in equilibrium 2 and the volume decrease inherent in the charge separation effect of reaction 3 are diminished.

The first prediction is borne out by recent results of ion association[40] and acid dissociation[41] studies of hexaamminemetal nitrates of the first-row transition elements in liquid ammonia. In this series $Co(NH_3)_6^{3+}$ is exceptional in showing abnormally low $\Delta S°$ values for both reactions, if compared to the lower oxidation-state complex $Co(NH_3)_6^{2+}$. In addition in the strongly electrostricted second coordination sphere of the complexes, the necessary creation of freedom of motion and free volume[42] for the anion is expected to cause the large recorded volume increase. The smaller volume increase for a neutral group as NH_3 can then be explained from a better fit of this group in the solvent structure of the second sphere.[38]

Registry No. $Co(NH_3)_5F^{2+}$, 15392-06-0; $Co(NH_3)_5Cl^{2+}$, 14970-14-0; $Co(NH_3)_5Br^{2+}$, 14970-15-1; $Co(NH_3)_5N_3^{2+}$, 14403-83-9; $Co(NH_3)_5NCS^{2+}$, 14970-18-4; $Co(NH_3)_5SO_4^{+}$, 18661-07-9; $Co(NH_3)_5PO_4$, 15612-03-0; $Co(NH_3)_5NO_3^{2+}$, 15077-47-1.

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Contribution from the Department of Chemistry,
Northwestern University, Evanston, Illinois 60201

Coordinated Nitrosyl Hydride: Structural and Spectroscopic Study of $OsCl_2(CO)(HNO)(P(C_6H_5)_3)_2$

ROBERT D. WILSON and JAMES A. IBERS*

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That $OsCl(CO)(NO)(PPh_3)_2$ (Ph = phenyl = C_6H_5) reacts with HCl to form $OsCl_2(CO)(HNO)(PPh_3)_2$ is confirmed by a structural and spectroscopic study of the product. The octahedrally coordinated Os(II) ion possesses trans phosphine ligands, cis chloro ligands, a carbonyl group, and a HNO molecule coordinated through the N atom. Important metrical details for this coordination are Os–N = 1.915 (6) Å, N–O = 1.193 (7) Å, N–H = 0.94 (11) Å, Os–N–O = 136.9 (6)°, Os–N–H = 123 (7)°, and O–N–H = 99 (7)°. These results have been derived from a three-dimensional X-ray study of $OsCl_2(CO)(HNO)(PPh_3)_2\cdot{}^1/_2CH_2Cl_2$, based on 185 variables and 5563 significant observations. The material crystallizes with four molecules in space group C_{2h}^5-$P2_1/n$ of the monoclinic system in a cell of dimensions a = 10.849 (2) Å, b = 33.272 (7) Å, c = 10.036 (3) Å, and β = 104.56 (1)°. The N–O stretching frequency has been identified at 1410 cm^{-1} from the spectra of the unlabeled and ^{15}N-labeled species. Coordination of HNO in solution has been established from the ^1H NMR spectra of $OsCl_2(CO)(H^{14}NO)(PPh_3)_2$ and the corresponding ^{15}N derivative, which show the chemical shift of the unique proton at $\delta = 21.2$. Consistent with the solid-state study, the ^1H–^{15}N coupling constant of 75 Hz implies that the ligand is HNO rather than HON. Reaction of a noncoordinating acid, HBF_4, with $OsCl(CO)(NO)(PPh_3)_2$ yields a variety of products, including $[OsCl_2(CO)(NO)(PPh_3)_2][BF_4]$ whose identity was established by crystallographic methods.

Introduction

Both nucleophilic and electrophilic attack of metal-coordinated nitric oxide have been reported. Typical of the nucleophilic attack, which occurs on linearly coordinated nitrosyls, is the reaction of $RuCl(NO)(bpy)_2^{2+}$ (bpy = 2,2′-bipyridine) with base to form $RuCl(NO_2)(bpy)_2$.[1] Typical of electrophilic attack, which occurs apparently on bent nitrosyls, is reaction with acid to convert the coordinated nitric oxide to coordinated nitrosyl hydride, HNO. Grundy, Reed, and Roper[2] provided the first example of such a reaction, namely, $OsCl(CO)(NO)(PPh_3)_2$ with HCl to form $OsCl_2(CO)(HNO)(PPh_3)_2$, but other examples[3,4] have now been proposed. In none of these instances is there direct, unequivocal evidence for the formation of coordinated HNO. The possibility of the alternative connectivity, NOH, cannot be discounted, as suggested for $[Fe(CN)_5(NOH)]^{2-}$[5,6] and $RhCl_3(NOH)(PPh_3)_2$,[7] although other formulations for these species have been suggested.[8,9]

In this paper we present structural and spectroscopic evidence that definitively establishes the presence in the solid state and in solution of the N-coordinated HNO molecule in the prototype example, $OsCl_2(CO)(HNO)(PPh_3)_2$.

Experimental Procedure

Infrared spectra (4000–600 cm^{-1}) were measured in Nujol mulls and dichloromethane solutions using Perkin-Elmer 727-B and IR 283

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Table I. Infrared Absorption Bands (cm^{-1}) for $OsCl(CO)(NO)(PPh_3)_2$ and $OsCl_2(CO)(HNO)(PPh_3)_2$[a]

	ν(NO)	ν(CO)
$OsCl(CO)(^{14}NO)(PPh_3)_2$	1769 w, 1629 m, 1560 s	1962 w, 1905 vs, 1894 vs
$OsCl(CO)(^{15}NO)(PPh_3)_2$	1742 w, 1598 m, 1534 s	1962 w, 1904 vs, 1894 vs
$OsCl(CO)(^{14}NO)(PPh_3)_2$[b]	1790 m, 1648 m, 1574 w	1906 vs
$OsCl(CO)(^{14}NO)(PPh_3)_2$[c]	1770, 1628, 1587	1963, 1896
$OsCl(CO)(H^{14}NO)(PPh_3)_2 \cdot {}^1/_2CH_2Cl_2$[d]	1410 s	1973 vs
$OsCl_2(CO)(H^{15}NO)(PPh_3)_2 \cdot {}^1/_2CH_2Cl_2$	1393 s	1971 vs
$OsCl_2(CO)(H^{14}NO)(PPh_3)_2$[e]		1976 vs

[a] As Nujol mulls except where indicated. [b] In CH_2Cl_2 solution; note the change in relative intensities of the three nitrosyl bands vs. the mull spectrum. [c] 23 well-formed, medium-sized (≃0.1–0.2 mm edge dimensions) uncrushed single crystals using a beam condenser on a Perkin-Elmer IR-283 spectrometer. [d] The IR spectrum of $OsCl_2(CO)(DNO)(PPh_3)_2$ is superimposable on that of $OsCl_2(CO)(HNO)(PPh_3)_2$. No bands assignable to ν(NH) or ν(ND) were found. [e] In CH_2Cl_2 solution; the region between 1460 and 1200 cm^{-1} is blank, in part because of solvent absorption.

spectrometers. ^1H and ^{31}P NMR spectra were recorded using a Varian FT-20 NMR spectrometer. All reactions involving osmium compounds were carried out under oxygen-free dinitrogen using standard Schlenk ware techniques.

Chlorohydridocarbonyltris(triphenylphosphine)osmium(II), $OsClH(CO)(PPh_3)_3$. The compound was prepared by literature methods,[10] with the substitution of 1.2 mmol of $(NH_4)_2OsCl_6$ (Matthey-Bishop) for the sodium salt. The off-white product was characterized by its infrared spectrum [ν(Os–H), 2105 (m) cm^{-1}; ν(CO), 1912 (vs), 1894 (s) cm^{-1}] which was in fair agreement with that of the literature.[10] The yield was 1.04 g (82%). Anal. Calcd for $C_{55}H_{46}ClOP_3Os$: C, 63.40; N, 0.0; H, 4.45. Found: C, 63.28; N, 0.0; H, 4.10.

Chlorocarbonylnitrosylbis(triphenylphosphine)osmium(0), $OsCl(CO)(NO)(PPh_3)_2$. The preparation followed that of Laing and Roper:[11,12] 0.38 g (0.36 mmol) of $OsClH(CO)(PPh_3)_3$ and 0.13 g (0.61 mmol) of *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide were made into a slurry with ethanol (15 mL) and refluxed under N_2 for 3 h. The yellow-brown powdered product was filtered, washed with pentane, and dried. This crude powder was typically used as is, but small portions of the material could be recrystallized by vapor diffusion (CH_2Cl_2 solution vs. $(C_2H_2)_2O$ under N_2) which afforded orange-brown parallelepipeds. The carbonyl and nitrosyl infrared absorption frequencies are given in Table I. Anal. Calcd for $C_{37}H_{30}ClNO_2P_2Os$: C, 54.98; H, 3.74; N, 1.73. Found: C, 54.24; H, 4.03; N, 1.73. From preliminary film data we find the compound crystallizes in the monoclinic space group *C*2/*c* or *Cc* in a cell of dimensions a = 15.99 Å, b = 9.64 Å, c = 22.01 Å, β = 105.3°, and V = 3273 Å^3, with ρ_{calcd} = 1.64 g cm^{-3} (for Z = 4) and ρ_{obsd} = 1.62 g cm^{-3}. Thus $OsCl(CO)(NO)(PPh_3)_2$ is not isomorphous with $RuI(CO)(NO)(PPh_3)_2$ which crystallizes in space group *Pbcn* of the orthorhombic system.[13]

Chlorocarbonyl[^{15}N]nitrosylbis(triphenylphosphine)osmium(0), $OsCl(CO)(^{15}NO)(PPh_3)_2$. The material was synthesized in the above manner but at one-quarter scale, utilizing ^{15}N-labeled *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (labeled at the nitroso nitrogen atom).

***N*-Methyl-*N*-[^{15}N]nitroso-*p*-toluenesulfonamide, $CH_3(C_6H_4)SO_2N(CH_3)(^{15}NO)$.** This compound was made according to the synthesis outlined by DeBoer and Backer[14] but at one-thousandth scale and with substitution of 99% $Na^{15}NO_2$ [Stohler Isotope Chemicals] for the unlabeled sodium nitrite. The purity of this material was checked by its infrared spectrum (Nujol mull) which differed from that of an authentic sample of unlabeled compound by a strong N–O vibration shifted to 1472 cm^{-1} from 1495 cm^{-1}.

Dichlorocarbonyl(nitrosyl hydride)bis(triphenylphosphine)osmium(II)–Hemi(dichloromethane), $OsCl_2(CO)(HNO)(PPh_3)_2 \cdot {}^1/_2CH_2Cl_2$. Approximately 0.04 g (0.05 mmol) of $OsCl(CO)(NO)(PPh_3)_2$ was placed in a 13 × 100 mm Pyrex test tube which was then put in a 250-mL Schlenk tube. After the vessel was evacuated and then refilled with N_2, ca. 3 mL of dry degassed benzene was added (during N_2 flushing) to the test tube, resulting in incomplete dissolution of the osmium complex. The N_2 atmosphere was later replaced by 1 atm of HCl (gas) [Matheson Gas] with rapid saturation of the reaction solution, subsequent reddening, and nearly complete dissolution of the remaining starting material. After ca. 10 min the atmosphere was again replaced by N_2 and during flushing ca. 50 mL of dry degassed pentane was syringed into the Schlenk vessel (outside the test tube) and vapor diffusion was allowed to proceed at room temperature overnight. The malformed red-orange crystals obtained were separated from the solution and from small amounts of yellow powder. Redissolution of these crystals in dry degassed methylene chloride (ca. 2 mL) was followed by vapor diffusion vs. diethyl ether (under N_2). Within 2 days well-formed red-orange needles developed. Pertinent infrared absorption data are given in Table I. Anal. Calcd for $C_{37.5}H_{32}Cl_3NO_2P_2Os$: C, 50.80; H, 3.64; N, 1.58; Cl, 11.99. Found: C, 50.77; H, 3.15; N, 1.72; Cl, 11.76.

Dichlorocarbonyl([^{15}N]nitrosyl hydride)bis(triphenylphosphine)osmium(II)–Hemi(dichloromethane), $OsCl_2(CO)(H^{15}NO)(PPh_3)_2 \cdot {}^1/_2CH_2Cl_2$. Crystals of this compound were obtained by reaction of 0.03 g (0.04 mmol) of $OsCl(CO)(^{15}NO)(PPh_3)_2$ with excess HCl gas in exactly the same manner as that employed for the unlabeled material. The unit cell parameters, as determined by precession photographs, were identical with those of the unlabeled compound. This nondestructive method of analysis obviated the need for elemental analysis.

Dichlorocarbonyl(nitrosyl deuteride)bis(triphenylphosphine)osmium(II), $OsCl_2(CO)(DNO)(PPh_3)_2$. DCl (gas) generated from benzoyl chloride and D_2O[15] was reacted with $OsCl(CO)(NO)(PPh_3)_2$ in benzene-d_6. Removal of solvent and excess DCl under vacuum afforded the compound as a red-brown powder. The IR spectrum (Nujol mull) of the powder was superimposable on that of $OsCl_2(CO)(HNO)(PPh_3)_2$, rendering unsuccessful the attempt to assign an N–H absorption band (or conceivably, at that point, an O–H band). A high degree of deuteration at the DNO group was established by the near disappearance of the δ = 21.2 signal in the ^1H NMR spectrum.

Dichlorocarbonylnitrosylbis(triphenylphosphine)osmium(II) Tetrafluorborate, $[OsCl_2(CO)(NO)(PPh_3)_2][BF_4]$. In 1 mL of dry degassed CH_2Cl_2 0.03 g (0.04 mmol) of $OsCl(CO)(NO)(PPh_3)_2$ was reacted with 0.2 mL of 0.2 M HBF_4 etherate in CH_2Cl_2 solution. This corresponds to a ca. 1:1 mole ratio. To the clear yellow-brown solution which immediately formed, diethyl ether was slowly added (by vapor diffusion) until pale yellow crystals appeared. Insufficient material was available for elemental analysis but a very sharp, strong IR absorption at 2127 cm^{-1} was assigned to ν(Os–H) since the Os–H stretching vibration in $OsClH(CO)(PPh_3)_2$ is found at 2099 cm^{-1}.[10] As a result of a subsequent crystallographic analysis, the material was found not to be a hydride but the new compound $[OsCl_2(CO)(NO)(PPh_3)_2][BF_4]$.

The 2127-cm^{-1} band can be assigned to ν(CO) in analogy with the value of 2135 cm^{-1} in $[OsI(CO)_3(PPh_3)_2][I]$.[16] A strong band at 1899 cm^{-1} may be ascribed to ν(NO) of a linear nitrosyl group.[17]

Attempted Deprotonation of $OsCl_2(CO)(HNO)(PPh_3)_2$. To a small quantity (ca. 0.02 g) of $OsCl_2(CO)(HNO)(PPh_3)_2$ in 5 mL of benzene was added a large excess of $[N(C_2H_5)_4](OH)$ in THF (wet). No immediate reaction was noted. After 4 h the solvents were removed under vacuum. The IR spectra (Nujol mull) of the crude dry yellow-orange powder was dominated in the 1300–2400-cm^{-1} region by appropriate bands from $OsCl_2(CO)(HNO)(PPh_3)_2$.

Data Collection and Structure Analysis for $OsCl_2(CO)(HNO)(PPh_3)_2 \cdot {}^1/_2CH_2Cl_2$. The compound $OsCl_2(CO)(HNO)(PPh_3)_2 \cdot {}^1/_2CH_2Cl_2$ crystallizes in space group C_{2h}^5-$P2_1/n$ of the monoclinic system. Hand-centering of 17 well-distributed reflections (60° < $2\theta(CuK\alpha_1)$ < 70°) led to the cell constants given in Table II. Acquisition of room-temperature data using a Picker FACS-I diffractometer proceeded by methods generally used in this laboratory.[18] Important parameters of data collection are listed in Table II.

The structure was solved using Patterson and Fourier methods. Trial positions for the heavy atoms (Os, P, Cl) were obtained from a three-dimensional, origin-removed Patterson function. All nonsolvent, nonhydrogen atoms were located on subsequent difference Fourier maps. After two cycles of full-matrix least-squares refinement of an isotropic model in which the carbon atoms of the phenyl rings were constrained to the rigid-group approximation, a difference Fourier map revealed the carbon and chlorine atoms of a dichloromethane molecule. The occupancy factor of these atoms was set at $^1/_2$ and was not refined since (i) the molecule was found to be in two different

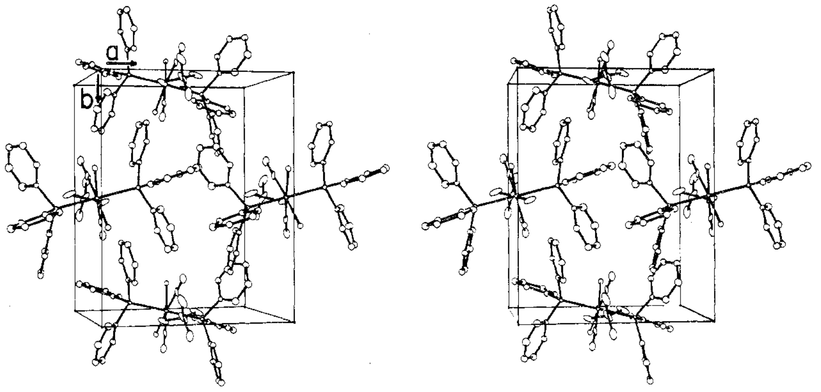

Figure 1. Stereoscopic view of a unit cell of $[OsCl_2(CO)(NO)(PPh_3)_2][BF_4]$. The 20% probability ellipsoids are shown.

Table II. Crystal Data and Data Collection Procedures for $OsCl_2(CO)(HNO)[P(C_6H_5)_3]_2 \cdot {}^1/_2CH_2Cl_2$

formula	$C_{37.5}H_{32}Cl_3NO_2P_2Os$
formula wt	887.18 amu
space group	$C_{2h}{}^5$-$P2_1/n$ (monoclinic)
a	10.849 (2) Å
b	33.272 (7) Å
c	10.036 (3) Å
β	104.56 (1)°
V	3506 Å^3
Z	4
ρ_{calcd}	1.681 g/cm^3
ρ_{obsd}	1.68 g/cm^3
temp	22 °C
crystal shape	hexagonal needle [011] of approx length 0.59 mm and width 0.09 mm, bounded by the faces {010}, {110}
crystal vol	0.0049 mm^3
radiation	Cu Kα (λ(Cu Kα_1) 1.540 562 Å), prefiltered through 0.03 mm Ni foil
linear absorption coeff (μ)	101.8 cm^{-1}
transmission factors	0.190–0.485
detector aperture	3.5-mm wide by 3.5-mm high, 30 cm from crystal
takeoff angle	3.5°
scan speed	2.0°/min
2θ limits	5.0–125.0° (bisecting mode), 125.0–160.0° (parallel mode)
bkgd counts	10 s at each end of scan with rescan option
scan range	0.8° below Kα_1 to 0.8° above Kα_2 (bisecting mode); 1.5 and 1.1° respectively, for the parallel mode
data collected	$\pm h, k \leqslant 0, l \geqslant 0$
p	0.04
unique data, $F_o{}^2 > 3\sigma(F_o{}^2)$	5563
final no. of variables	185
error in observn of unit weight, electrons	1.58 e
R	0.040
R_w	0.051

orientations in the vicinity of an inversion center and (ii) carbon and chlorine elemental analyses are in very good agreement with the hemi-solvate formulation. Inspection of the thermal parameters of the atoms of the assigned CO and NO groups supported the assignment, rather than interchange of C and N. Similarly, inspection of the N and O parameters suggests that these atoms are assigned correctly, with the linkage being Os–N–O, rather than Os–O–N. On a subsequent difference Fourier map, the major feature was a peak of height 0.67 e/Å^3 in the equatorial plane within 1.1 Å of the N atom of the bent NO group. This provides reasonable evidence for the presence of the HNO group in this complex. Anisotropic least-squares refinement (unique H atom isotropic), in which the contributions of all phenyl and methylene H atoms positioned in idealized calculated positions were ultimately included, converged to values of R and R_W of 0.040 and 0.051, respectively. The standard deviation of an observation of unit weight, based on 185 variables and 5563 observations, is 1.58 electrons. A survey of $\sum w(|F_o| - |F_c|)^2$ as a function of $|F_o|$, Miller indices, and setting angles exposed no anomalous trends.

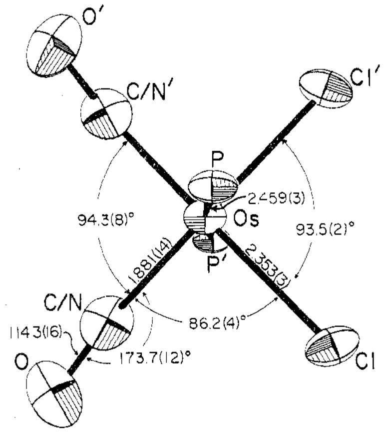

Figure 2. Inner coordination sphere of the octahedral cation $OsCl_2(CO)(NO)(PPh_3)_2{}^+$. Here vibrational ellipsoids are plotted at the 50% probability level. Primed atoms are related to unprimed atoms by the crystallographically imposed twofold axis. The C and N atoms are disordered and are denoted by C/N.

Final positional and thermal parameters are given in Tables III and IV. Tabulations of root-mean-square amplitudes of vibrations appear in Table V.[19] Calculated and observed structure amplitudes appear in Table VI.[19]

Crystallographic Study of $[OsCl_2(CO)(NO)(PPh_3)_2][BF_4]$. The crystallographic study of the material thought to be $[OsClH(CO)(NO)(PPh_3)_2][BF_4]$ proceeded along the lines described above. Data were collected at −158 °C using a cold gas system designed by Huffman.[20] On the basis of the eventual structural refinement the compound is actually $[OsCl_2(CO)(NO)(PPh_3)_2][BF_4]$ with both cation and ion having crystallographically imposed C_2 symmetry. Pertinent details of data collection and refinement are given in Table VII.

Final positional and thermal parameters are tabulated in Tables VIII and IX. Root-mean-square amplitudes of motion are given in Table X.[19] A listing of the observed and calculated structure amplitudes appears as Table XI.[19]

Results and Discussion

Structure of $[OsCl_2(CO)(NO)(PPh_3)_2][BF_4]$. With two formula units in space group $P2_12_12$, twofold symmetry is imposed crystallographically on the cation and anion of this compound. In view of the method of preparation from the reaction of HBF_4 with $OsCl(CO)(NO)(PPh_3)_2$ and the presence of a sharp, strong band at 2127 cm^{-1} we believed the cation could be $OsClH(CO)(NO)(PPh_3)_2{}^+$. However, this formulation is precluded by the results of a least-squares refinement of the X-ray data in which the occupancy of the Cl atom was included as a variable. Starting at 0.5 (for the chlorohydrido formulation), the occupancy converged to 0.95

Table III. Positional and Thermal Parameters for the Nongroup Atoms of $OsCl_2(CO)(HNO)(PPh_3)_2\cdot{}^1/_2CH_2Cl_2$

ATOM	X[A]	Y	Z	B11[B]	B22	B33	B12	B13	B23
OS	-0.010818(22)	0.132805(7)	0.028641(25)	5.870(21)	0.644(2)	4.722(31)	0.076(5)	1.190(17)	0.115(6)
P(1)	0.15991(13)	0.17405(4)	0.16827(15)	6.41(12)	0.65(1)	5.77(17)	0.00(3)	1.40(11)	0.09(4)
P(2)	-0.18427(13)	0.09273(4)	-0.10646(15)	6.53(12)	0.68(1)	5.45(16)	-0.02(3)	1.20(11)	0.11(4)
CL(1)	-0.15574(14)	0.15725(5)	0.15956(16)	7.81(13)	0.96(1)	8.24(19)	0.39(3)	2.74(12)	-0.15(4)
CL(2)	0.06191(16)	0.07858(5)	0.19326(17)	9.75(16)	0.94(1)	9.29(20)	0.26(4)	1.84(14)	0.45(4)
C(1)	-0.05483(60)	0.17258(23)	-0.11089(75)	6.91(57)	1.32(9)	8.09(88)	-0.99(18)	1.76(55)	-0.28(22)
O(1)	-0.07448(49)	0.19267(15)	-0.19178(59)	11.22(57)	1.06(5)	12.06(78)	-0.13(14)	1.11(51)	0.68(17)
N	0.10691(51)	0.10938(19)	-0.06267(62)	7.41(50)	1.30(7)	8.44(75)	-0.58(15)	2.62(49)	-1.11(18)
O(2)	0.14164(51)	0.11568(18)	-0.16442(58)	11.36(59)	1.79(7)	10.93(76)	-0.68(17)	5.37(55)	-0.84(19)
H(1)	0.1645(110)	0.0889(33)	-0.0237(126)	5.3(39)					
C(2)	0.4756(66)	-0.0063(15)	0.5561(58)	61.5(148)	5.9(8)	41.3(121)	-11.7(29)	17.8(111)	6.2(21)
CL(3)	0.3254(9)	0.0236(3)	0.4846(8)	36.3(16)	2.4(1)	22.1(13)	-2.3(3)	6.1(11)	-0.6(3)
CL(4)	0.5883(17)	0.0033(4)	0.4916(16)	40.4(24)	2.9(2)	27.7(16)	2.7(5)	14.3(18)	0.4(4)

[A] ESTIMATED STANDARD DEVIATIONS IN THE LEAST SIGNIFICANT FIGURE(S) ARE GIVEN IN PARENTHESES IN THIS AND ALL SUBSEQUENT TABLES. [B] THE FORM OF THE ANISOTROPIC THERMAL ELLIPSOID IS: $EXP[-(B11H^2+B22K^2+B33L^2+2B12HK+2B13HL+2B23KL)]$. THE QUANTITIES GIVEN IN THE TABLE ARE THE THERMAL COEFFICIENTS X 10^3.

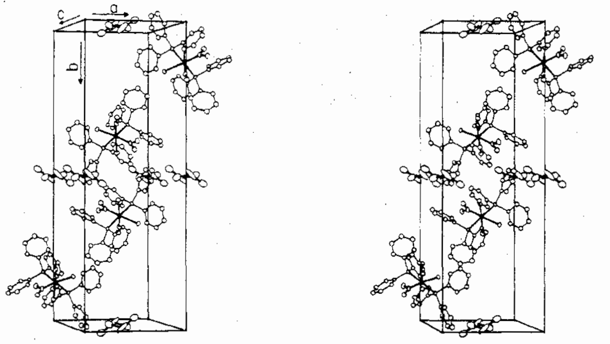

Figure 3. Stereoscopic view of the unit cell of $OsCl_2(CO)(HNO)(PPh_3)_2$. Hydrogen atoms are omitted. The 20% probability ellipsoids are shown.

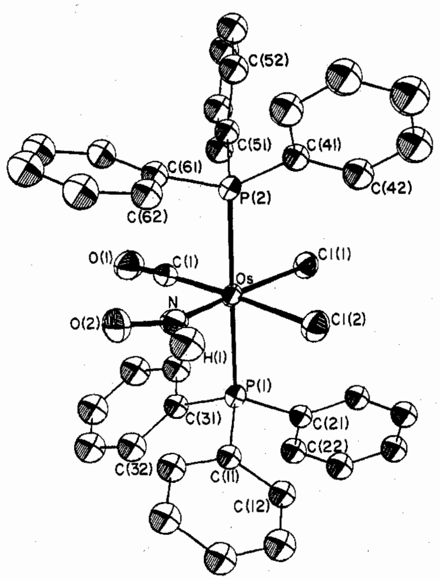

Figure 4. Drawing of $OsCl_2(CO)(HNO)(PPh_3)_2$ with phenyl hydrogen atoms removed for clarity. The 40% probability ellipsoids are shown.

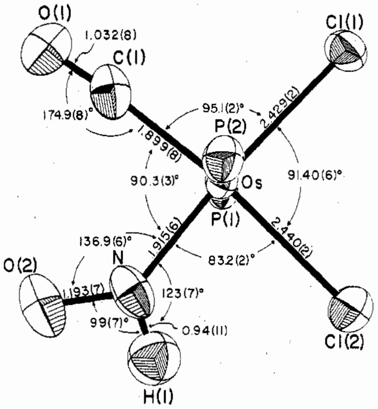

Figure 5. Inner coordination sphere of $OsCl_2(CO)(HNO)(PPh_3)_2$. Vibrational ellipsoids are drawn at the 40% level.

(2), clearly consistent with the dichloro formulation. Moreover, the final thermal parameters of the Cl ligand are reasonable.

The structure consists of discrete ions, as illustrated in Figure 1. The imposed twofold symmetry brings about disorder of the NO and CO groups of the cation (Figure 2) and precludes a useful discussion of the structure. Distances and angles are given in Table XII.

Structure of $OsCl_2(CO)(HNO)(PPh_3)_2\cdot{}^1/_2CH_2Cl_2$. The crystal structure of $OsCl_2(CO)(HNO)(PPh_3)_2\cdot{}^1/_2CH_2Cl_2$ consists of discrete molecules with no unusual intermolecular contacts. A stereoview of the unit cell packing is depicted in Figure 3, which also shows the disorder of the CH_2Cl_2 solvate molecules. Intramolecular distances and angles are given in Table XIII.

The molecular structure is illustrated in Figure 4 and the inner coordination sphere, with important metric parameters, is shown in Figure 5. The geometry about the Os center is octahedral with trans phosphine groups, cis chloro ligands, a carbonyl group, and the HNO ligand. This is precisely the structure proposed by Grundy et al.[2] The Os–P, Os–Cl, and Os–C(O) distances found in the present structures are within

Table IV. Derived Parameters for the Rigid-Group Atoms of $OsCl_2(CO)(HNO)(PPh_3)_2 \cdot {}^1/_2CH_2Cl_2$

ATOM	X	Y	Z	B,A^2	ATOM	X	Y	Z	B,A^2
C(11)	0.31294(30)	0.14815(11)	0.20416(42)	2.87(9)	C(41)	-0.22560(42)	0.04669(11)	-0.03117(45)	3.11(10)
C(12)	0.36799(37)	0.13468(12)	0.33749(37)	3.29(10)	C(42)	-0.23764(46)	0.04835(12)	0.10388(44)	4.24(13)
C(13)	0.48283(38)	0.11363(13)	0.36553(36)	4.42(14)	C(43)	-0.28381(53)	0.01516(16)	0.16117(40)	5.47(17)
C(14)	0.54263(32)	0.10604(12)	0.26023(48)	4.32(13)	C(44)	-0.31794(53)	-0.01970(13)	0.08342(55)	6.05(19)
C(15)	0.48758(39)	0.11950(13)	0.12690(41)	4.29(13)	C(45)	-0.30590(51)	-0.02137(11)	-0.05163(53)	5.12(16)
C(16)	0.37274(39)	0.14056(13)	0.09886(33)	3.79(12)	C(46)	-0.25973(47)	0.01183(14)	-0.10893(38)	4.61(14)
C(21)	0.14734(37)	0.19053(11)	0.33812(32)	2.82(10)	C(51)	-0.34092(31)	0.11700(11)	-0.16743(48)	3.12(10)
C(22)	0.19695(39)	0.22772(10)	0.38935(41)	3.72(12)	C(52)	-0.44476(41)	0.09290(9)	-0.22930(50)	4.16(13)
C(23)	0.19209(41)	0.23971(10)	0.52113(44)	4.31(13)	C(53)	-0.56528(34)	0.11000(13)	-0.27648(54)	4.88(15)
C(24)	0.13761(43)	0.21451(12)	0.60168(34)	4.09(13)	C(54)	-0.58198(33)	0.15117(13)	-0.26180(56)	4.74(14)
C(25)	0.08800(40)	0.17732(11)	0.55045(39)	3.78(12)	C(55)	-0.47814(44)	0.17527(9)	-0.19993(54)	4.77(15)
C(26)	0.09286(37)	0.16533(9)	0.41867(41)	3.14(10)	C(56)	-0.35761(36)	0.15819(11)	-0.15275(50)	4.04(13)
C(31)	0.17877(42)	0.22103(11)	0.08118(45)	3.22(11)	C(61)	-0.14090(39)	0.07849(12)	-0.26325(38)	3.18(10)
C(32)	0.28782(34)	0.23178(13)	0.03988(53)	4.54(14)	C(62)	-0.05470(42)	0.04722(12)	-0.26074(41)	3.93(13)
C(33)	0.28933(41)	0.26712(15)	-0.03450(56)	5.39(17)	C(63)	-0.00886(42)	0.03949(12)	-0.37620(52)	4.98(16)
C(34)	0.18178(52)	0.29170(12)	-0.06759(54)	5.66(18)	C(64)	-0.04921(48)	0.06303(15)	-0.49417(42)	5.29(17)
C(35)	0.07273(41)	0.28095(13)	-0.02630(57)	5.53(17)	C(65)	-0.13542(46)	0.09430(13)	-0.49667(39)	4.80(15)
C(36)	0.07122(35)	0.24561(14)	0.04809(52)	4.50(14)	C(66)	-0.18126(38)	0.10203(11)	-0.38121(46)	3.74(12)

RIGID GROUP PARAMETERS

GROUP	X_C[A]	Y_C	Z_C	DELTA[B]	EPSILON	ETA
GRP 11	0.42779(26)	0.12709(8)	0.23219(32)	0.9988(29)	2.6427(23)	1.6623(30)
GRP 12	0.14247(24)	0.20252(8)	0.46990(30)	2.6569(26)	-2.9000(21)	-1.7372(26)
GRP 13	0.18027(31)	0.25637(9)	0.00679(33)	1.3711(28)	-2.8593(31)	2.5469(31)
GRP 21	-0.27177(29)	0.01349(9)	0.02612(36)	2.9530(60)	2.1084(27)	-1.7649(61)
GRP 22	-0.46145(29)	0.13408(9)	-0.21462(32)	-0.3987(24)	-2.9202(31)	0.1066(31)
GRP 23	-0.09506(28)	0.07076(9)	-0.37871(34)	0.6298(31)	2.7760(25)	1.7419(30)

[A] X_C, Y_C, AND Z_C ARE THE FRACTIONAL COORDINATES OF THE ORIGIN OF THE RIGID GROUP. [B] THE RIGID GROUP ORIENTATION ANGLES DELTA, EPSILON, AND ETA(RADIANS) HAVE BEEN DEFINED PREVIOUSLY: S.J. LA PLACA AND J.A. IBERS, ACTA CRYSTALLOGR., 18, 511(1965).

the normal ranges. However, it is curious that the Os–Cl distance of 2.353 (3) Å in the cationic complex is so much shorter than those of 2.429 (2) and 2.440 (2) Å in the closely related neutral complex.

The HNO group is the focus of major interest in the neutral complex since this is the first structural characterization of that group as a coordinated ligand. The HNO ligand is coplanar with the $OsCl_2(CO)$ portion of the molecule, the largest deviation from the plane being 0.1 (1) Å for H(1). The distances and angle within the coordinated HNO ligand of H–N = 0.94 (11) Å, N–O = 1.193 (7) Å, and H–N–O = 99 (7)° compare favorably with those of 1.026 Å, 1.211 Å, and 108.5° in the thermally unstable free molecule.[21] The closest metal complex for structural comparison is $PdCl_2(PhNO)_2$,[22] in which the nitrogen atoms of the N-bound nitrosobenzene ligands are also sp^2 hybridized in the square plane of the metal and have N–O distances of 1.209 (3) Å.

The species $[OsCl_2(CO)(NO)(PPh_3)_2]^+$ and $OsCl_2(CO)(HNO)(PPh_3)_2$ are closely related, differing mainly in the presence or absence of H$^-$. This suggests that here the hydrogen atom on the coordinated nitrosyl hydride ligand, which has been referred to as a "protonated nitrosyl",[4] is not protonic but hydridic. In support of this idea the osmium nitrosyl hydride complex was not deprotonated by excess $[N(C_2H_5)_4]OH$ over a 4-h period. It would be interesting to compare the metal–HNO interaction with analogous metal–HCO interactions. However, we have been unsuccessful in finding a description of a metal–formyl structure in the literature.

Proton and Phosphorus-31 NMR Spectra for $OsCl_2(CO)(HNO)(PPh_3)_2$. We felt that the solid-state structural definition of $OsCl_2(CO)(HNO)(PPh_3)_2$ could be usefully complemented by examining the solution structure, especially if the technique employed were inherently more sensitive to the position of the hydrogen nucleus than is the X-ray method. For that reason ^1H NMR spectra were recorded. Figure 6 (top) shows the ^1H NMR spectrum of $OsCl_2(CO)(H^{14}NO)(PPh_3)_2$ in C_6D_6 between $\delta = 5.5$ and $\delta = 23.0$. The singlet at low field ($\delta = 21.2$) we attribute to the HNO proton

Table VII. Crystal Data and Data Collection Parameters for $[OsCl_2(CO)(NO)(P(C_6H_5)_3)_2][BF_4]$

formula	$C_{37}H_{30}BCl_2F_4NO_2OsP_2$
formula weight	930.52 amu
space group	$D_2{}^3$-$P2_12_12$
a	11.295 (7) Å
b	14.618 (10) Å
c	10.657 (8) Å
V	1759.6 Å^3
Z	2
ρ_{calcd} (−158 °C)	1.756 g cm^{-3}
ρ_{obsd} (room temp.)	1.70 g cm^{-3}
data collection temp	−158 ± 1 °C[a]
crystal shape	needle of approx dimensions 0.13 × 0.13 × 0.35 mm
crystal vol	0.0064 mm^3
radiation	Mo Kα (λ(Mo Kα_1) 0.709 30 Å), monochromatized from the (002) face of mosaic graphite
linear absorption coeff	39.2 cm^{-1}
transmission factors	0.533–0.696
detector aperture	5.5-mm wide by 3.5-mm, 30 cm from sample
takeoff angle	2.8°
scan speed	2.0° in 2θ/min
2θ limits	3.5–66.5°
bkgd counts	10 s at each end of scan with rescan option
scan range	0.9° below Kα_1 to 0.9° above Kα_2
data collected	$h \geq 0, k \geq 0, l \geq 0$
p	0.04
unique data, $F_o{}^2 > 3\sigma(F_o{}^2)$	3228
final no. of variables	101
error in observn of unit weight, electrons	2.30 e
R	0.069
R_w	0.081

[a] This error was estimated by frequent monitoring of the temperature of the cold stream ca. 1 cm upstream from the sample.

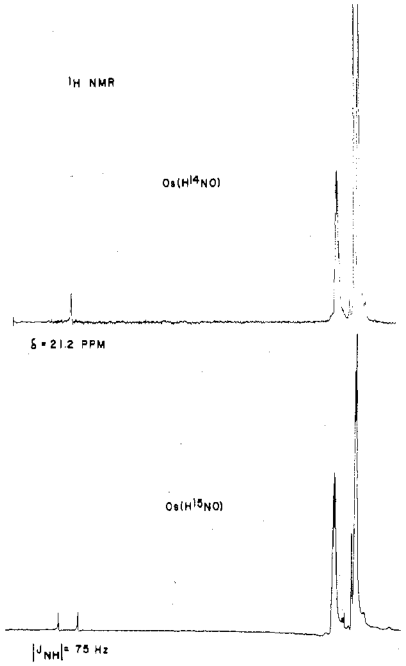

Figure 6. ^{1}H NMR spectra of $OsCl_2(CO)(H^{14}NO)(PPh_3)_2$ (top) and $OsCl_2(CO)(H^{15}NO)(PPh_3)_2$ (bottom) in C_6D_6 for the 5.5–23.0-ppm region.

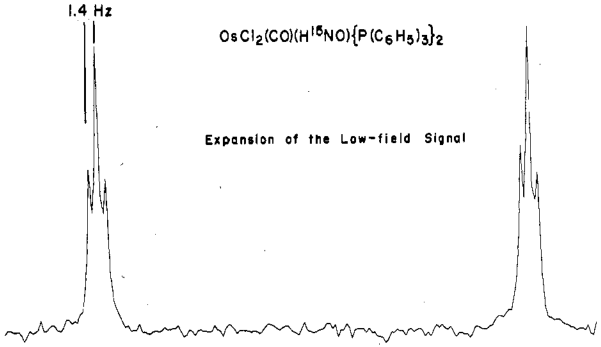

Figure 7. High-resolution view of the signal centered at δ = 21.2 for $OsCl_2(CO)(H^{15}NO)(PPh_3)_2$.

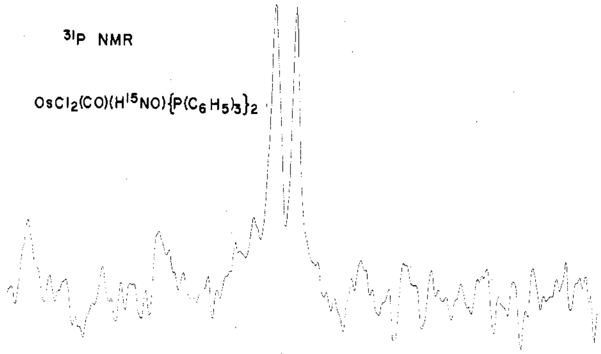

Figure 8. ^{31}P NMR spectrum of $OsCl_2(CO)(H^{15}NO)(PPh_3)_2$. The center of the doublet is −13.51 ppm from H_3PO_4.

on the basis of the similarly low-field proton resonance for metal–formyl complexes[23] and for OsC(=S)H and OsC(=NR)H systems.[24] This represents the first time the ^{1}H NMR signal for the nitrosyl hydride hydrogen nucleus in M(HNO) complexes has been clearly observed, and the chemical shift reported here is very different from the value of δ = 7.9 indirectly deduced for the HNO proton resonance in $[CoBr(das)_2(HNO)][ClO_4]_2$ (das = *o*-phenylenebis(dimethylarsine)).[4]

As further proof of the correct assignment of the δ = 21.2 signal, the spectrum of $OsCl_2(CO)(H^{15}NO)(PPh_3)_2$ in C_6D_6 was recorded over the same region. (Figure 6, bottom). A splitting of the low-field resonance by the spin = $^1/_2$ ^{15}N nucleus is evident. The |^{1}H–^{15}N| coupling constant of 75 Hz observed here is in the range 65–75 Hz reported for the one-bond coupling constant in coordinated PhN=^{15}NH[25] and is very different from the smaller (4–5 Hz) two-bond coupling constant for phenyldiazene complexes. This implies the connectivity of the ligand is HNO as opposed to HON, and taken together with the X-ray results provides unequivocal evidence for the presence of the N-bound HNO ligand in $OsCl_2(CO)(HNO)(PPh_3)_2$.

The apparent doublet in the low-field region of the proton spectrum of the ^{15}N-labeled material is actually more complex when viewed at higher resolution. Figure 7 shows an expansion of this region. Virtual coupling of the proton to the two equivalent phosphorus atoms is indicated by this spectrum. It is noteworthy that the 1.4-Hz splitting within the triplets of Figure 7 is of the same order of magnitude as the |^{31}P–^{15}N| coupling constant (2.1 Hz) found in the ^{31}P spectrum (Figure 8).

Infrared Spectroscopic Study of $OsCl_2(CO)(HNO)(PPh_3)_2$ and $OsCl(CO)(NO)(PPh_3)_2$. A concomitant benefit of the NMR analysis of both ^{14}N and ^{15}N-labeled material was the availability of these compounds for IR study. The N–O stretching frequency of 1410 cm^{-1} reported[2] for $OsCl_2(CO)(HNO)(PPh_3)_2$ had not been substantiated by isotopic substitution, although this assignment had been used as primary evidence for the existence of new (HNO) complexes.[3] An inspection of Table I will show that the assignment by Grundy et al.[2] is indeed correct. On ^{15}N substitution only the band at 1410 cm^{-1} shifts significantly, with a frequency de-

Table VIII. Positional and Thermal Parameters for the Nongroup Atoms of $[OsCl_2(CO)(NO)(PPh_3)_2][BF_4]$

ATOM	X	Y	Z	B11	B22	B33	B12	B13	B23
OS	0	1/2	0.148992(55)	18.46(30)	19.15(20)	56.66(48)	5.05(39)	0	0
P	0.21096(22)	0.45911(17)	0.13988(29)	21.3(15)	14.74(94)	57.1(25)	-0.8(10)	-3.1(19)	1.2(14)
CL	-0.03209(23)	0.38539(19)	-0.00224(33)	37.8(19)	26.1(11)	87.7(29)	0.6(11)	-0.7(18)	-13.4(16)
C/N	-0.03394(89)	0.40943(97)	0.2690(13)	16.4(57)	56.2(75)	85.(13)	-6.3(56)	9.3(73)	-8.8(84)
O	-0.05642(94)	0.34911(89)	0.3329(10)	59.6(87)	73.1(74)	95.(12)	2.5(68)	1.5(83)	26.8(80)
B	1/2	0	0.4025(17)	115.(18)	102.(14)	9.(13)	75.(18)	0	0
F(1)	0.4077(10)	0.01696(65)	0.48499(96)	217.(14)	45.1(65)	150.(11)	57.3(76)	133.(11)	43.7(70)
F(2)	0.5194(11)	0.07206(92)	0.3351(12)	82.(14)	126.6(94)	302.(20)	33.0(94)	66.(16)	153.(11)

Table IX. Derived Parameters for the Rigid-Group Atoms of $[OsCl_2(CO)(NO)(PPh_3)_2][BF_4]$

ATOM	X	Y	Z	B,A^2	ATOM	X	Y	Z	B,A^2
C(11)	0.23423(73)	0.35596(40)	0.23205(65)	1.99(18)	C(24)	0.40238(69)	0.39611(62)	-0.23142(61)	2.88(22)
C(12)	0.21894(75)	0.36106(42)	0.36175(68)	2.45(19)	C(25)	0.28575(70)	0.42724(60)	-0.23703(55)	3.03(22)
C(13)	0.23227(84)	0.28283(56)	0.43536(51)	3.31(24)	C(26)	0.22498(52)	0.44815(54)	-0.12675(70)	2.58(20)
C(14)	0.26089(79)	0.19949(44)	0.37927(67)	3.19(26)	C(31)	0.30155(73)	0.55164(44)	0.20482(78)	1.91(17)
C(15)	0.27618(74)	0.19438(39)	0.24957(70)	2.39(20)	C(32)	0.30659(76)	0.63079(53)	0.13189(64)	2.80(21)
C(16)	0.26284(77)	0.27262(49)	0.17596(50)	2.30(19)	C(33)	0.37072(85)	0.70641(45)	0.17382(80)	3.27(26)
C(21)	0.28083(63)	0.43793(54)	-0.01085(56)	2.09(17)	C(34)	0.42980(83)	0.70287(51)	0.28866(87)	3.23(24)
C(22)	0.39746(64)	0.40679(59)	-0.00523(59)	2.74(21)	C(35)	0.42476(88)	0.62372(63)	0.36159(72)	4.40(31)
C(23)	0.45824(52)	0.38588(61)	-0.11552(78)	3.40(25)	C(36)	0.36063(88)	0.54811(50)	0.31967(77)	4.10(32)

RIGID GROUP PARAMETERS

GROUP	X_C	Y_C	Z_C	DELTA	EPSILON	ETA
GRP 1	0.24756(41)	0.27772(35)	0.30566(50)	-2.7753(95)	2.1811(41)	-1.765(10)
GRP 2	0.34161(47)	0.41702(33)	-0.12113(51)	1.2699(63)	2.5759(41)	1.5073(63)
GRP 3	0.36568(53)	0.62726(39)	0.24674(57)	-2.6740(91)	-2.1657(55)	-0.6083(95)

Table XII. Selected Distances (Å) and Angles (deg) for $[OsCl_2(CO)(NO)(PPh_3)_2][BF_4]$

Distances

Os–Cl	2.353 (3)	P–C(21)	1.816 (7)
Os–C/N	1.881 (14)	P–C(31)	1.832 (8)
Os–P	2.459 (3)	B–F(1)	1.386 (14)
C/N–O	1.143 (16)	B–F(2)	1.294 (15)
P–C(11)	1.819 (7)		

Angles

Cl–Os–Cl′	93.5 (2)	P–C(11)–C(16)	121.7 (5)
Cl–Os–C/N	86.2 (4)	P–C(21)–C(22)	115.3 (5)
Cl–Os–C/N′	177.1 (3)	P–C(21)–C(26)	124.6 (5)
C/N–Os–C/N′	94.3 (8)	P–C(31)–C(32)	115.1 (6)
P–Os–Cl	87.1 (1)	P–C(31)–C(36)	124.8 (6)
P–Os–Cl′	89.8 (1)	C(11)–P–C(21)	105.9 (4)
P–Os–C/N	93.1 (3)	C(11)–P–C(31)	109.1 (4)
P–Os–C/N′	90.0 (3)	C(21)–P–C(31)	102.6 (4)
P–Os–P′	175.5 (1)	F(1)–B–F(2)	109.5 (7)
Os–P–C(11)	108.7 (3)	F(1)–B–F(1)′	101.3 (15)
Os–P–C(21)	119.8 (3)	F(1)–B–F(2)′	111.8 (8)
Os–P–C(31)	110.3 (3)	F(2)–B–F(2)′	112.5 (19)
P–C(11)–C(12)	118.2 (5)		

Table XIII. Distances (Å) and Angles (deg) in $OsCl_2(CO)(HNO)(PPh_3)_2 \cdot {}^1/_2CH_2Cl_2$

Distances

Os–Cl(1)	2.429 (2)	P(1)–C(11)	1.824 (4)
Os–Cl(2)	2.440 (2)	P(1)–C(21)	1.828 (4)
Os–P(1)	2.444 (2)	P(1)–C(31)	1.827 (4)
Os–P(2)	2.424 (2)	P(2)–C(41)	1.814 (4)
Os–C(1)	1.899 (8)	P(2)–C(51)	1.842 (4)
Os–N	1.915 (6)	P(2)–C(61)	1.815 (5)
C(1)–O(1)	1.032 (8)	C(2)–Cl(3)	1.89 (8)
N–O(2)	1.193 (7)	C(2)–Cl(4)	1.55 (4)
N–H(1)	0.94 (11)		

Angles

Cl(1)–Os–Cl(2)	91.40 (6)	Os–N–O(2)	136.9 (6)
Cl(1)–Os–P(1)	90.13 (5)	Os–N–H(1)	123 (7)
Cl(1)–Os–P(2)	88.26 (5)	O(2)–N–H(1)	99 (7)
Cl(1)–Os–C(1)	95.1 (2)	Os–P(1)–C(11)	111.6 (1)
Cl(1)–Os–N	174.6 (2)	Os–P(1)–C(21)	118.7 (1)
Cl(2)–Os–P(1)	87.56 (5)	Os–P(1)–C(31)	111.5 (1)
Cl(2)–Os–P(2)	92.60 (5)	Os–P(2)–C(41)	118.0 (1)
Cl(2)–Os–C(1)	173.5 (2)	Os–P(2)–C(51)	117.8 (1)
Cl(2)–Os–N	83.2 (2)	Os–P(2)–C(61)	107.1 (1)
P(1)–Os–P(2)	178.38 (5)	C(11)–P(1)–C(21)	103.6 (2)
P(1)–Os–C(1)	92.6 (2)	C(11)–P(1)–C(31)	107.0 (2)
P(1)–Os–N	90.1 (2)	C(21)–P(1)–C(31)	103.5 (2)
P(2)–Os–C(1)	87.4 (2)	C(41)–P(2)–C(51)	101.8 (2)
P(2)–Os–N	91.5 (2)	C(41)–P(2)–C(61)	106.6 (2)
C(1)–Os–N	90.3 (3)	C(51)–P(2)–C(61)	104.2 (2)
Os–C(1)–O(1)	174.9 (8)	Cl(3)–C(2)–Cl(4)	115 (2)

crease of 17 cm^{-1}. Weakening of the N–O bond upon coordination is implied by this $\nu(NO)$ value since in the free HNO molecule a value of 1563 cm^{-1} has been found.[26]

An unsuccessful attempt was made to assign the N–H stretching vibration. Failure to observe a $\nu(NH)$ band above 3100 cm^{-1} in the IR spectrum was also noted for $ReCl_2(NO)(HNO)(PPh_3)_2$.[3] There hydrogen bonding was thought to be a possible cause. There is no evidence for hydrogen bonding in the present structure.

Grundy et al.[2] reported a single value of 1560 cm^{-1} for the strong $\nu(NO)$ absorption of $OsCl(CO)(NO)(PPh_3)_2$. There are actually three nitrosyl bands in this compound, as verified by isotopic substitution (Table I). These occur in the Nujol mulls of crushed single crystals, in uncrushed single crystals, and even in solution. The relative intensities of the three bands change in going from CH_2Cl_2 solution to the mull. This paradox of an excessive number of observed nitrosyl stretching bands is not novel, another example being that of $CoCl_2(NO)(PMePh_2)_2$.[27] A possible explanation for the present system is that there are actually three structures in dynamic equilibrium in solution.

Summary

We have provided unequivocal structural and spectroscopic evidence for the presence of the N-bound HNO ligand in $OsCl_2(CO)(HNO)(PPh_3)_2$. Since the HNO molecule is thermally unstable, the present compound is another illustration of the stabilization of molecular species on transition metals.

The mechanism of formation of this compound from the reaction of HCl with $OsCl(CO)(NO)(PPh_3)_2$ is unknown. The reaction could be concerted, or there could be a metal hydride or a cationic five-coordinate HNO complex as an intermediate. Potentially, substitution of the noncoordinating acid HBF_4 for HCl in the reaction could result in species that would aid in distinguishing among these several possibilities. Unfortunately, only $[OsCl_2(CO)(NO)(PPh_3)_2][BF_4]$ was isolated from this reaction mixture. Its isolation provides no clues as to the mechanism of the original reaction.

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Registry No. $OsCl(CO)(NO)(PPh_3)_2$, 22186-54-5; $OsCl(CO)(^{15}NO)(PPh_3)_2$, 68378-76-7; $OsCl_2(CO)(HNO)(PPh_3)_2 \cdot {}^1/_2CH_2Cl_2$, 68378-77-8; $OsCl_2(CO)(H^{15}NO)(PPh_3)_2$, 68378-78-9; $[OsCl_2(CO)(NO)(PPh_3)_2](BF_4)$, 68378-80-3; $OsCl_2(CO)(DNO)(PPh_3)_2$, 68378-63-2; $OsClH(CO)(PPh_3)_3$, 16971-31-6; $(NH_4)_2OsCl_6$, 12125-08-5; $CH_3(C_6H_4)SO_2N(CH_3)(NO)$, 80-11-5; $CH_3(C_6H_4)SO_2N(CH_3)(^{15}NO)$, 68378-95-0; $Na^{15}NO_2$, 68378-96-1.

Supplementary Material Available: Root-mean-square amplitudes of vibration (Tables V and X) and listings of structure amplitudes (Tables VI and XI) (62 pages). Ordering information is given on any current masthead page.

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