g scale, a pale yellow band appeared between the orange one of $Ru_3(CO)_{12}$ and the green one of $Ru_3(CO)_{10}(NO)_2$. Careful removal of solvent yielded pale lemon yellow crystals remarkably soluble in pentane and air sensitive in solution. After being placed in the freezer overnight, the pentane solution yielded 2.41 mg of recrystallized $Ru_4C_{12}N_2O_{13}$ (**3**). *Anal.* Calcd for $Ru_4C_{12}N_2O_{13}$: C, 18.37; H, 0.0; N, 3.57; Ru, 51.5; mol wt 784. Found: C, 18.70; H, 0.0; N, 3.48; Ru, 49.7 (done by weighing reduced combustion residue; some loss by sublimation during combustion); mol wt 784 (mass spectrometric). Infrared spectra showed ν_{CO} (hexane) at 2074 (s), 2067 (s), 2055 (m), 2035 (s), 2027 (m), and 1999 (m) cm^{-1} and ν_{NO} (KBr) at 1510 (b) cm^{-1}.

Preparation of 2 Directly from $Ru_3(CO)_{10}(NO)_2$.—$Ru_3(CO)_{10}(NO)_2$ (15 mg) was dissolved in 25 ml of benzene purged by a stream of nitrogen. The nitrogen was replaced by nitric oxide and, as soon as the system was filled with that gas, the reaction was lowered into a 100° oil bath and refluxed for 10 min. After cooling and flushing with nitrogen, the solution was filtered and the brown solid obtained was shown by comparison of its infrared spectrum to be identical with **2** obtained from the reaction of $Ru_3(CO)_{12}$ with nitric oxide.

Dodecacarbonyltriosmium, $Os_3(CO)_{12}$.—Commercial osmium trichloride (3 g, 61.89% Os), 75 ml of absolute ethanol, and 1.3 g of mossy zinc were placed in a glass liner in a 300-cm^3 Magne-Drive autoclave. The apparatus was filled with 1200 psi of carbon monoxide and then stirred for 8.5 hr at 135°. After cooling and venting, the reaction mixture was removed, filtered, and washed with ethanol, and $Os_3(CO)_{12}$ (2.02 g, 69%) was then extracted from the residue with dichloromethane in a Soxhlet apparatus.

Di-μ-nitrosyl-decacarbonyltriosmium, $Os_3(CO)_{10}(NO)_2$ (4).—Dodecacarbonyltriosmium (150 mg) and 10 ml of benzene were placed in a Fischer-Porter pressure vessel which was then thoroughly purged with argon and charged with 60 psi of nitric oxide. The sealed reaction mixture was then heated to 100° for 24 hr with magnetic stirring. Upon cooling, a solid (largely unreacted $Os_3(CO)_{12}$) precipitated. After flushing with argon, the mixture was filtered to give a pale green solution. Addition of heptane and removal of benzene on the rotary evaporator gave 20 mg of light green crystals of $Os_3(CO)_{10}(NO)_2$. Purification for analysis and spectroscopy was effected by chromatography on silica gel under nitrogen with 3:1 hexane–CCl_4 as described above. *Anal.* Calcd for $Os_3C_{10}N_2O_{12}$: C, 13.19; H, 0.0; N, 3.07; mol wt 911. Found: C, 13.11; H, 0.2; N, 2.83; mol wt 911 (mass spectrometric). Infrared spectra showed ν_{CO} (tetrachloroethylene) at 2108 (w), 2068 (s), 2063 (s), 2054 (sh), 2025 (s), 2017 (w), 2008 (s), and 1996 (m) cm^{-1}, ν_{NO} (KBr) at 1503 (m) and 1484 (s) cm^{-1}, and a strong band (KBr) at 739 cm^{-1}.

Collection and Reduction of the Intensity Data

Pale green, needle-shaped crystals of $Ru_3(CO)_{10}(NO)_2$, mol wt 643, were obtained from both benzene–heptane and dichloromethane–hexane. Several of these, from three different batches, were examined by precession photography and found to be twinned or polycrystalline. The twinned crystals gave photographs consistent with the monoclinic space groups $P2_1$ or $P2_1/m$ whereas a genuine single crystal (obtained from dichloromethane–hexane) showed symmetry and systematic absences uniquely consistent with space group no. 14[18] $P2_1/b$. Throughout this analysis the first setting of this space group (*c* axis unique) was

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[12] C. W. Bradford and R. S. Nyholm, *Chem. Commun.*, 384 (1967).

[13] B. F. G. Johnson, J. Lewis, and P. A. Kilty, *J. Chem. Soc. A*, 2859 (1968).

[14] R. B. King and M. B. Bisnette, *Inorg. Chem.*, **3**, 791 (1964); R. B. King, *ibid.*, **6**, 30 (1967).

[15] R. C. Elder, F. A. Cotton, and R. A. Schunn, *J. Amer. Chem. Soc.*, **89**, 3645 (1967).

[15a] NOTE ADDED IN PROOF.—Since the writing of this paper X-ray structural analyses of two other compounds containing nitrosyl bridges have been reported: one [L. Y. Y. Chan and F. W. Einstein, *Acta Crystallogr.*, **26B**, 1899 (1970)] containing a nitrosyl bridge disordered with an amido bridge, and another [J. L. Calderon, F. A. Cotton; B. G. DeBoer, and N. Martinez, *Chem. Commun.*, 1476 (1971)] containing a double-nitrosyl bridge with a type of asymmetry unlike that sometimes observed in double-carbonyl bridges.

[16] M. I. Bruce and F. G. A. Stone, *J. Chem. Soc. A*, 1238 (1967).

[17] F. E. Hughes, *J. Chem. Phys.*, **35**, 1531 (1961).

TABLE I[a]

FINAL POSITIONAL AND THERMAL PARAMETERS FOR $[Ru_3(CO)_{10}(NO)_2]$

Atom	X	Y	Z	B or β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ru(1)	0.1088 (1)	0.10547 (9)	−0.11908 (3)	0.0141 (2)	0.0088 (1)	0.00120 (2)	0.0037 (1)	0.00015 (5)	0.00022 (4)
Ru(2)	−0.0210 (1)	−0.24521 (9)	−0.09230 (3)	0.0123 (2)	0.0086 (1)	0.00114 (1)	0.0024 (1)	0.00025 (5)	0.00022 (4)
Ru(3)	0.2843 (1)	−0.10449 (9)	−0.15793 (3)	0.0125 (2)	0.0113 (1)	0.00110 (2)	0.0047 (1)	0.00040 (5)	0.00025 (4)
O(11)	0.488 (1)	0.3410 (8)	−0.0947 (3)	0.027 (2)	0.018 (1)	0.0032 (2)	−0.004 (1)	−0.0016 (6)	−0.0002 (4)
O(12)	0.086 (1)	0.2490 (9)	−0.2234 (3)	0.039 (3)	0.024 (2)	0.0017 (2)	0.009 (2)	−0.0008 (6)	0.0027 (4)
O(13)	−0.122 (1)	0.2793 (7)	−0.0681 (3)	0.032 (2)	0.016 (1)	0.0029 (2)	0.010 (1)	0.0031 (6)	−0.0004 (4)
O(21)	0.204 (1)	−0.4199 (8)	−0.0361 (3)	0.032 (2)	0.019 (1)	0.0027 (2)	0.013 (2)	−0.0006 (6)	0.0017 (4)
O(22)	−0.167 (1)	−0.5039 (9)	−0.1698 (3)	0.035 (3)	0.020 (2)	0.0024 (2)	−0.002 (2)	0.0007 (6)	−0.0025 (4)
O(23)	−0.359 (1)	−0.3434 (7)	−0.0214 (3)	0.025 (2)	0.019 (1)	0.0024 (2)	0.005 (1)	0.0044 (6)	−0.0010 (4)
O(30)	0.346 (1)	−0.4131 (8)	−0.1751 (3)	0.035 (3)	0.015 (1)	0.0030 (2)	0.012 (2)	0.0013 (6)	−0.0008 (4)
O(31)	0.528 (1)	−0.0447 (8)	−0.0623 (3)	0.023 (2)	0.030 (2)	0.0017 (2)	0.009 (2)	−0.0021 (5)	−0.0009 (4)
O(32)	0.014 (1)	−0.1304 (9)	−0.2471 (3)	0.032 (3)	0.030 (2)	0.0017 (2)	0.017 (2)	−0.0020 (6)	−0.0010 (5)
O(33)	0.604 (1)	0.110 (1)	−0.2180 (3)	0.028 (3)	0.030 (2)	0.0041 (2)	0.009 (2)	0.0037 (7)	0.0073 (6)
O(1)	0.1794 (9)	−0.0081 (7)	−0.0191 (3)	4.1 (2)					
O(2)	−0.234 (1)	−0.1120 (7)	−0.1609 (3)	5.0 (2)					
N(1)	0.110 (1)	−0.0377 (7)	−0.0603 (3)	3.2 (2)					
N(2)	−0.100 (1)	−0.0934 (8)	−0.1323 (3)	3.8 (2)					
C(11)	0.344 (2)	0.252 (1)	−0.1047 (4)	4.6 (3)					
C(12)	0.100 (2)	0.199 (1)	−0.1856 (4)	4.9 (3)					
C(13)	−0.032 (2)	0.212 (1)	−0.0862 (4)	4.3 (3)					
C(21)	0.119 (2)	−0.356 (1)	−0.0572 (4)	3.9 (2)					
C(22)	−0.116 (2)	−0.411 (1)	−0.1399 (4)	4.7 (3)					
C(23)	−0.234 (2)	−0.309 (1)	−0.0476 (4)	3.9 (3)					
C(30)	0.320 (2)	−0.297 (1)	−0.1687 (4)	4.3 (3)					
C(31)	0.437 (2)	−0.067 (1)	−0.0983 (4)	4.2 (3)					
C(32)	0.114 (2)	−0.123 (1)	−0.2134 (4)	4.6 (3)					
C(33)	0.481 (2)	0.033 (1)	−0.1955 (4)	4.6 (3)					

[a] The form of the anisotropic ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

used in the equivalent setting $P2_1/n$ for which the general equivalent positions are x, y, z; $\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} + z$; $\bar{x}, \bar{y}, \bar{z}$; and $\frac{1}{2} + x, \frac{1}{2} + y, \frac{1}{2} - z$. Unit cell dimensions of a = 7.639 (3), b = 9.231 (2), c = 26.293 (9) Å, and γ = 108.45 (3)° were obtained by least-squares refinement of the setting angles of eight reflections accurately centered in a 1.5-mm diameter, circular receiving aperture, on a Hilger and Watts four-circle, computer-controlled diffractometer (λ(Mo Kα_1) 0.7093 Å; 24°). Here, and elsewhere in this paper, digits in parentheses are estimated standard deviations in the least significant figures quoted and were usually derived from the inverse matrix in the course of normal least-squares refinement calculations. The density calculated for four molecules in this unit cell (2.44 g cm^{-3}) lies within the range observed in a calibrated density gradient tube (2.42 ± 0.05 g cm^{-3}).[19]

Diffraction data were collected from a well-formed thin, platelike crystal of noncentric habit. Its seven bounding faces were identified and their distances from an arbitrary crystal origin measured using a calibrated graticule in a binocular microscope. Minimum and maximum crystal dimensions were 0.04 and 0.30 mm, respectively, and its volume was 0.0019 mm^3. Its mosaicity was examined by means of open-counter ω scans at a takeoff angle of 3°. The widths at half-height, for strong low-angle reflections, ranged from 0.10 to 0.13°.[20] Zirconium-filtered Mo Kα X-radiation and the θ–2θ scan technique were used to record the intensities of 4903 reflections in the positive l hemisphere of reciprocal space for which $0 \leqslant 2\theta \leqslant 46°$. A symmetric scan range of 1.20° in 2θ, centered on the calculated peak position (λ(Mo K$\bar{\alpha}$) 0.7107 Å), was composed of 60 steps of 1-sec duration. Stationary-crystal, stationary-counter background counts of 15 sec were measured at each end of the scan range. No reflections required attenuation to bring them within the linear response range of the scintillation counter, which was located with its 5-mm diameter receiving aperture 230 mm from the crystal.

During data collection the intensities of three standard reflections, monitored at regular intervals, dropped to 93% of their starting values. These observations were used to place all intensities on the same relative scale.[21a] Data were corrected for Lp[21b] and then for absorption (μ(Mo Kα) 25.6 cm^{-1}) using Gaussian integration.[22] Minimum and maximum values of transmission coefficients were 0.706 and 0.891, respectively. After averaging reflections recorded more than once and also the equivalent forms, the data reduced to 2444 reflections of which 1237 had $F^2 > 3\sigma_{F^2}$ where σ_{F^2} was estimated from counting statistics.[23] These were the data used in final refinements of the structure parameters.

Solution and Refinement of the Structure

Full-matrix least-squares refinements[24] were based on F and the function was minimized as $\Sigma w(|F_o| - |F_c|)^2$. The weights w were taken as $4F_o^2/\sigma^2_{F_o^2}$ where $|F_o|$ and $|F_c|$ are observed and calculated structure amplitudes. The atomic scattering factors for Ru were taken from Cromer and Waber[25] while those for C, N, and O were from the tabulation by Ibers.[19] The effects of anomalous dispersion of ruthenium were included in F_c[26] using Cromer's[27] values for $\Delta f'$ and $\Delta f''$. Agreement factors are defined as $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2}$.

Positions for three ruthenium atoms were obtained from Harker peaks in a three-dimensional Patterson synthesis. Refinement of these coordinates and isotropic temperature factors gave values for R_1 and R_2 of 0.264 and 0.289, respectively. From this point two different Fourier syntheses with an intermediate least-squares refinement enabled development of a model containing all 27 atoms of the structure. Using isotropic temperature factors refinement of the model converged with R_1 = 0.070 and R_2 = 0.063. Examination of residual electron density maps at this stage suggested that the thermal motion of the ruthenium atoms and the terminal carbonyl oxygen atoms might be better described by anisotropic temperature factors. In addition the isotropic temperature factors for these oxygen atoms were consistently higher than those of the nitrosyl atoms and of every carbon atom in the structure. Refinement of this model ultimately converged with R_1 = 0.028 and R_2 = 0.018.

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(18) "International Tables for X-Ray Crystallography," Vol. I, Kynoch Press, Birmingham, England, 1962.

(19) "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962.

(20) T. C. Furnas, "Single Crystal Orienter Instruction Manual," General Electric Co., Milwaukee, Wis., 1957.

(21) (a) Calculations were carried out at the University of Canterbury using an IBM 360/44 computer with 32K words of core storage and twin 2315 disk drives. (b) The data processing program HILGOUT is based on programs DRED (J. F. Blount) and PICKOUT (R. J. Doedens).

(22) Numerical absorption corrections are applied using program DABS which is a modified version of DATAPH (P. Coppens). Mathematical methods are fully described in "Crystallographic Computing," Munksgaard, Copenhagen, 1970.

(23) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

(24) Structure factor calculations and least-squares refinements were carried out using program CUCLS and Fourier summations using program FOURIER. These are highly modified versions of the well-known programs ORFLS (W. R. Busing, K. O. Martin, and H. A. Levy) and FORDAP (A. Zalkin), respectively.

(25) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 511 (1965).

(26) J. A. Ibers and W. C. Hamilton, *ibid.*, **17**, 781 (1964).

(27) D. T. Cromer, *ibid.*, **18**, 17 (1965).

Shifts in the last cycle of refinement were all less than half of their estimated standard deviations.

Final difference Fourier calculations gave peaks approximately one-tenth the height at which atoms were located earlier in the analysis. The relative weighting scheme appeared very satisfactory in that average values of the minimized function appear to be independent of $|F_o|$ and $\lambda^{-1} \sin \theta$. The error in an observation of unit weight is 0.930. Structure factor calculations for the 1207 reflections having $F_o^2 < 3\sigma_{F_o^2}$ show none that has $|F_o^2 - F_c^2| > 3\sigma_{F_o^2}$. There is no evidence of secondary extinction among the strong, low-angle reflections.

In order to check that the bridging groups were nitrosyl and not carbonyl, two cycles of refinement were completed using carbon scattering factors in place of nitrogen. This resulted in a very significant increase in both agreement factors and a concomitant decrease in both bridging atom isotropic temperature factors, from values typical of all nonterminal light atoms in the molecule (~4.5 Å^2) to abnormally low values (1.08 and 1.45 Å^2). In view of the observation of nitrides and not oxides in the mass spectrum (see below) no calculations were performed which considered the possibility of O-bound bridging nitrosyls; however, similar abnormalities in the temperature factors would clearly result from switching the N and O atoms. There is no doubt the only nitrogen atoms in the molecule are in the bridging positions.

The positional and vibrational parameters obtained from the final cycle of least-squares refinement are listed in Table I. Derived root-mean-square amplitudes of vibration for the anisotropic atoms are listed in Table II. An appendix[28] contains final values of $|F_o|$ and $|F_o|$ for the 1237 reflections used in the refinement.

TABLE II

ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION (Å)

Atom	Min	Intermed	Max
Ru(1)	0.182 (1)	0.193 (2)	0.207 (1)
Ru(2)	0.173 (1)	0.192 (1)	0.202 (1)
Ru(3)	0.174 (2)	0.195 (2)	0.214 (1)
O(11)	0.21 (1)	0.32 (1)	0.36 (1)
O(12)	0.19 (1)	0.32 (1)	0.35 (1)
O(13)	0.21 (1)	0.27 (1)	0.35 (1)
O(21)	0.21 (1)	0.30 (1)	0.33 (1)
O(22)	0.22 (1)	0.29 (1)	0.38 (1)
O(23)	0.18 (1)	0.27 (1)	0.34 (1)
O(30)	0.20 (1)	0.30 (1)	0.34 (1)
O(31)	0.20 (1)	0.28 (1)	0.35 (1)
O(32)	0.22 (1)	0.27 (1)	0.36 (1)
O(33)	0.20 (1)	0.28 (1)	0.46 (1)

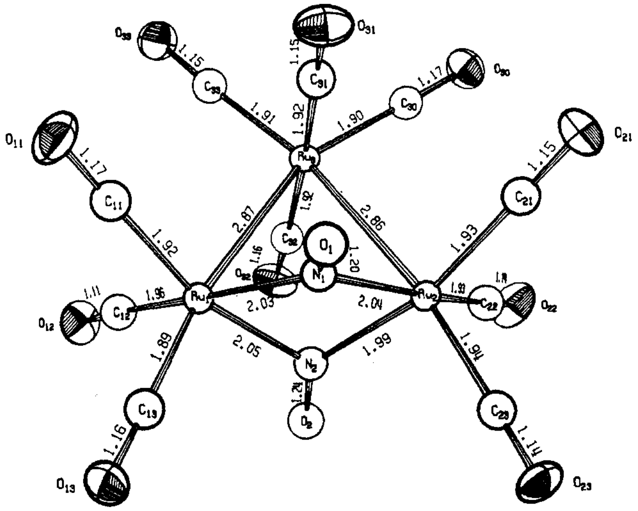

Figure 1.—A perspective view of $[Ru_3(CO)_{10}(NO_2]$ defining the atom-numbering scheme.

TABLE III

BOND DISTANCES (Å) FOR $Ru_3(CO)_{10}(NO)_2$

Ru(1)–Ru(2)	3.150 (1)		
Ru(1)–Ru(3)	2.870 (1)	Ru(2)–Ru(3)	2.861 (1)
Ru(1)–N(1)	2.03 (1)	Ru(1)–N(2)	2.05 (1)
Ru(2)–N(1)	2.04 (1)	Ru(2)–N(2)	1.99 (1)
N(1)–O(1)	1.20 (1)	N(2)–O(2)	1.24 (1)
		N(1)–N(2)	2.43 (1)
Ru(1)–C(11)	1.92 (1)	C(11)–O(11)	1.17 (1)
Ru(1)–C(12)	1.96 (1)	C(12)–O(12)	1.11 (1)
Ru(1)–C(13)	1.89 (1)	C(13)–O(13)	1.16 (1)
Ru(2)–C(21)	1.93 (1)	C(21)–O(21)	1.15 (1)
Ru(2)–C(22)	1.93 (1)	C(22)–O(22)	1.14 (1)
Ru(2)–C(23)	1.94 (1)	C(23)–O(23)	1.14 (1)
Ru(3)–C(30)	1.90 (1)	C(30)–O(30)	1.17 (1)
Ru(3)–C(31)	1.92 (1)	C(31)–O(31)	1.15 (1)
Ru(3)–C(32)	1.92 (1)	C(32)–O(32)	1.16 (1)
Ru(3)–C(33)	1.91 (1)	C(33)–O(33)	1.15 (1)

TABLE IV

BOND ANGLES (DEG) FOR $Ru_3(CO)_{10}(NO)_2$

Ru–Ru–Ru Angle			
Ru(2)–Ru(3)–Ru(1)	66.69 (4)		
Ru–N–Ru Angles			
Ru(1)–N(1)–Ru(2)	101.3 (3)	Ru(2)–N(2)–Ru(1)	102.5 (4)
Ru–N–O Angles			
O(1)–N(1)–Ru(1)	129.1 (6)	O(1)–N(1)–Ru(2)	129.4 (6)
O(2)–N(2)–Ru(2)	130.2 (6)	O(2)–N(2)–Ru(1)	127.2 (6)
Ru–C–O Angles			
O(11)–C(11)–Ru(1)	178.4 (9)	O(23)–C(23)–Ru(2)	178.9 (9)
O(12)–C(12)–Ru(1)	176.9 (11)	O(30)–C(30)–Ru(3)	178.7 (9)
O(13)–C(13)–Ru(1)	177.0 (10)	O(31)–C(31)–Ru(3)	179.4 (9)
O(21)–C(21)–Ru(2)	179.1 (9)	O(32)–C(32)–Ru(3)	178.3 (4)
O(22)–C(22)–Ru(2)	176.4 (10)	O(33)–C(33)–Ru(3)	176.6 (4)
Angles around Ru(1)			
N(1)–Ru(1)–N(2)	73.0 (3)		
C(13)–Ru(1)–C(11)	95.9 (4)	C(11)–Ru(1)–N(2)	163.7 (4)
C(13)–Ru(1)–C(12)	94.1 (5)	C(11)–Ru(1)–Ru(3)	90.8 (3)
C(13)–Ru(1)–N(1)	96.4 (4)	C(12)–Ru(1)–N(1)	166.2 (4)
C(13)–Ru(1)–N(2)	97.7 (3)	C(12)–Ru(1)–N(2)	96.7 (4)
C(13)–Ru(1)–Ru(3)	169.3 (3)	C(12)–Ru(1)–Ru(3)	94.0 (3)
C(11)–Ru(1)–C(12)	91.2 (4)	N(1)–Ru(1)–Ru(3)	74.6 (2)
C(11)–Ru(1)–N(1)	96.6 (4)	N(2)–Ru(1)–Ru(3)	74.5 (2)
Angles around Ru(2)			
N(2)–Ru(2)–N(1)	74.0 (3)		
C(21)–Ru(2)–C(22)	91.4 (4)	C(22)–Ru(2)–N(1)	163.9 (4)
C(21)–Ru(2)–C(23)	95.9 (4)	C(22)–Ru(2)–Ru(3)	91.0 (3)
C(21)–Ru(2)–N(2)	165.0 (4)	C(23)–Ru(2)–N(2)	96.9 (4)
C(21)–Ru(2)–N(1)	96.4 (4)	C(23)–Ru(2)–N(1)	98.5 (3)
C(21)–Ru(2)–Ru(3)	91.2 (3)	C(23)–Ru(2)–Ru(3)	170.7 (3)
C(22)–Ru(2)–C(23)	94.8 (4)	N(2)–Ru(2)–Ru(3)	75.4 (2)
C(22)–Ru(2)–N(2)	95.3 (4)	N(1)–Ru(2)–Ru(3)	74.7 (2)
Angles around Ru(3)			
C(30)–Ru(3)–C(33)	103.0 (3)	C(33)–Ru(3)–Ru(2)	166.5 (1)
C(30)–Ru(3)–C(31)	91.6 (4)	C(33)–Ru(3)–Ru(1)	100.1 (1)
C(30) Ru(3)–C(32)	95.6 (3)	C(31)–Ru(3)–C(32)	172.0 (3)
C(30)–Ru(3)–Ru(2)	90.2 (3)	C(31)–Ru(3)–Ru(2)	87.2 (3)
C(30)–Ru(3)–Ru(1)	156.9 (3)	C(31)–Ru(3)–Ru(1)	88.7 (3)
C(33)–Ru(3)–C(31)	89.8 (3)	C(32)–Ru(3)–Ru(2)	89.2 (1)
C(33)–Ru(3)–C(32)	92.0 (1)	C(32)–Ru(3)–Ru(1)	83.3 (1)

Description of Structure and Discussion

The crystal structure consists of well-separated molecules of $[Ru_3(CO)_{10}(NO)_2]$. A perspective view is shown in Figure 1, which contains the atom-numbering scheme used in the text. Selected interatomic distances are given in Table III and bond angles in Table IV.

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[28] This appendix will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

There is a noncrystallographic twofold axis of symmetry coincident with one median of the triruthenium triangle. Furthermore, this triangle defines an approximate mirror plane in the molecule with N(1), C(11), C(21), and C(31) lying above the plane and N(2), C(12), C(22), and C(32) lying below it. Thus the point group of the whole molecule is approximately C_{2v}, with the other plane containing Ru(3), C(31), C(32), N(1), and N(2).

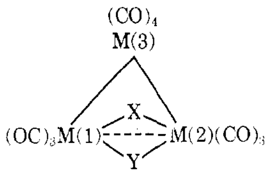
The Ru–C and C–O distances are not significantly different from those in $Ru_3(CO)_{12}$.[29] The structure, however, rather resembles that of $Fe_3(CO)_{12}$[30] with a double-nitrosyl bridge replacing the double-carbonyl bridge present in the latter molecule. As might be expected, these bridging ligands have qualitatively similar structural properties. For example, the average N–O distance of 1.22 Å is comparable to the longest N–O distances observed for terminal nitrosyl ligands,[31] just as slightly longer C–O distances are found in connection with bridging carbonyl groups.[3a] Furthermore, the average Ru–N distance of 2.03 Å is longer even than the metal–nitrogen distances found in bent nitrosyl complexes such as $[IrCl(CO)(Ph_3P)_2(NO)][BF_4]$, where Ir–N is 1.97 Å.[32] (Metal–nitrogen distances involving more nearly linear nitrosyl ligands are considerably shorter.[32]) The same pattern is well-known for bridging carbonyl groups: their metal–carbon distances are longer than those of terminal carbonyl groups.[33–36] The N(1)–N(2) distance of 2.43 Å in $Ru_3(CO)_{10}(NO)_2$ is much too long for any direct interaction between the two nitrosyl ligands.

In contrast to the results obtained for $Fe_3(CO)_{12}$[30] and $Fe_3(CO)_{11}(PPh_3)$,[37] there is little or no asymmetry in the present double-nitrosyl bridge: the average of the Ru(1)–N(1) and Ru(2)–N(2) distances related by the C_2 axis is 2.01 Å, compared to the value of 2.04 Å for the other pair (Ru(1)–N(2) and Ru(2)–N(1))—a difference of only 3σ. In even greater contrast to $Fe_3(CO)_{12}$, the ruthenium nitrosyl carbonyl cluster displays none of the disorder that so long plagued crystallographers investigating the iron trimer. This difference is probably due to the greater distortion of the triruthenium triangle from the equilateral: its apical Ru(1)–Ru(3)–Ru(2) angle is 66.7° compared to 57.2° in the iron cluster.[30]

The Ru(1)–Ru(3) and Ru(2)–Ru(3) distances (2.87 and 2.86 Å, respectively) agree with that (2.85 Å) found in $Ru_3(CO)_{12}$[29] and may be considered normal Ru–Ru single bonds. The Ru(1)–Ru(2) distance, spanned by the double nitrosyl bridge, of 3.15 Å is considerably longer than the usual Ru–Ru single bond and suggests a very low bond order. However, it is becoming increasingly clear that metal–metal distances alone are not a definitive criterion for bond order. The recent structural literature includes similar Ru–Ru distances which are in one case considered nonbonded and in the other bonded: the dimeric complex $Ru_2(CO)_5Cl_3(SnCl_3)$[38] has a triple μ-chloro bridge, an Ru–Ru distance of 3.16 Å, and no evidence for formation of a metal–metal bond, whereas $[Me_3Sn(CO)_3RuSnMe_2]_2$[39] displays an Ru–Ru distance of 3.12 Å and fulfills all the criteria (principally major distortions of normal bridging ligand geometry)[40] for direct metal–metal bonding in bridged dimers.

A comparison of the metal framework of $Ru_3(CO)_{10}(NO)_2$ with that of $Fe_3(CO)_{12}$ and other isostructural systems is illuminating. Values of M–C–M angles associated with bridging carbonyls in metal clusters fall into a rather narrow range (79–87°), and a multiple-carbonyl bridge invariably results in a slight *contraction* (about 0.1 Å) of the bridged metal–metal bond.[3a,30] For instance, in $Fe_3(CO)_{12}$ the unbridged Fe–Fe single-bond distance is 2.69 Å, whereas the distance between the pair of iron atoms connected by the double-carbonyl bridge is shortened by 0.11 Å (to 2.58 Å).[30] On the other hand, the Ru–N–Ru angles associated with the bridging nitrosyls in $Ru_3(CO)_{10}(NO)_2$ average 101° and the Ru(1)–Ru(2) distance is *lengthened* 0.29 Å by the double-nitrosyl bridge.

In terms of the noble gas formalism the structural difference between $Ru_3(CO)_{10}(NO)_2$ and $Fe_3(CO)_{12}$ can be explained by the presence of two more ligand electrons in the former compound and the consequent formation of one less metal–metal bond. The validity of such reasoning can be assessed by further comparisons to other compounds of structure



with different bridging ligands X and Y. Table V summarizes the results of structural investigations[41,42]

TABLE V

Metal	Bridging ligands	Av unbridged M–M distance, Å	Bridged M–M distance, Å
Ru	X = Y = NO[a]	2.87	3.15
Os	X = Y = OCH_3[b]	2.82	3.08
Os	X = Br, Y = Ph_3PAu[c]	2.87	2.87
Os	X = Cl, Y = Ph_3PAu[c]	2.82	2.86
Os	X = H, Y = SC_2H_5[b]	2.84	2.86
Os	X = Y = H[b]	2.81	2.67

[a] This work. [b] Professor R. Mason, Sheffield University, personal communication. [c] J. Gee and H. M. Powell, ref 9 of C. W. Bradford, W. van Bronswijk, R. J. H. Clark, and R. S. Nyholm, *J. Chem. Soc. A*, 2889 (1970).

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(29) R. Mason and A. I. M. Rae, *J. Chem. Soc. A*, 778 (1968).

(30) C. H. Wei and L. F. Dahl, *J. Amer. Chem. Soc.*, **91**, 1351 (1969).

(31) These include (a) 1.21 Å found in $[Co(en)_3][Cr(CN)_5(NO)]$ by J. H. Enemark, M. S. Quinby, L. L. Reed, M. J. Steuck, and K. L. Walther, *Inorg. Chem.*, **9**, 2397 (1970); (b) 1.207 Å found in $Mo(C_5H_5)_3(NO)$ by J. L. Calderon, F. A. Cotton, and P. Legzdins, *J. Amer. Chem. Soc.*, **91**, 2528 (1969).

(32) D. J. Hodgson and J. A. Ibers, *Inorg. Chem.*, **7**, 2345 (1968), and references therein.

(33) For example, in $Co_2(CO)_8$[34] the average Co–C distance is 1.92 Å for bridging carbonyls and 1.80 Å for terminal ones; in $Fe_3(CO)_{12}$ the comparable figures are 2.21 Å (bridging) and 1.85 Å (terminal); in $Cs_2[Co_6(CO)_{15}]$[35] 1.90 Å (bridging) and 1.74 Å (terminal); in $Ru_6C(CO)_{14}(1,3,5\text{-}(CH_3)_3C_6H_3)$[36] 2.06 Å (bridging) and 1.92 Å (terminal).

(34) G. G. Sumner, H. P. Klug, and L. E. Alexander, *Acta Crystallogr.*, **17**, 732 (1964).

(35) V. Albano, P. Chini, and V. Scatturin, *J. Organometal. Chem.*, **15**, 423 (1968).

(36) R. Mason and W. R. Robinson, *Chem. Commun.*, 468 (1968).

(37) D. J. Dahm and R. A. Jacobson, *J. Amer. Chem. Soc.*, **90**, 5106 (1968).

(38) R. K. Pomeroy, M. Elder, D. Hall, and W. A. G. Graham, *Chem. Commun.*, 381 (1969).

(39) S. F. Watkins, *J. Chem. Soc. A*, 1552 (1969).

(40) L. F. Dahl, E. R. deGil, and R. D. Feltham, *J. Amer. Chem. Soc.*, **91**, 1653 (1969).

(41) Professor R. Mason, Sheffield University, personal communication.

(42) J. Gee and H. M. Powell, ref 9 of C. W. Bradford, W. van Bronswijk, R. J. H. Clark, and R. S. Nyholm, *J. Chem. Soc. A*, 2889 (1970).

on a series of osmium clusters. (The covalent radii of ruthenium and osmium are virtually identical, and hence such considerations do not affect comparisons of clusters of the two elements.) It is clear that ligands which are formal three-electron donors, such as nitrosyl and methoxide, span the largest M(1)–M(2) distances (formally nonbonds), whereas hydride ligands, one-electron donors, span the shortest distance (formally a double bond). (It is unclear what formal electron-donating capacity should be assigned a bridging Ph_3PAu species.) However, in view of (a) the lack of correlation between bond order and bond length noted above and (b) the fact that formally nonbonded metal–metal distances between double carbonyl-bridged metal atoms are never found in metal carbonyl clusters (including anions), we ascribe only limited validity to such noble gas formalism reasoning. The one statement which can be made with certainty is that the trimetallic framework in these complexes, while remaining unaffected in other respects, can accept a wide range of M(1)–M(2) distances depending upon the nature of the bridging ligands. This situation contrasts to that in binuclear complexes, where a metal–metal bond imposes distortions upon the bridging ligand geometry.[40] One may then regard the bridging nitrosyl ligands in $Ru_3(CO)_{10}(NO)_2$ as "structure determining" and suggest that future examples of this species are likely to have large M–N–M angles and expanded metal–metal distances also.

Infrared Spectra and Structures of Nitrosyl Carbonyl Clusters in Solution.—As is clear from Figure 2, the carbonyl region infrared spectra are very similar for $Ru_3(CO)_{10}(NO)_2$ (1) and $Os_3(CO)_{10}(NO)_2$ (4). The pattern observed was shown by Knight and Mays[43] to be characteristic of the terminal carbonyl region in trimetallic complexes believed to have C_{2v} symmetry in solution, such as $RuFe_2(CO)_{12}$, $OsFe_2(CO)_{12}$, $[MnFe_2(CO)_{12}]^-$, $[TcFe_2(CO)_{12}]^-$, $[ReFe_2(CO)_{12}]^-$, and $Ru_3(CO)_{10}(NO)_2$. We therefore conclude that in solution 4 has the same structure as 1. The solid-state (KBr) spectra of the two compounds are also similar, especially in such characteristic features as ν_{NO} at 1517 and 1500 cm^{-1} (1) and 1503 and 1484 cm^{-1} (4) and sharp peaks at 723 (1) and 739 cm^{-1} (4). Inasmuch as no such feature is present in spectra of metal carbonyl clusters, we attribute the latter bands to a vibration of the double-nitrosyl bridge. Similar peaks, also without any reasonable alternative assignment, are reported[14] for cyclopentadienyl complexes presumed to contain bridging nitrosyls.

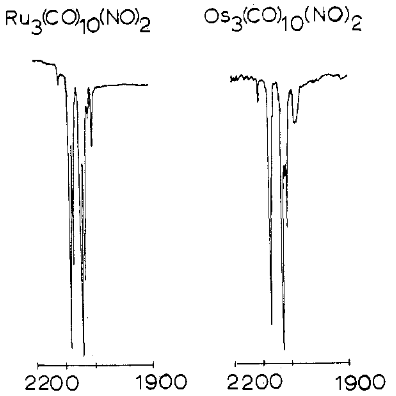

Figure 2.—Solution infrared spectra in the carbonyl region (2200–1900 cm^{-1}) of $Ru_3(CO)_{10}(NO)_2$ and $Os_3(CO)_{10}(NO)_2$.

In a recent communication Poliakoff and Turner[44] showed that molecular $Ru_3(CO)_{10}(NO)_2$ condensed in an argon matrix at 20°K had the same ir spectrum as in solution at room temperature. This evidence implies that the solid-state structure of 1, described in this paper, is maintained in solution. (Indeed, reasoning from infrared spectra, these workers were able to predict the structure of 1.)

In consideration of all of the above spectral evidence it is clear that both $Ru_3(CO)_{10}(NO)_2$ and $Os_3(CO)_{10}(NO)_2$ have the structure shown in Figure 1 in solution as well as in the solid state.

Mass Spectra.—Compounds 1, 3, and 4 were examined by low-resolution mass spectrometry. In view of the complex ruthenium and osmium isotopic distributions the parent ions and all overlapping multiplets of significance were analyzed by a computer program based upon the procedure of Brauman[45] and modified to include multiple heteroatoms. The detailed fragmentation patterns of 1 and 4 are shown in Tables VI and VII.

TABLE VI
MASS SPECTRUM OF $Ru_3(CO)_{10}(NO)_2$

m/e^a	Identity	Rel intens^b	m/e^a	Identity	Rel intens^b
643	$Ru_3(CO)_{10}(NO)_2^+$	25	375	$Ru_3(NO)_2C^+$ or $Ru_3(CO)(NO)N^+$	12
615	$Ru_3(CO)_9(NO)_2^+$	21	373	$Ru_3(CO)(NO)C^+$ or $Ru_3(CO)_2N^+$	5
587	$Ru_3(CO)_8(NO)_2^+$	49	361	$Ru_3(CO)(NO)^+$	50
559	$Ru_3(CO)_7(NO)_2^+$	18	347	$Ru_3(NO)N^+$	10
531	$Ru_3(CO)_6(NO)_2^+$	12	345	$Ru_3(NO)C^+$ or $Ru_3(CO)N^+$	8
503	$Ru_3(CO)_5(NO)_2^+$	34	333	$Ru_3(NO)^+$	43
501	$Ru_3(CO)_6(NO)^+$	44	331	$Ru_3(CO)^+$	17
475	$Ru_3(CO)_4(NO)_2^+$	100	317	Ru_3N^+	11
473	$Ru_3(CO)_5(NO)^+$	41	303	Ru_3^+	51
447	$Ru_3(CO)_3(NO)_2^+$	25	216	Ru_2N^+	8
445	$Ru_3(CO)_4(NO)^+$	35	202	Ru_2^+	14
419	$Ru_3(CO)_2(NO)_2^+$	14			
417	$Ru_3(CO)_3(NO)^+$	31			
389	$Ru_3(CO)_2(NO)^+$	49			

[a] For ^{101}Ru peaks. [b] Most intense peak = 100.

TABLE VII
MASS SPECTRUM OF $Os_3(CO)_{10}(NO)_2$^{a}

m/e^b	Ion	Rel intens^c	m/e^b	Ion	Rel intens^c
916	$Os_3(CO)_{10}(NO)_2^+$	25	692	$Os_3(CO)_2(NO)_2^+$	8
888	$Os_3(CO)_9(NO)_2^+$	33	690	$Os_3(CO)_3(NO)^+$	39
860	$Os_3(CO)_8(NO)_2^+$	13	674	$Os_3(CO)_2(NO)C^+$ or $Os_3(CO)_3N^+$	4
842	$Os_3(CO)_8(NO)C^+$ or $Os_3(CO)_9N^+$	13	662	$Os_3(CO)_2(NO)^+$	46
832	$Os_3(CO)_7(NO)_2^+$	3	646	$Os_3(CO)(NO)C^+$ or $Os_3(CO)_2N^+$	7
830	$Os_3(CO)_8(NO)^+$	2	634	$Os_3(CO)(NO)^+$	36
804	$Os_3(CO)_6(NO)_2^+$	6	632	$Os_3(CO)_2^+$	12
802	$Os_3(CO)_7(NO)^+$	11	618	$Os_3(CO)N^+$ or $Os_3(NO)C^+$	9
776	$Os_3(CO)_5(NO)_2^+$	30	606	$Os_3(NO)^+$	34
774	$Os_3(CO)_6(NO)^+$	100	604	$Os_3(CO)^+$	12
748	$Os_3(CO)_4(NO)_2^+$	37	590	Os_3N^+	17
746	$Os_3(CO)_5(NO)^+$	30	576	Os_3^+	29
720	$Os_3(CO)_3(NO)_2^+$	15			
718	$Os_3(CO)_4(NO)^+$	43			

[a] Doubly charged ions corresponding substantially to the above spectrum are observed in relative abundance of 48%. [b] For ^{192}Os peaks. [c] Most intense peak = 100.

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(43) J. Knight and M. J. Mays, *Chem. Commun.*, 1006 (1970).

(44) M. Poliakoff and J. J. Turner, *J. Chem. Soc. A*, 654 (1971).

(45) J. I. Brauman, *Anal. Chem.*, **38**, 607 (1966).

In both cases the decomposition path appears to be successive loss of all ligands to produce an M_3^+ ion. This pattern is like that observed[46] for $Os_3(CO)_{12}$ and $Ru_3(CO)_{12}$ and is quite common for second- and third-row transition metal clusters. A large number of doubly charged ions are observed in the mass spectrum of **4**; this behavior is also seen with $Os_3(CO)_{12}$[46] and reflects the greater stability of third-row transition element clusters toward oxidation.

Both **1** and **4** display strong $M_3(NO)^+$ peaks and in general lose CO in preference to NO. This observation is in accord with experience on mononuclear nitrosyl carbonyls[46,47] and suggests that the nitrosyl ligand is more tightly bound. Indeed, in the case of $Ru_3(CO)_{10}(NO)_2$, Ru_2N^+ (but not Ru_2C^+) is observed after the cluster begins to fragment.

The mechanism of loss of the first nitrosyl ligand appears to vary somewhat between **1** and **4**. In the mass spectrum of $Ru_3(CO)_{10}(NO)_2$, ions below $Ru_3(CO)_6(NO)_2^+$ begin to display NO loss in competition with further CO loss; for $Os_3(CO)_{10}(NO)_2$ the same pattern begins with $Os_3(CO)_8(NO)_2^+$. However, with the osmium cluster a peak ($^{192}Os_3(CO)_8(NO)C^+$ or $^{192}Os_3(CO)_9N^+$) is observed at m/e 842—far higher than other deoxygenated fragments, which do not appear until nearly all ligands are gone from the cluster. This observation suggests that some nitrogen is lost as NO_2 from $Os_3(CO)_9(NO)_2^+$.

Acknowledgment.—The authors thank Professor J. T. Moelwyn-Hughes for his assistance with the chromatography and mass spectral interpretation and Professor J. McLeod (Australian National University, Canberra) for his assistance in obtaining the MS 9 mass spectra. Support for this work was generously provided by National Science Foundation Grant No. GP20273X and Petroleum Research Fund Grant No. 3635-C3.

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Metal Ion–Aromatic Complexes. XII. The Crystal and Molecular Structures of Acenaphthenesilver Perchlorate and Acenaphthylenesilver Perchlorate

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The crystal and molecular structures of acenaphthenesilver perchlorate and acenaphthylenesilver perchlorate have been determined by single-crystal X-ray diffraction from counter-measured intensities at room temperature. Crystals of acenaphthenesilver perchlorate were found to be orthorhombic: a = 18.531 (2) Å, b = 15.586 (5) Å, c = 7.877 (3) Å; space group $Pmnb$, Z = 8. The structure was refined to a conventional R factor of 0.074 by full-matrix least-squares methods based upon 1236 independent reflections. The structure may be described in terms of one-dimensional infinite chains of $AgClO_4$ with the aromatic groups lying on either side of the chain. The Ag–O interactions range from 2.34 to 2.46 Å (±0.02 Å or less). The Ag–C distances are all "short" at 2.44–2.51 Å (±0.01 Å). Crystals of acenaphthylenesilver perchlorate were found to be orthorhombic: a = 6.416 (1) Å, b = 10.286 (2) Å, c = 18.056 (2) Å; space group $P22_12_1$, Z = 4. Disorder and large thermal motions limited the accuracy of this structure determination and full-matrix least-squares refinement converged to a conventional R of 0.20 with 547 independent reflections. The structure consists of one-dimensional chains of alternating aromatic and perchlorate groups and is different from the structure found for acenaphthenesilver perchlorate. The five-membered ring is not involved in bonding to the silver atom.

Introduction

The crystal and molecular structures of a number of complexes between Ag(I) and aromatic moieties have now been determined. These structures cover a wide range of stoichiometries but yet have some common features. $(Aryl)_2Ag^IClO_4$ complexes are formed with cyclohexylbenzene[1] and o-,[2] m-,[3] and p-xylenes.[4] Unfortunately, the last structure is badly disordered and little useful information can be derived from its crystal structure analysis. However, $(cyclohexylbenzene)_2AgClO_4$ and $(m\text{-xylene})_2AgClO_4$ are composed of sheets or chains of $AgClO_4$ in which each Ag(I) is bound to two aromatic entities, one on either side of the chain or sheet such that each silver has two close Ag–C distances at 2.47 ± 0.02 Å. The coordination polyhedron of silver is completed by Ag–O interactions. The next nearest Ag–C distance can vary over wide limits up to the 2.96 Å observed in $C_6H_6 \cdot AgAlCl_4$.[5] On the other hand, a discrete dimer is observed for $(o\text{-xylene})_2AgClO_4$ with Ag–O–Ag bridges and the distorted tetrahedral geometry of Ag(I) is completed by interaction with the aromatic moieties at the usual 2.47 Å distance. One to one stoichiometries are also observed in $C_6H_6 \cdot AgClO_4$,[6] dibenzyl·$AgClO_4$,[7] and indene·$AgClO_4$,[8] but in spite of different coordination numbers and Ag–O distances the common 2.47-Å nearest Ag–C distance persists. Higher ratios of silver to aromatic moieties have been found in naphthalene·$4AgClO_4 \cdot 4H_2O$[9] and anthracene·$4AgClO_4 \cdot H_2O$.[9] Only the naphthalene

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