form IIIa or IIIb. However the infrared spectra of hexadecane solutions exhibit three CO stretching bands at 1997, 1986, and 1976 cm^{-1}, and the NMR spectra at room temperature show the resonance due apparently to a single isomer. A variable-temperature experiment revealed that an exchange phenomenon occurs but the slow-exchange limits were not reached. It is possible therefore to consider that an exchange between the two IIIa and IIIb isomers occurs in solution, only one isomer being present in the solid state.

For the phenylthiolato-bridged complexes the constraint occurring in the *tert*-butyl group no longer exists and the seven isomers can be expected. In Table IV, the infrared and NMR data show that in the solid state the compound can exist as a cis isomer (**18**) whereas in solution the trans isomer (**17**) can be observed.

Finally, it is of interest to compare the reactivity of thiolato-bridged carbonyl complexes to that of their chloro-bridged analog $[RhCl(CO)_2]_2$. Indeed it has been shown[21] that addition of a phosphine ligand to $[RhCl(CO)_2]_2$ gives rise to a series of equilibria between monomeric and dimeric species. On the contrary, in the present study, no monomeric species have been detected, but pentacoordinated dinuclear complexes are obtained. Both observations are in favor of more stable thiolato-bridged complexes toward bridge splitting by nucleophilic ligands.

Registry No. $[Rh(SPh)(CO)_2]_2$, 24818-80-2; $[RhCl(CO)_2]_2$, 14523-22-9; $[RhCl(CO)P(CH_3)_3]_2$, 49634-24-4; $[Rh(S\text{-}t\text{-}C_4H_9)(CO)_2]_2$, 54032-58-5; $[Rh(SC_6H_5)(CO)_2P(CH_3)_3]_2$, 56348-51-7; $[Rh(SC_6H_5)(CO)_2P(C_6H_{11})_3]_2$, 56348-52-8; $[Rh(SC_6H_5)(CO)_2P(C_6H_5)_3]_2$, 56348-53-9; $[Rh(SC_6H_5)(CO)_2P(N(CH_3)_2)_3]_2$, 56348-54-0; $[Rh(SC_6H_5)(CO)_2P(OCH_3)_3]_2$, 56348-55-1; $[Rh(S\text{-}t\text{-}C_4H_9)(CO)_2P(C_6H_{11})_3]_2$, 56348-56-2; $[Rh(S\text{-}t\text{-}C_4H_9)(CO)_2P(C_6H_5)_3]_2$, 56348-57-3; $[Rh(S\text{-}t\text{-}C_4H_9)(CO)_2P(CH_3)_2C_6H_5]_2$, 56390-02-4; $[Rh(S\text{-}t\text{-}C_4H_9)(CO)_2P(N(CH_3)_2)_3]_2$, 56348-58-4; $[Rh(S\text{-}t\text{-}C_4H_9)(CO)_2P(OCH_3)_3]_2$, 56348-59-5; $[Rh(S\text{-}t\text{-}C_4H_9)(CO)P(CH_3)_3]_2$, 54032-62-1; $[Rh(S\text{-}t\text{-}C_4H_9)(CO)P(CH_3)_2C_6H_5]_2$, 54032-64-3; $[Rh(S\text{-}t\text{-}C_4H_9)(CO)P(N(CH_3)_2)_3]_2$, 54032-66-5; $[Rh(S\text{-}t\text{-}C_4H_9)(CO)P(OCH_3)_3]_2$, 54032-68-7; $[Rh(SC_6H_5)(CO)P(CH_3)_3]_2$, 54032-61-0; $[Rh(SC_6H_5)(CO)P(N(CH_3)_2)_3]_2$, 54032-65-4; $[Rh(SC_6H_5)(CO)P(OCH_3)_3]_2$, 54032-67-6; $P(CH_3)_3$, 594-09-2; $P(OCH_3)_3$, 121-45-9.

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Aryldiazo Complexes. Syntheses and Reactions of New Complexes of Osmium and Ruthenium

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Aryldiazo complexes, $[M(CO)_2(NNPh)(PPh_3)_2][PF_6]$ (M = Os, Ru; Ph = C_6H_5), have been prepared by allowing diazonium salts to react with $M(CO)_3(PPh_3)_2$. Infrared spectra of the Ru complex suggest the presence of two isomers both in solution and in the solid state. These complexes react with a variety of coordinating anions (X^-), to form $MX(CO)_2(NNPh)(PPh_3)_2$. The osmium derivatives have $\nu(NN)$ near 1455 cm^{-1}, which is the lowest value yet reported for a nonbridging aryldiazo ligand. The first aryldiazo–hydrido complexes, $MH(CO)_2(NNPh)(PPh_3)_2$ and $MH(CO)(NNPh)(PPh_3)_2$, were prepared by deprotonation of the respective phenyldiazene complexes, $MH(CO)_2(HNNPh)(PPh_3)_2^+$ and $MH(CO)(HNNPh)(PPh_3)_3^+$. The compound $OsCl_3(NNPh)(PPh_3)_2$ has also been prepared. A large number of the foregoing complexes have been synthesized with selective ^2H and ^{15}N labels. Infrared and NMR spectra show $MX(CO)_2(NNPh)(PPh_3)_2$ and the analogous hydrido complex to be pseudooctahedral with trans phosphine ligands, cis carbonyl ligands, and a doubly bent phenyldiazenido ($NNPh^-$) ligand. Similarly, $MH(CO)(NNPh)(PPh_3)_2$ possesses a trigonal-bipyramidal geometry with trans phosphine ligands and an equatorial, singly bent phenyldiazoniumato ($NNPh^+$) ligand. Isotopic substitution of the diazo ligand shows that $\nu(NN)$ is often vibrationally coupled with phenyl vibrational modes and that two or three bands sometimes shift upon ^{15}N substitution. Vibrational coupling is also observed in the higher energy region (1850–1900 cm^{-1}) in the compound $RuCl_3(NNC_6D_5)(PPh_3)_2$. The wide range in the values of $\nu(NN)$, $RuCl_3(NNPh)(PPh_3)_2$ (1882 cm^{-1}), vs. $RuCl(CO)_2(NNPh)(PPh_3)_2$ (1462 cm^{-1}), indicates that the N–N stretching frequencies are sensitive to the electronic and steric environment of the diazo ligand. The aryldiazo complexes are compared with analogous, isoelectronic nitrosyl complexes of Os and Ru.

Introduction

Although the first molybdenum–[2] and platinum–aryldiazo[3] complexes were reported over 10 years ago, it has been only in the last several years that appreciable numbers of aryldiazo complexes have been prepared. Even so, there are relatively few such complexes known when compared with the number of analogous nitrosyl complexes. Aryldiazo complexes have been reported for all members of the Cr, Mn, Fe, Co, and Ni triads with the exception of Ni, Pd, and Tc.[4,5] Part of the interest in aryldiazo and other diazo ligands has been generated by the close relationship of these ligands to dinitrogen and nitrosyl ligands. Recent work has shown that diazo ligands can be prepared from coordinated dinitrogen in Re, Mo, and W complexes.[6] Furthermore, aryldiazo ligands resemble nitrosyl ligands, adopting both a singly bent geometry ($ArNN^+$ vs. NO^+) and a doubly bent geometry ($ArNN^-$ vs. NO^-).[7-9]

To date, only one osmium–aryldiazo complex has been reported, $OsBr_3(NNTo)(PPh_3)_2$.[9,10] Although several ruthenium complexes have been reported,[10,11] only two have been carefully characterized, $RuCl_3(NNAr)(PPh_3)_2$ and its bromo analog.[10] We now report the syntheses and characterization of a variety of new Ru and Os complexes of the type $M(CO)_2(NNAr)(PPh_3)_2^+$, $MH(CO)(NNAr)(PPh_3)_2$, $MH(CO)_2(NNAr)(PPh_3)_2$, and $MX(CO)_2(NNAr)(PPh_3)_2$, M = Ru or Os and X = halide or pseudohalide. We also report the preparation of $OsCl_3(NNPh)(PPh_3)_2$ and the preparations of many of these complexes with selective ^2H and ^{15}N isotopic labels. A preliminary report of this work has appeared previously.[8] Recently, Cenini et al. have also reported the complex $[Ru(CO)_2(NNAr)(PPh_3)_2][BF_4]$.[12]

Experimental Section

Unless otherwise noted, all reactions were performed at ambient room temperature (20–25°) in freshly distilled solvents under a nitrogen atmosphere. Most of the reactions were repeated in the presence of air without any obvious deleterious effects except when the five-coordinate ruthenium–monocarbonyl complexes were prepared. The following compounds were synthesized by the respective literature methods: $Ru(CO)_3(PPh_3)_2$,[13] $Os(CO)_3(PPh_3)_2$,[14] $RuCl_3(NNAr)(PPh_3)_2$,[10] $OsH_2(CO)(PPh_3)_3$,[13] $OsH_2(CO)_2(PPh_3)_2$,[13] $RuH_2(CO)(PPh_3)_3$,[13] $RhCl(PPh_3)_3$,[15] $OsCl_2(PPh_3)_3$,[16] $RuCl_2(PPh_3)_3$,[17] $IrCl(N_2)(PPh_3)_2$;[18] $[Et_4N]_2[OsCl_6]$ and $[Et_4N]_2[OsBr_6]$ were used instead of the analogous sodium and ammonium salts. The following compounds were prepared by modifications of published procedures: $OsBr_2(PPh_3)_3$,[16] $OsBr_2(CO)_2(PPh_3)_2$,[14] $[Et_4N]_2[OsCl_6]$,[19] $[Et_4N]_2[OsBr_6]$,[19] $[(n\text{-}Bu)_4N]_2[OsBr_6]$,[19] $OsHCl(CO)_2(PPh_3)_2$,[20] $OsHBr(CO)_2(PPh_3)_2$,[20] $RuHCl(CO)_2(PPh_3)_2$,[20] $RuHBr(CO)_2(PPh_3)_2$.[20] All of the precious metal was obtained from Matthey-Bishop, Inc., Malvern, Pa., with the exception of OsO_4 which was obtained from D. F. Goldsmith, Inc., Evanston, Ill. Aniline-d_5 was purchased from Aldrich Chemical Co., Milwaukee, Wis. Sodium nitrite-^{15}N, potassium azide-^{15}N (single nitrogen label), and aniline-^{15}N were purchased from Stohler Isotope Chemicals, Waltham, Mass. 18-Crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) was purchased from PCR, Inc., Gainesville, Fla. Elemental analyses were performed by H. Beck of Northwestern's Analytical Services Laboratory and by Micro-Tech Laboratories, Inc., Skokie, Ill. The results of these analyses appear in Table I. Infrared spectra were recorded in perfluorohydrocarbon, hexachlorobutadiene, and Nujol mulls using a Perkin-Elmer 457 double-beam spectrometer and calibrated using a polystyrene film. The NMR spectra were recorded using a Perkin-Elmer R20B spectrometer or a Bruker HFX-90 spectrometer at ambient temperatures in C_6D_6 or CD_2Cl_2 with tetramethylsilane as an internal standard. Conductivities were measured in nitrobenzene. Attempts were made to record Raman spectra of many of these compounds but with very little success. The majority decomposed even with spinning and cooling (~190 K, 6471-Å exciting frequency, 20 mW at sample). The few which did not decompose gave spectra in which were visible coordinated triphenylphosphine bands and sometimes weak carbonyl bands. Although not reported here in detail for the sake of brevity, almost all of the complexes have been prepared with substituted aryldiazonium cations (*p*-fluorophenyl, *p*-tolyl) or with a different anion (BF_4). The physical properties and chemical stabilities are all similar to those herein reported which were prepared with phenyldiazonium hexafluorophosphate.

Dicarbonyl(phenyldiazo)bis(triphenylphosphine)osmium Hexafluorophosphate (I). (a) $Os(CO)_3(PPh_3)_2$, 0.80 g, and 0.30 g of $[PhN_2][PF_6]$ were stirred in 25 ml of dichloromethane until the vigorous evolution of carbon monoxide ceased. Reaction times were about 3–4 min and no longer than 6–7 min; longer times resulted in the formation of other products. The mixture was immediately filtered to remove the excess diazonium salt, and the solvent was rapidly removed. The crude product was recrystallized from dichloromethane–ether to yield yellow crystals of the CH_2Cl_2 solvate. The yield was 89%.

(b) $Os(CO)_3(PPh_3)_2$, 0.80 g, and 0.25 g of $[PhN_2][PF_6]$ were vigorously stirred in 40 ml of benzene for 15–30 min during which time carbon monoxide was evolved, and a yellow solid deposited from solution. The reaction mixture was quickly and briefly heated to just below the boiling temperature of the solvent and *immediately* filtered while hot. The yellow microcrystalline solid was washed with benzene and dried on the filter. The yield was 90% of the benzene solvate; conductivity 21.4 Ω^{-1} cm^2 mol^{-1}.

Dicarbonyl(phenyldiazo)bis(triphenylphosphine)ruthenium Hexafluorophosphate (II). This salt was prepared exactly as its osmium analog starting with 0.71 g of $Ru(CO)_3(PPh_3)_2$. Both methods were used and similar yields were obtained; conductivity 22.5 Ω^{-1} cm^2 mol^{-1}.

Chlorodicarbonyl(phenyldiazo)bis(triphenylphosphine)osmium (IIIb). To 0.51 g of $[Os(CO)_2(NNPh)(PPh_3)_2][PF_6]$ dissolved in 6 ml of dry acetone, a solution of LiCl (0.09 g) in anhydrous methanol (1 ml) was added dropwise with stirring until the color had completely changed from yellow to deep green; a few extra drops of the lithium chloride solution were added. Almost immediately, blue-green crystals of the product crystallized out of solution as the 1:1 acetone solvate in good yield (81%). If crystallization did not take place within 30 sec of the chloride addition, the glass reaction flask was rubbed with a metal spatula to induce crystallization. The product was washed with a small amount of 50:50 acetone–ether. The product can be recrystallized from dichloromethane–acetone.

Fluorodicarbonyl(phenyldiazo)bis(triphenylphosphine)osmium (IIIa). This compound was prepared exactly as IIIb using a solution of $[Et_4N][F]\cdot 2H_2O$, 0.30 g in 2 ml of methanol; 72% yield.

Bromodicarbonyl(phenyldiazo)bis(triphenylphosphine)osmium (IIIc). Preparation was exactly as for IIIb using a solution of LiBr, 0.18 g in 1 ml methanol; 79% yield.

Iododicarbonyl(phenyldiazo)bis(triphenylphosphine)osmium (IIId). This compound was prepared exactly as IIIb using a solution of LiI, 0.27 g in 1 ml of methanol; 75% yield.

Isocyanatodicarbonyl(phenyldiazo)bis(triphenylphosphine)osmium (IIIe). The procedure was exactly as that for IIIb using 10 ml of acetone (instead of 6 ml) and a basic solution of NaNCO, 0.13 g in 3 ml of water with a trace of NaOH (pH 12); 80% yield. A neutral solution of $[KC_{12}H_{24}O_6][NCO]$ was also used, 0.16 g of KNCO and 0.6 g of recrystallized 18-crown-6 in 2 ml of methanol.

Azidodicarbonyl(phenyldiazo)bis(triphenylphosphine)osmium (IIIf). This compound was prepared exactly as IIIb using a solution of LiN_3, 0.10 g in 1 ml of methanol; 61% yield.

Azido-^{15}N-dicarbonyl(phenyldiazo)bis(triphenylphosphine)osmium. This compound was prepared exactly as IIIb using a solution of $[KC_{12}H_{24}O_6][^{15}N^{14}N_2]$, 0.16 g of labeled KN_3 and 0.6 g of recrystallized 18-crown-6 in 2 ml of methanol; 57% yield.

Nitritodicarbonyl(phenyldiazo)bis(triphenylphosphine)osmium (IIIg). Preparation was exactly as IIIb using a solution of $LiNO_2\cdot H_2O$, 0.15 g in 1 ml of methanol; 82% yield.

Nitrito-^{15}N-dicarbonyl(phenyldiazo)bis(triphenylphosphine)osmium. This compound was prepared exactly as IIIb using 10 ml of acetone and a basic solution of labeled $NaNO_2$, 0.14 g in 3 ml of water with a trace of NaOH (pH 12); 80% yield. A neutral solution of $[NaC_{12}H_{24}O_6][^{15}NO_2]$ was also used, 0.14 g of labeled $NaNO_2$ and 1.0 g of recrystallized 18-crown-6 in 2 ml of methanol.

Formatodicarbonyl(phenyldiazo)bis(triphenylphosphine)osmium (IIIh). This compound was prepared exactly as IIIb using a solution of $LiHCO_2\cdot H_2O$, 0.14 g in 1 ml of methanol; 74% yield.

Acetatodicarbonyl(phenyldiazo)bis(triphenylphosphine)osmium (IIIi). The procedure was exactly as IIIb using a solution of $LiCH_3CO_2\cdot 2H_2O$, 0.20 g in 1 ml of methanol; 72% yield.

Chlorodicarbonyl(phenyldiazo)bis(triphenylphosphine)ruthenium (IVa). This compound was prepared exactly as IIIb using 0.47 g of II, $[Ru(CO)_2(NNPh)(PPh_3)_2][PF_6]$; 86% yield of chocolate brown crystals.

Bromodicarbonyl(phenyldiazo)bis(triphenylphosphine)ruthenium (IVb). This compound was prepared exactly as IIIc using 0.47 g of II; 74% yield.

Isocyanatodicarbonyl(phenyldiazo)bis(triphenylphosphine)ruthenium (IVc). This compound was prepared exactly as IIIe using 0.47 g of II; 76% yield.

Iododicarbonyl(phenyldiazo)bis(triphenylphosphine)ruthenium (IVd). This compound was prepared as IIId except that the reaction was performed at −10°C and 0.47 g of II was used; 69% yield. Although the elemental analyses were satisfactory, the infrared spectra showed the presence of about 10% of the five-coordinate monocarbonyl complex (ν(CO) 1899 cm^{-1}).

Reaction of $[Os(CO)_2(NNPh)(PPh_3)_2][PF_6]$ with $NaBH_4$. Compound I (0.51 g) was refluxed with 0.20 g of $NaBH_4$ in 25 ml

Table I. Analytical Data for Aryldiazo Complexes

Compd	Color	C[a]	H	N	Cl, Br, or I
$[Os(CO)_2(NNPh)(PPh_3)_2][PF_6]\cdot{}^1/_2C_6H_6$	Yellow	53.52 (53.26)	3.35 (3.61)	2.92 (2.64)	
$[Ru(CO)_2(NNPh)(PPh_3)_2][PF_6]\cdot C_6H_6$	Lemon yellow	59.41 (59.47)	3.87 (4.09)	2.86 (2.77)	
$OsCl_3(NNPh)(PPh_3)_2\cdot CH_2Cl_2$	Yellow-brown	51.01 (51.08)	3.50 (3.63)	3.00 (2.77)	17.63 (17.53)
$OsBr_3(NNPh)(PPh_3)_2\cdot CH_2Cl_2$	Yellow-brown	45.03 (45.12)	3.03 (3.26)	2.55 (2.45)	
$RuCl_3(4\text{-}FC_6H_4NN)(PPh_3)_2\cdot CH_2Cl_2$	Green-brown	54.65 (54.94)	3.75 (3.86)	2.83 (2.98)	18.63 (18.86)
$RuCl_3(2,6\text{-}F_2C_6H_3NN)(PPh_3)_2\cdot CH_2Cl_2$	Ruby red	54.16 (53.91)	3.98 (3.68)	3.07 (2.92)	
$OsF(CO)_2(NNPh)(PPh_3)_2$	Blue-green	58.92 (59.05)	3.65 (3.94)	3.32 (3.13)	
$OsCl(CO)_2(NNPh)(PPh_3)_2\cdot C_3H_6O$	Blue-green	57.96 (58.23)	4.47 (4.26)	2.96 (2.89)	3.60 (3.66)
$OsBr(CO)_2(NNPh)(PPh_3)_2\cdot C_3H_6O$	Olive green	55.97 (55.68)	4.30 (4.08)	2.99 (2.76)	7.94 (7.88)
$OsI(CO)_2(NNPh)(PPh_3)_2\cdot{}^1/_2C_3H_6O$	Green	53.21 (52.96)	3.96 (3.71)	2.62 (2.72)	12.50 (12.30)
$Os(NCO)(CO)_2(NNPh)(PPh_3)_2\cdot{}^1/_2C_3H_6O$	Blue-green	59.16 (58.98)	3.82 (4.05)	4.64 (4.44)	
$Os(N_3)(CO)_2(NNPh)(PPh_3)_2\cdot{}^1/_2C_3H_6O$	Olive green	57.45 (57.71)	4.25 (4.05)	7.29 (7.40)	
$Os(ONO)(CO)_2(NNPh)(PPh_3)_2\cdot{}^1/_2C_3H_6O$	Gray-green	57.66 (57.47)	4.26 (4.03)	4.22 (4.42)	
$Os(HCO_2)(CO)_2(NNPh)(PPh_3)_2\cdot{}^1/_2C_3H_6O$	Blue-green	59.00 (58.79)	4.36 (4.14)	2.85 (2.95)	
$Os(CH_3CO_2)(CO)_2(NNPh)(PPh_3)_2\cdot{}^1/_2C_3H_6O$	Blue-green	58.98 (59.18)	4.13 (4.29)	2.83 (2.91)	
$OsH(CO)_2(NNPh)(PPh_3)_2$	Blue-green	60.03 (60.27)	4.22 (4.14)	2.99 (3.19)	
$OsD(CO)_2(NNPh)(PPh_3)_2$	Blue-green	60.08 (60.20)	4.40 (4.13)	3.11 (3.19)	
$RuCl(CO)_2(NNPh)(PPh_3)_2\cdot C_3H_6O$	Chocolate brown	63.99 (64.13)	4.82 (4.69)	3.44 (3.18)	3.80 (4.03)
$RuBr(CO)_2(NNPh)(PPh_3)_2\cdot C_3H_6O$	Chocolate brown	60.78 (61.04)	4.56 (4.47)	3.19 (3.03)	8.80 (8.64)
$Ru(NCO)(CO)_2(NNPh_3)_2\cdot{}^1/_2C_3H_6O$	Chocolate brown	64.94 (65.11)	4.38 (4.47)	5.17 (4.90)	
$RuI(CO)_2(NNPh)(PPh_3)_2\cdot{}^1/_2C_3H_6O$	Brown	57.89 (57.97)	3.82 (4.06)	3.21 (2.97)	
$RuH(CO)_2(NNPh)(PPh_3)_2$	Lime green; brown[b]	66.93 (67.08)	4.47 (4.61)	3.66 (3.56)	
$RuD(CO)_2(NNPh)(PPh_3)_2$	Lime green; brown[b]	67.26 (67.00)	4.71 (4.60)	3.80 (3.55)	
$OsH(CO)(NNPh)(PPh_3)_2$	Orange; brown[b]	61.03 (60.84)	4.12 (4.27)	3.44 (3.30)	
$OsD(CO)(NNPh)(PPh_3)_2$	Orange; brown[b]	60.99 (60.77)	4.40 (4.27)	3.35 (3.30)	
$RuH(CO)(NNPh)(PPh_3)_2$	Brown	68.18 (67.98)	4.98 (4.78)	3.59 (3.69)	
$RuD(CO)(NNPh)(PPh_3)_2$	Brown	68.05 (67.89)	4.68 (4.77)	3.81 (3.68)	

[a] Theoretical values in parentheses. [b] See text regarding the two solid-state forms. Both forms of the same compound gave essentially identical analyses.

of 2-methoxyethanol for 1 hr under a CO atmosphere. The solution was filtered while warm (about 50°C) and washed with methanol to yield a white, microcrystalline powder of $OsH_2(CO)_2(PPh_3)_2$; 92% yield. This same reaction was carried out at room temperature in ethanol for 1 hr under a nitrogen atmosphere. The crude product which contained substantial amounts of $OsH_2(CO)_2(PPh_3)_2$ was recrystallized from benzene–ethanol to yield the pure osmium dihydride; 59% yield.

Reaction of $[Ru(CO)_2(NNPh)(PPh_3)_2][PF_6]$ with $NaBH_4$. Compound II (0.47 g) was refluxed with 0.20 g of $NaBH_4$ and 0.50 g of triphenylphosphine in 25 ml of ethanol for 1 hr under a nitrogen atmosphere. The mixture was cooled to room temperature and filtered. The white, microcrystalline solid was washed with methanol to yield $RuH_2(CO)(PPh_3)_3$; 85% yield. This same reaction was carried out in the absence of triphenylphosphine both at room temperature and in refluxing ethanol. In both cases, a yellow, insoluble product of unknown composition was obtained.

Hydridocarbonyl(phenyldiazo)bis(triphenylphosphine)osmium (Va). In 10 ml of acetone, 1.01 g of $OsH_2(CO)(PPh_3)_3$ and 0.35 g of $[PhN_2][PF_6]$ were stirred vigorously for 15 min. An additional 0.05 g of the diazonium salt was added, and the mixture was stirred until all of the hydride dissolved and the reaction was complete (about 15–30 min more). Twenty milliliters of methanol was added to the stirring solution and it was then cooled to about –20°C. About 3 ml of a concentrated solution of NaOH in methanol was added dropwise with stirring over a period of 1–2 min. If the product did not immediately crystallize from solution, the inside of the glass reaction vessel was rubbed with a metal rod which quickly induced crystallization. The reaction mixture was removed from the cold-temperature bath and stirred for 3–5 min in order to ensure complete crystallization. The product was immediately filtered, washed with methanol, and dried under vacuum to give a brown solvent-free microcrystalline powder. The yield was 61%. The product was not allowed to remain in contact with the basic solution any longer than necessary. If the deprotonation reaction was performed at room temperature, a bright orange crystalline modification was produced in about 50% yield. The brown and orange forms had almost identical elemental analyses and infrared spectra; in solution they were identical (ir and NMR spectra). The conversion of the orange form to the more stable brown form took place immediately in solution but required about 10–20 hr in the solid state; conductivity 0.9 Ω^{-1} cm^2 mol^{-1}. When Va was recrystallized from dichloromethane, beautiful brown crystals of the 1:1 solvate resulted.

Deuteridocarbonyl(phenyldiazo)bis(triphenylphosphine)osmium (Vb). This compound was prepared exactly as Va using $OsD_2(CO)(PPh_3)_3$, CH_3OD, and $(CD_3)_2CO$. The solution of the base was made by preparing a concentrated solution of $NaOCH_3$ in CH_3OD which contained 10% D_2O by volume. The yield was 60%.

Hydridodicarbonyl(phenyldiazo)bis(triphenylphosphine)osmium (IIIj). Preparation was exactly as Va using 0.77 g of $OsH_2(CO)_2(PPh_3)_2$; there was a 74% yield of a solvent-free, blue-green, crystalline powder. This complex was washed several times with neutral methanol, but it was not allowed to remain in contact with the methanol more than 5–10 sec per washing. The product can be recrystallized from benzene–hexane; conductivity 0.8 Ω^{-1} cm^2 mol^{-1}. Attempts to prepare the analogous chloro and bromo complexes (IIIb, IIIc) by this technique using $OsHX(CO)_2(PPh_3)_2$ failed.

Deuteridodicarbonyl(phenyldiazo)bis(triphenylphosphine)osmium (IIIk). This compound was prepared exactly as IIIi using $OsD_2(CO)_2(PPh_3)_2$; yield 58%. Deuterated solvents and bases were used; see preparation of Vb.

Hydridocarbonyl(phenyldiazo)bis(triphenylphosphine)ruthenium (VIa). (a) This compound was prepared exactly as Va using 0.92 g of $RuH_2(CO)(PPh_3)_3$; yield 44%.

(b) $RuH(CO)_2(NNPh)(PPh_3)_2$, 0.40 g, was dissolved in 50 ml of oxygen-free benzene and stirred in a quartz flask at room temperature under ambient light conditions for 60 min. Most of the solvent was removed under vacuum, and the product was crystallized from benzene–hexane to give a brown crystalline powder in low yield (14%). The product prepared by this method was identical with that prepared by the first method.

Deuteridocarbonyl(phenyldiazo)bis(triphenylphosphine)ruthenium (VIb). Preparation was exactly as that for VIa, method (a), using $RuD_2(CO)(PPh_3)_3$; yield 39%. Deuterated solvents and bases were used; see preparation of Vb.

Hydridodicarbonyl(phenyldiazo)bis(triphenylphosphine)ruthenium (IVe). This compound was prepared exactly as VIa with one modification. Just prior to cooling and addition of base, carbon monoxide was added to the orange solution of $[RuH(CO)(HNNPh)(PPh_3)_3][PF_6]$ forming a yellow solution of $[RuH(CO)_2(HNNPh)(PPh_3)_2][PF_6]$ (15-min reaction time at 3 atm of CO or 30-min reaction time at 1 atm of CO). The yield was 71% of bright green crystals which slowly converted to a more stable brown form in the solid state. This conversion took place instantly in solution, and both forms had identical solution properties. Attempts to prepare the analogous chloro and bromo complexes (IVa, IVb) by this technique using $RuHX(CO)_2(PPh_3)_2$ failed.

Deuteridodicarbonyl(phenyldiazo)bis(triphenylphosphine)ruthenium (IVf). The procedure was exactly as that for IVe using $RuD_2(CO)(PPh_3)_3$; yield 57%. Deuterated solvents and bases were used; see preparation of Vb.

Trichloro(phenyldiazo)bis(triphenylphosphine)osmium (VIIa). This compound was prepared according to the published procedure for $OsBr_3(p\text{-}NNC_6H_4CH_3)(PPh_3)_2$[10] using $OsCl_2(PPh_3)_3$, $[PhN_2][PF_6]$, and LiCl. The crude product crystallized from solution as the acetone solvate which was recrystallized from dichloromethane–methanol to yield yellow-brown crystals of the 1:1 dichloromethane solvate; yield 78%.

Tribromo(phenyldiazo)bis(triphenylphosphine)osmium (VIIb). This complex was prepared exactly as VIIa except $OsBr_2(PPh_3)_3$ and LiBr were used as starting materials. The yield was 61% of yellow-brown crystals of the dichloromethane solvate.

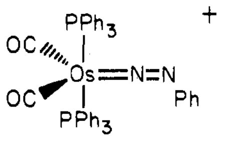
^{2}H- and ^{15}N-labeled Benzenediazonium Hexafluorophosphate. The following procedure was used to prepare small quantities of isotopically labeled benzenediazonium salts.[21] Aniline (633 mg), distilled water (2.0 ml), and concentrated aqueous hydrochloric acid (1.7 ml) were added to a small reaction flask which was cooled to about 0°C. The temperature throughout the reaction was maintained between −10 and 0°C by carefully stirring the solution and periodically immersing it in a Dry Ice–acetone bath. A sodium nitrite solution, 500 mg of $NaNO_2$ in 1.5 ml of distilled water, was added dropwise over a period of about 3 min. The solution was stirred for an additional 1 min and then tested with starch–potassium iodide paper in order to ensure that the nitrite was present in slight excess. Finally, a solution of 1.0 ml of 65% aqueous hexafluorophosphoric acid in 4.0 ml of distilled water was slowly added with stirring. The white precipitate was filtered and washed with 20 ml of distilled water at room temperature. The damp solid was then dissolved in 10 ml of acetone, and the solution was filtered. Enough absolute ethanol was added in order to begin precipitation of the salt, followed by the slow addition of a large volume of diethyl ether in order to complete precipitation. The product was filtered, washed with ether, dried under vacuum for 10 min, and stored in the dark at −10 to −20°C. The yield was 84–88% of fine, white needles which could be kept in excess of 6 months without significant decomposition. The following labeled cations were prepared: $C_6H_5{}^{14}N^{15}N^+$, $C_6H_5{}^{15}N^{14}N^+$, $C_6H_5{}^{15}N_2{}^+$, $C_6D_5{}^{14}N_2{}^+$, $C_6D_5{}^{14}N^{15}N^+$, and $2,6\text{-}F_2C_6H_3{}^{14}N^{15}N^+$.

Discussion

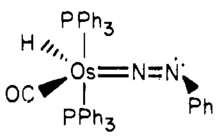
Preparations of New Compounds. Similar to the reaction with the iron analog,[22,23] $Ru(CO)_3(PPh_3)_2$ and $Os(CO)_3(PPh_3)_2$ both react with aryldiazonium salts in dichloromethane or benzene at room temperature with the evolution of 1 mol of carbon monoxide (see eq 1). Although others have claimed that these ruthenium and osmium tricarbonyl complexes are resistant to substitution,[24,25] the reaction with benzenediazonium cations takes place smoothly and rapidly under mild conditions. The resulting yellow, crystalline products are 1:1 electrolytes in nitrobenzene. They are slightly sensitive to light in the solid state but are stable for several months when stored at 0°C in the dark. In acetone or methylene chloride solution, they are less stable. As judged by infrared spectra of acetone solutions, the half-lives of the Ru and Os complexes are about 1 and 3 hr, respectively, yielding unidentified carbonyl-containing decomposition products. If the reaction solvents were not completely free from moisture or alcohols, the products sometimes contained small amounts of a phenyldiazene impurity which appeared to be the PF_6 analogs of $[Ru(OClO_3)(CO)_2(HNNPh)(PPh_3)_2][ClO_4]$ (ν(CO) 2041, 2090 cm^{-1}) and $[Os(OClO_3)(CO)_2(HNNPh)(PPh_3)_2][ClO_4]$ (ν(CO) 2028, 2080 cm^{-1}). These phenyldiazene complexes are easily prepared by adding $HClO_4$, HBF_4, etc., to II or I in ether–ethanol. The unwanted diazene impurities could be easily removed by stirring the impure aryldiazo complexes in a dilute solution of methanolic NaOH in diethyl ether. If the solutions were not maintained free from dust and other foreign particulates, decomposition via N_2 evolution was enhanced. In fact, the addition of activated alumina or charcoal to solutions of the complexes caused a noticeable increase in the rate of gas evolution from solution.

$$Os(CO)_3(PPh_3)_2 + [PhN_2][PF_6] \rightarrow \underset{\text{I}}{[Os(CO)_2(NNPh)(PPh_3)_2][PF_6]} + CO\uparrow \qquad (1)$$

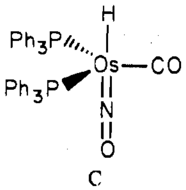
It is likely that the cations of $[Ru(CO)_2(NNPh)(PPh_3)_2][PF_6]$ (II) and of $[Os(CO)_2(NNPh)(PPh_3)_2][PF_6]$ (I) have the same trigonal-bipyramidal geometry (A) with trans phosphine ligands and singly bent aryldiazo ligands



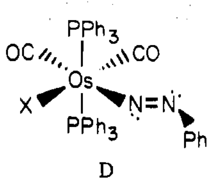
A



B



C



D

Table II. Infrared Spectral Data (cm^{-1}) for Aryldiazo Complexes

Compd[a]	ν(NN)	ν(CO)	Other	ν(NN) with isotopic labels
$[Os(CO)_2(NNPh)(PPh_3)_2][PF_6]\cdot{}^1/_2C_6H_6$	1577 sh, 1668	1967, 2051		1572, 1644;[b] 1572, 1647;[c] 1560, 1625;[d] 1663;[e] 1633[f]
$[Ru(CO)_2(NNPh)(PPh_3)_2][PF_6]\cdot C_6H_6$	1555, 1592, 1605, 1680	1978, 2064		1540, 1591, 1597, 1655;[b] 1539, 1590, 1598, 1657;[c] 1518, 1587, 1590 sh, 1633;[d] 1530, 1572, 1595, 1675;[e] 1520, 1571, 1585, 1650[f]
$OsCl_3(NNPh)(PPh_3)_2\cdot CH_2Cl_2$	1807, 1833		ν(OsCl) 308, 321	1746, 1753[d]
$OsBr_3(NNPh)(PPh_3)_2\cdot CH_2Cl_2$	1810, 1828			1787, 1807;[c] 1756, 1762[d]
$RuCl_3(4\text{-}FC_6H_4NN)(PPh_3)_2\cdot CH_2Cl_2$	1850			
$RuCl_3(2,6\text{-}F_2C_6H_3NN)(PPh_3)_2\cdot CH_2Cl_2$	1835–1895[m]			1810–1870[m,n]
$RuCl_3(NNPh)(PPh_3)_2\cdot CH_2Cl_2$	1882		ν(RuCl) 323 sh, 332	1850;[b] 1852;[c] 1820;[d] 1853, 1886;[c] 1838, 1886[f]
$RuCl_3(4\text{-}CH_3C_6H_4NN)(PPh_3)_2\cdot CH_2Cl_2$	1895			
$OsF(CO)_2(NNPh)(PPh_3)_2$	1457[h]	1962, 2036;[l] 1950, 1965, 2022, 2034		1406, 1449;[d] 1459[e,g]
$OsCl(CO)_2(NNPh)(PPh_3)_2\cdot C_3H_6O$	1454[h]	1963, 2034	ν(OsCl) 278	1452;[b,h] 1451[c,h] 1402, 1447;[d] 1455[e,g]
$OsBr(CO)_2(NNPh)(PPh_3)_2\cdot C_3H_6O$	1454[h]	1963, 2036		1404, 1448;[d] 1456[e,g]
$OsI(CO)_2(NNPh)(PPh_3)_2\cdot{}^1/_2C_3H_6O$	1455[h]	1956, 2035		1410, 1449;[d] 1456[e,g]
$Os(NCO)(CO)_2(NNPh)(PPh_3)_2\cdot{}^1/_2C_3H_6O$	1454[h]	1962, 2036	ν_s(NCO) 2231 ν_{as}(NCO) 1348	
$Os(N_3)(CO)_2(NNPh)(PPh_3)_2\cdot{}^1/_2C_3H_6O$	1440, 1462	1959, 2020	ν_s(NNN) 2056 ν_{as}(NNN) 1282	
$Os(N_3{}^*)(CO)_2(NNPh)(PPh_3)_2\cdot{}^1/_2C_3H_6O$[i]	1440, 1462	1959, 2020	ν_s(NNN) 2039, 2051[i] ν_{as}(NNN) 1262, 1271[i]	
$Os(ONO)(CO)_2(NNPh)(PPh_3)_2\cdot{}^1/_2C_3H_6O$	1456[h]	1960, 2034	ν_s(ONO) 1435 sh, 1493 ν_{as}(ONO) 988, 1059	1455[e,g]
$Os(ONO^*)(CO)_2(NNPh)(PPh_3)_2\cdot{}^1/_2C_3H_6O$[i]	1457[h]	1960, 2034	ν_s(ONO) 1411, 1467[i] ν_{as}(ONO) 968, 1040[i]	1455[e,g]
$Os(HCO_2)(CO)_2(NNPh)(PPh_3)_2\cdot{}^1/_2C_3H_6O$	1457[h]	1955, 2035	ν_s(OCO) 1638 ν_{as}(OCO) 1286	1455;[b,h] 1457[e,g]
$Os(CH_3CO_2)(CO)_2(NNPh)(PPh_3)_2\cdot{}^1/_2C_3H_6O$	1457[h]	1955, 2033	ν_s(OCO) 1632 ν_{as}(OCO) 1323	1455;[b,h] 1457[e,g]
$OsH(CO)_2(NNPh)(PPh_3)_2$	1453[h]	1979, 2025	ν(OsH) 1913	1450;[b,h] 1450;[c,h] 1447, 1409;[d] 1454[e,g]
$OsD(CO)_2(NNPh)(PPh_3)_2$		1946, 2018	ν(OsD) 1397	1457[e]
$RuCl(CO)_2(NNPh)(PPh_3)_2\cdot C_3H_6O$	1455[h]	1983, 2042	ν(RuCl) 272	1448;[b,h] 1449;[c,h] 1407, 1446;[d] 1462,[e] 1440[f]
$RuBr(CO)_2(NNPh)(PPh_3)_2\cdot C_3H_6O$	1455[h]	1984, 2043		1449;[b,h] 1449;[c,h] 1407, 1446;[d] 1464;[e] 1442[f]
$Ru(NCO)(CO)_2(NNPh)(PPh_3)_2\cdot{}^1/_2C_3H_6O$	1414 sh, 1466	1985, 2045	ν_s(NCO) 2248 ν_{as}(NCO) 1334	1452;[b,h] 1470;[e] 1447[f]
$RuI(CO)_2(NNPh)(PPh_3)_2\cdot{}^1/_2C_3H_6O$	1458[h]	1970, 2043		1453;[b,h] 1471;[e] 1448[f]
$RuH(CO)_2(NNPh)(PPh_3)_2$[o]	1455[h]	1973, 2026	ν(RuH) 1915	
$RuD(CO)_2(NNPh)(PPh_3)_2$[o]	1455[h]	1943, 2020	ν(RuD)[k]	
$OsH(CO)(NNPh)(PPh_3)_2$	1472 sh, 1541, 1605	1911	ν(OsH) 2010[j]	1469, 1524, 1598;[b] 1469, 1528, 1595;[c] 1465, 1507, 1595;[d] 1519, 1581;[e] 1506, 1567[f]
$OsD(CO)(NNPh)(PPh_3)_2$	1472, 1541, 1605	1911	ν(OsD) 1446[j]	1519, 1581[e]
$RuH(CO)(NNPh)(PPh_3)_2$[o]	1475 sh, 1550, 1611	1928	ν(RuH) 2012	
$RuD(CO)(NNPh)(PPh_3)_2$[o]	1475 sh, 1550, 1611	1928	ν(RuD)[k]	

[a] Unless otherwise noted, spectra were measured in Nujol and/or hexachlorobutadiene mulls; sh = shoulder, br = broad. [b] For $C_6H_5{}^{14}N^{15}N$. [c] For $C_6H_5{}^{15}N^{14}N$. [d] For $C_6H_5{}^{15}N_2$. [e] For $C_6D_5{}^{14}N_2$. [f] For $C_6D_5{}^{14}N^{15}N$. [g] Band for ν(NN) not visible for $C_6D_5{}^{14}N^{15}N$. [h] There probably are other bands associated with ν(NN) which are hidden by other interfering bands. [i] Single ^{15}N label in NO_2 and N_3 (terminal nitrogen). [j] Observed in the complex with C_6D_5NN in order to avoid interfering bands. [k] This band could not be observed. [l] Measured in CH_2Cl_2 solution. [m] Four moderately intense bands lie in this region. [n] For $C_6H_3F_2{}^{14}N^{15}N$. [o] Measured in perfluorokerosene mulls.

located in equatorial sites. The N–N stretching frequencies of these compounds also indicate a singly bent geometry for the aryldiazo ligands in these complexes (vide infra). This is the same general coordination geometry found in $Fe(CO)_2(NNPh)(PPh_3)_2{}^+$ [26] and $Os(CO)_2(NO)(PPh_3)_2{}^+$.[24] The infrared spectra of the Fe (1978, 2030 cm^{-1}), Ru (1978, 2064 cm^{-1}), and Os (1967, 2051 cm^{-1}) analogs of $M(CO)_2(NNPh)(PPh_3)_2{}^+$ all contain two strong carbonyl bands in the 1950–2100-cm^{-1} region (see Table II).

The osmium complex $[Os(CO)_2(NNPh)(PPh_3)_2][PF_6]$ (I) reacts with a large number of coordinating anions to form green six-coordinate complexes (see eq 2). This reaction must

$$\underset{\text{IIIa–IIIi}}{Os(CO)_2(NNPh)(PPh_3)_2^+ + X^- \rightarrow OsX(CO)_2(NNPh)(PPh_3)_2} \qquad (2)$$

$$X = F, Cl, Br, I, NCO, N_3, NO_2, HCO_2, CH_3CO_2$$

be performed in a neutral or slightly basic medium (acetone) because the slightest trace of acid will result in the protonation of the rather basic phenyldiazo (phenyldiazenido) ligand forming the stable, pale yellow cis phenyldiazene complexes $[OsX(CO)_2(HN{=}NPh)(PPh_3)_2][PF_6]$. The deprotonated complexes will slowly extract protons from freshly distilled methanol or ethanol; thus, the freshly prepared complexes must be rapidly filtered and removed from the reaction solvent since it contains small amounts of methanol or water. The reaction of I with BH_4 does not produce the aryldiazo–hydrido complex but rather results in the destruction of the diazo ligand and the production of $OsH_2(CO)_2(PPh_3)_2$ in good yield. With

$$Os(CO)_2(NNPh)(PPh_3)_2^+ + BH_4^- \rightarrow OsH_2(CO)_2(PPh_3)_2 \qquad (3a)$$

$$Ru(CO)_2(NNPh)(PPh_3)_2^+ + BH_4^- \xrightarrow{PPh_3} RuH_2(CO)(PPh_3)_3 \qquad (3b)$$

other anions such as CN^-, PhS^-, NCS^-, or OH^-, only decomposition products without aryldiazo ligands could be observed. The only product obtained from these reactions in appreciable yield was a yellow solid which analyzed for $Os(NCS)_2(CO)_2(PPh_3)_2$. Although the reaction of I with azide ion produced the expected six-coordinate product IIIf, the yields were somewhat low, and other osmium carbonyl complexes remained in solution after precipitation of IIIf. IIIb–IIIi all crystallize from solution as acetone solvates. Except for the chloro and bromo derivatives, which are stable as solvates, the others seem to desolvate partially unless they are maintained in a solvent atmosphere. The approximate extent of solvation was determined by elemental analyses and integration of appropriate solvent and phenyl peaks in the NMR spectra. The fluoro complex IIIa crystallizes from solution as an unsolvated microcrystalline powder whose infrared spectra have four strong carbonyl bands at 1950, 1965, 2022, and 2034 cm^{-1}. The two extra carbonyl bands are caused by solid-state splitting, and only two bands appear in solution (CH_2Cl_2) at 1962 and 2036 cm^{-1}. When stored under nitrogen in the dark at 0°C, these complexes seem to be indefinitely stable. The compounds are distinctly photosensitive and blacken at exposed surfaces when placed in a well-lighted room for 6–12 hr.

The ruthenium complex $[Ru(CO)_2(NNPh)(PPh_3)_2][PF_6]$ (II) shows somewhat different behavior. It reacts with Cl^-, Br^-, NCO^-, and I^- analogous to reaction 2 yielding the respective chocolate-brown six-coordinate phenyldiazo complexes IVa–IVd. They too crystallize as acetone solvates and in general have the same properties as their osmium analogs. These compounds also readily react with H^+ forming diazene complexes, but they are somewhat less basic than the osmium complexes and are stable in the presence of neutral alcohols. Compound II does not react with fluoride, acetate, or formate anions owing to the reduced coordinating ability of a second-row metal in comparison with a third-row metal. Compound II reacts with BH_4^- forming an insoluble, yellow residue. The same reaction with excess triphenylphosphine present yields $RuH_2(CO)(PPh_3)_3$ in good yield. The reaction of II with azide ion yields several different products which are difficult to isolate and purify; it is being studied further.

The stereochemistry of compounds III and IV is certainly the same as that of the stable isomers of $MX_2(CO)_2(PPh_3)_2$ which contain trans phosphine ligands and cis carbonyl ligands (D). The stereochemistry about the N–N double bond must be trans because molecular models suggest the presence of highly unfavorable steric interactions in the cis form. The infrared spectra show two strong bands near 2040 and 1980 cm^{-1} for the Ru complexes and near 2035 and 1960 cm^{-1} for the Os complexes arising from the symmetric and antisymmetric stretching vibrations of the cis carbonyl ligands. Solvent bands (acetone) appear near 1712 and 1357 cm^{-1}. The values of ν(NN) are near 1462 cm^{-1} for the Ru complexes and 1455 cm^{-1} for the Os complexes.

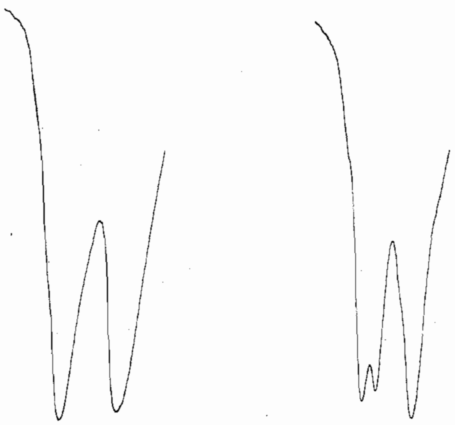
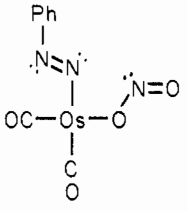


Figure 1. Infrared spectra of $Os(N_3)(CO)_2(NNPh)(PPh_3)_2$ in the 2000–2100-cm^{-1} region measured in hexachlorobutadiene mulls; energy increases to the left. On the left is the spectrum of the complex containing $Os^{14}N_3$. On the right is the spectrum of the mixture containing $Os^{14}N_2{}^{15}N$ and $Os^{15}N^{14}N_2$.

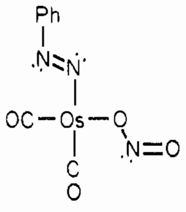
The value of ν(Os–Cl) at 278 cm^{-1} in the chloro complex IIIb is typical of such a vibration when the chloro ligand is trans to a carbonyl ligand in a six-coordinate complex; a lower value would be expected if the chloro ligand were trans to the aryldiazo or phosphine ligands. The proton-decoupled ^{31}P NMR spectrum (in C_6D_6) of IIIb which contained a $Ph^{15}N_2$ labeled diazo ligand shows only one sharp peak indicating the absence of measurable ^{31}P–^{15}N coupling and the presence of two chemically equivalent phosphine ligands. Thus, the only possible isomer compatible with the spectroscopic results is that depicted in D.

The two carbonyl ligands are chemically different, though both C–O stretching vibrations are certainly strongly coupled. The higher energy band is insensitive to the nature of the anionic ligand, X, but the lower energy band changes somewhat suggesting that the carbonyl ligand which is trans to X contributes most strongly to the lower energy band. The cyanato and azido complexes IIIe and IIIf have ligand vibrations at 2231 [ν_{as}(NCO)], 1345 [ν_{as}(NCO)], 2062 [ν_s(NNN)], and 1280 cm^{-1} [ν_{as}(NNN)] which are typical of unidentate N-bonded ligands.[27] The CO and NCO vibrations in IIIe do not seem to be coupled. The symmetric azide stretching frequency in IIIf was conclusively identified by preparing the isotopically substituted complex ($^{15}N^{14}N_2$). For this purpose, a soluble potassium azide–cyclic polyether complex was prepared using 18-crown-6 since potassium azide itself is only slightly soluble in methanol. Of the three high-energy bands at 2056, 2020, and 1959 cm^{-1}, the highest energy band was shown to be the azide vibration since it splits into two bands at 2051 and 2039 cm^{-1} in the labeled complex (see Figure 1). These two bands have about equal intensity and result from two isomers, one in which the ^{15}N atom is attached to the metal and the other in which the ^{14}N atom is attached to the metal. Although the carbonyl bands (2020 and 1959 cm^{-1}) are invariant with ^{15}N substitution, it is difficult to rule out vibrational coupling between trans azido and carbonyl ligands owing to the small isotopic shifts in the azido frequencies. As expected, the HCO_2 and CH_3CO_2 groups in the formato and acetato complexes IIIh and IIIi are unidentate and O bound with the respective values of ν_s(OCO) 1638 and 1632 cm^{-1} and ν_{as}(OCO) 1286 and 1323 cm^{-1}.

The isoelectronic NO_2 group is also unidentate and O bound in the nitrito complex IIIg. The formation of the O-bonded nitrito complex instead of the N-bonded nitro complex was not unexpected because others have observed the affinity of class B metals for hard donor ligands when a soft ligand is in the trans position,[28] in this case, the preference of Os(II) for oxygen over nitrogen when PhN_2 is in the trans position. Of special interest in the nitrito complex is the presence of *four* distinct bands for the NO_2 group in the region where symmetric and antisymmetric vibrations usually occur.[27] The four bands are found at 1493, 1435, 1059, and 988 cm^{-1} which shift to 1467, 1411, 1040, and 968 cm^{-1} in the isotopically labeled ($^{15}NO_2$) complex. There is no vibrational coupling between ν(ONO) of the nitrito ligand and ν(NN) of the diazo ligand. It is doubtful that there is isomerism about the Os–N bond owing to the specific steric demands of the bulky, doubly bent phenyldiazo ligand. Thus, the four bands seem to indicate the existence of two O-bound isomers, probably resulting from rotation about the Os–O bond (E and F). The two isomers exist in about a 50:50 ratio. There are no indications from the infrared spectra or elemental analyses of the presence of $Os(ONO)_2(CO)_2(PPh_3)_2$, $Os(ONO)(CO)(NNPh)(PPh_3)_2$, $Os(ONO_2)(CO)_2(NNPh)(PPh_3)_2$, or any other impurity. A solution spectrum (CH_2Cl_2) of IIIg revealed the presence of all four bands, thus eliminating the possibility of solid-state splitting. Although no crystal structure of $MX(CO)_2(NNAr)(PPh_3)_2$ is yet known, the structure of a similar complex, $RuCl(CO)_2(HNNPh)(PPh_3)_2^+$, shows that the diazene ligand is oriented away from the chloro ligand toward a carbonyl ligand and located in the Ru–Cl–C–C plane.[29] Furthermore, the molecule is rather crowded, and a phenyl group belonging to one of the phosphine ligands distorts somewhat the pseudooctahedral geometry by pushing the chloro ligand away from the cis carbonyl group toward the diazo ligand. Although the changes which take place upon protonation are not known with certainty, the basic structure of the ruthenium phenyldiazene complex suggests that there are grounds for believing that isomers of the type shown by E and F can exist. The six-coordinate ruthenium–phenyldiazenido complexes IVa–IVd have spectral properties similar to those of their osmium analogs (see Table II).



E



F

The ruthenium complex II reacts with I^- and NO_2^- according to eq 2 followed by decarbonylation (reaction 4) to

$$RuX(CO)_2(NNPh)(PPh_3)_2 \rightarrow RuX(CO)(NNPh)(PPh_3)_2 + CO\uparrow \quad (X = I, NO_2) \qquad (4)$$

yield mixtures of mono- and dicarbonyl complexes. At 25°C approximately a 50:50 mixture (monocarbonyl:dicarbonyl) is obtained for the iodo complexes and a 90:10 mixture for the NO_2 complexes. If the same reactions are performed at −10°C, the decarbonylation reaction is less favored and one obtains a 10:90 mixture for the respective iodo complex. Thus, the decarbonylation reaction is promoted by the higher temperature and by the presence of nitrite and iodide anions. The ease of decarbonylation seems to follow the trends $NO_2 > I > Br, Cl, NCO$ and $Ru > Os$.

While no accurate rate measurements have been carried out, this evidence suggests that the substitution reactions, $Ru(CO)_2(NNPh)(PPh_3)_2^+ + X^- \rightarrow RuX(CO)(NNPh)(PPh_3)_2 + CO$, proceed via six-coordinate dicarbonyl intermediates, IV. Such intermediates are possible only because of the amphoteric nature of the aryldiazo ligand. Although no CO was released from solution when these reactions were carried out in the presence of carbon monoxide scavengers such as $RhCl(PPh_3)_3$ or $IrCl(N_2)(PPh_3)_2$, neither the rate of reaction nor the extent of reaction seemed to increase suggesting that decarbonylation of the six-coordinate intermediates is the rate-limiting step. In the analogous osmium system, the six-coordinate complexes are sufficiently stable so that decarbonylation usually does not take place, and the reaction stops at the six-coordinate complexes. In the analogous iron system, no six-coordinate intermediates have been observed and loss of CO takes place in every case;[30] a kinetic study of these iron complexes would be enlightening in this regard. Thus we see that a first-row metal (Fe) loses the CO, a third-row metal (Os) retains the CO, and a second-row metal (Ru) is a borderline case which does both depending on the specific circumstances.

Table III. Proton Nuclear Magnetic Resonance Spectra for Nonaromatic Protons

Compd^a		Chem shift^b	J_{PH}^{c}
$Os(CH_3CO_2)(CO)_2(NNPh)(PPh_3)_2$^{d}	Singlet	8.61	
$Os(HCO_2)(CO)_2(NNPh)(PPh_3)_2$^{d}	Singlet	2.53	
$OsH(CO)_2(NNPh)(PPh_3)_2$^{d}	Triplet	12.76	20
$OsH(CO)_2(NNPh)(PPh_3)_2$^{e}	Triplet	12.38	20
$OsH(CO)(NNPh)(PPh_3)_2$^{d,f}	Triplet	19.51	21
$RuH(CO)_2(NNPh)(PPh_3)_2$^{e}	Triplet	12.63	18
$RuH(CO)(NNPh)(PPh_3)_2$^{e}	Triplet	18.79	21

[a] Abbreviations: Ph = C_6H_5; diazo ligand has single ^{15}N label, $^{15}N^{14}NPh$. [b] Values given in units of τ with tetramethylsilane as internal reference. [c] Coupling constants given in units of Hz. [d] Solvent is CD_2Cl_2 at ambient temperatures. [e] Solvent is C_6D_6 at ambient temperatures. [f] Chemical shift of hydridic proton in $OsH(CO)(NO)(PPh_3)_2$ is τ 14.6, $J_{PH} = 25$ Hz (C_6H_6), or τ 15.04, $J_{PH} = 24$ Hz (CH_2Cl_2); see ref 24 and 25.

Laing and Roper have made an interesting parallel observation concerning the unique behavior of the iodo complex in analogous ruthenium–nitrosyl complexes, $RuX(CO)(NO)(PPh_3)_2$.[31] For X = Cl, Br, and NCO, the values of ν(NO) fall in the small range 1580–1596 cm^{-1}, but the value for the iodo complex is anomalously high at 1642 cm^{-1}. Although disordered, the structure of the iodo complex has been described as trigonal bipyramidal with a linear, equatorial nitrosyl ligand.[32] Assuming that a higher value of ν(NO) indicated a greater tendency to form a trigonal-bipyramidal geometry with a linear nitrosyl ligand and a lower value indicated a tendency to form a square-pyramidal geometry with a bent nitrosyl ligand, then the iodo complex would have the greatest tendency to go toward the trigonal-bipyramidal geometry. This same preference for the trigonal-bipyramidal geometries in the iodo–phenyldiazo complex would account for more fascile decarbonylation of IVd compared with IVa–IVc. Similarly, using the same criterion the nitro complexes $Ir(NO_2)_2(NO)(PPh_3)_2$,[33] ν(NO) 1639 cm^{-1}, and $IrCl(NO_2)(NO)(PPh_3)_2$,[33] ν(NO) 1600 cm^{-1}, would be more inclined toward a trigonal-bipyramidal geometry than the corresponding dichloro (1560 cm^{-1}), dibromo (1563 cm^{-1}), or diiodo (1561 cm^{-1}) complexes.[34]

The reverse of reaction 4 does not take place; apparently the monocarbonyl complexes are more stable. Using CO pressures up to 5 atm at room temperature, only starting materials could be obtained. During the same attempted reaction with CO in refluxing solvent (benzene), the diazo complexes decomposed, and only small amounts of $RuX_2(CO)_2(PPh_3)_2$ (X = I, NO_2) were isolated. Similarly, attempted decarbonylation of IV under a nitrogen atmosphere in refluxing benzene also led to decomposition of aryldiazo complexes and formation of small amounts of the dihalodicarbonyl complexes.

The hydrido analogs of III and IV could not be prepared from I and II by the addition of a source of H^- because the reducing conditions destroyed the aryldiazo ligand. Although Laing et al. apparently attempted and failed to deprotonate hydridophenyldiazene complexes,[10] we have been able to do so under the proper conditions with acceptable yields. Although a series of reactions is required to prepare these diazo complexes, none of the intermediates is isolated so that only one synthetic step is required (see eq 5). Conveniently, all

$$\begin{tikzcd}
\mathrm{RuH_2(CO)(PPh_3)_3} \arrow[r, "+\mathrm{PhN_2PF_6}"] & \mathrm{[RuH(CO)(HNNPh)(PPh_3)_3][PF_6]} \arrow[d, "+\mathrm{CO}"', "-\mathrm{PPh_3}", "20^\circ"'] \\
\mathrm{OsH_2(CO)_2(PPh_3)_2} \arrow[r, "+\mathrm{PhN_2PF_6}"] & \mathrm{[MH(CO)_2(HNNPh)(PPh_3)_2][PF_6]} \arrow[d, "\mathrm{NaOH}"', "-20^\circ"] \\
 & \mathrm{MH(CO)_2(NNPh)(PPh_3)_2}\downarrow + \mathrm{NaPF_6} + \mathrm{H_2O} \\
 & \text{IIIj, M = Os} \\
 & \text{IVe, M = Ru}
\end{tikzcd} \qquad (5)$$

products and intermediates were soluble in the solvent (acetone–methanol) except the final desired product which crystallized out of solution as solvent-free crystals. Like the other members of the series, IIIj is blue-green, and in general it has similar properties. Infrared spectra of IIIj in the 1900–2100-cm^{-1} region show three bands, at 1913, 1979, and 2025 cm^{-1}; the first has medium intensity and the others have strong intensity. The intensity identifies the lower energy band as ν(OsH), and its position relative to the carbonyl bands suggests that the hydride is trans to a carbonyl ligand rather than trans to a phosphine ligand. This is substantiated by the spectrum of $\mathrm{OsD(CO)_2(NNPh)(PPh_3)_2}$ (IIIk) whose bands appear at 1397, 1946, and 2018 cm^{-1}. The direction of the shift of ν(CO) (to lower energy), the magnitude of the shift (33 cm^{-1}), and the ratio of $\nu(\mathrm{OsH})/\nu(\mathrm{OsD})$ (1.369) all show that the hydride and carbonyl stretching frequencies are coupled and that the hydride ligand is trans to the carbonyl ligand which is associated with the lower energy carbonyl band (1979 cm^{-1}).[35] The proton NMR spectrum of IIIj in $\mathrm{CD_2Cl_2}$ showed a sharp 1:2:1 triplet at τ 12.76 with $J_{\mathrm{PH}} = 20$ Hz (see Table III). The chemical shift in IIIj and absence of the resonance in IIIk both confirm the presence of the hydride. The resonance pattern and coupling constant are only consistent with the presence of two chemically equivalent phosphine ligands both of which are cis to the hydrido ligand. The only stereochemistry compatible with all of these data is D. The proton NMR spectrum of IIIj with a $\mathrm{Ph^{15}N_2}$ isotopic label showed the same single sharp triplet for the hydride resonance; there was no observable ^{15}N–^{1}H coupling.

The six-coordinate ruthenium–hydrido complex IVe crystallizes out of solution as bright green crystals. This is unusual since all of the other analogous ruthenium complexes, IV, are brown in color. Indeed, IVe exists in two forms in the solid state, green and brown, the brown being more stable (see eq 6). Elemental analyses and infrared spectra are virtually

$$\underset{\substack{\text{green}\\ \text{IVe}}}{\mathrm{RuH(CO)_2(NNPh)(PPh_3)_2}} \rightarrow \underset{\substack{\text{brown}\\ \text{VIa}}}{\mathrm{RuH(CO)_2(NNPh)(PPh_3)_2}} \rightarrow \underset{\substack{\text{brown}\\ \text{VIa}}}{\mathrm{RuH(CO)(NNPh)(PPh_3)_2}} + \mathrm{CO}\uparrow \qquad (6)$$

identical for both forms. The green to brown conversion takes place instantly upon dissolution in benzene and requires about 2 hr in the solid state at room temperature. The thermally induced (30°C) decarbonylation reaction has a half-life of about 50 min in benzene solution and about 12 hr in the solid state. The monocarbonyl, VI, is only moderately stable; it has a half-life in benzene solution of about 6 hr and is somewhat sensitive to oxygen. However, we found no evidence for a dioxygen adduct among the decomposition products. Compound VI decomposes rapidly in a matter of a few minutes, in chlorinated solvents such as methylene chloride or chloroform, but the solid is stable for 1 week or so without significant decomposition when it is maintained at −20°C in the dark under an inert atmosphere. The decarbonylation of IVe can be conveniently followed by observing carbonyl frequencies in the infrared spectrum or by observing the hydride resonance in the NMR spectrum. The facile decarbonylation can be explained by the strong trans-labilizing influence of the hydrido ligand. The infrared spectra of the ruthenium–hydrido and –deuterido complexes IVe and IVf are similar to those of their osmium analogs and indicate the same coupling between the carbonyl and hydride vibrations. The proton NMR spectrum of IVe in benzene also shows a 1:2:1 triplet at τ 12.63 with $J_{\mathrm{PH}} = 18$ Hz indicating the same stereochemistry as found in the osmium complex. Our attempts to prepare the chloro and bromo derivatives IIIb, IIIc, IVa, and IVb by deprotonation of the respective phenyldiazene complexes failed. The expected color changes were observed, yellow → green (Os) or yellow → brown (Ru), but no product could be isolated from solution. However, preliminary results suggest that five-coordinate monocarbonyl–halo complexes $\mathrm{MX(CO)(NNPh)(PPh_3)_2}$ can be prepared by deprotonation of the respective diazene complexes; the details of these reactions will be reported later.

The osmium complex $\mathrm{OsH(CO)_2(NNPh)(PPh_3)_2}$ is more stable than its Ru analog and does not spontaneously lose carbon monoxide. However, in the presence of ultraviolet light (mercury vapor lamp) a green to brown color change is observed. When the experiment is conducted using a quartz NMR tube and benzene as the solvent, the strong signal from the hydridic proton in the starting material was completely replaced by that of the hydridic proton in $\mathrm{OsH(CO)(NNPh)(PPh_3)_2}$. However, the intensity of the hydridic

$$\mathrm{OsH(CO)_2(NNPh)(PPh_3)_2} \xrightarrow[-\mathrm{CO}]{h\nu} \mathrm{OsH(CO)(NNPh)(PPh_3)_2} \xrightarrow{h\nu} \text{other product}$$

resonance for the monocarbonyl complex was only about 30% of that expected. Indeed, a solution of the pure five-coordinate monocarbonyl complex also reacted, but more slowly, upon irradiation to form as yet unidentified products. It is noteworthy that we have been unable thermally or photolytically to induce a hydride migration. There is no evidence in the NMR spectra for resonances which could result from any five-coordinate Os(0) complexes of the type $\mathrm{Os(CO)_2(HN{=}NPh)(PPh_3)_2}$ or $\mathrm{Os(HC{=}O)(CO)(NNPh)(PPh_3)_2}$.

The brown five-coordinate monocarbonyl–hydrido complexes V and VI were conveniently prepared in one synthetic step in a reaction analogous to (5) using the respective monocarbonyl–tris(phosphine)–phenyldiazene complexes (see eq 7). V and VI were the only complexes which were prepared

$$\begin{tikzcd}
\mathrm{MH_2(CO)(PPh_3)_3} + \mathrm{[PhN_2][PF_6]} \xrightarrow{20^\circ} \\
\mathrm{[MH(CO)(HNNPh)(PPh_3)_3][PF_6]} \arrow[d, "+\mathrm{NaOH}"', "-20^\circ"] \\
\mathrm{MH(CO)(NNPh)(PPh_3)_2} + \mathrm{NaPF_6} + \mathrm{H_2O} + \mathrm{PPh_3} \\
\text{Va, M = Os} \\
\text{VIa, M = Ru}
\end{tikzcd} \qquad (7)$$

by two different methods; their physical and spectral properties were the same when prepared by either method.

The spectra of these five-coordinate complexes suggest that both have trigonal-bipyramidal geometries (B). The infrared spectra show the presence of one strong carbonyl band near 1915 cm^{-1} and a medium band associated with ν(NN) near 1545 cm^{-1}. Careful inspection of the spectra shows the presence of two weaker bands associated with ν(NN) near 1610 and 1475 cm^{-1}. The metal–hydride stretching frequencies occur near 2010 cm^{-1}; this band has medium intensity in the osmium complex but weak intensity in the ruthenium complex. There were no shifts in the carbonyl frequencies and ν(MH) were missing in both respective deuterido complexes (Vb, VIb). Although ν(RuD) could not be observed, ν(OsD) appeared at 1446 cm^{-1} with $\nu(\mathrm{OsH})/\nu(\mathrm{OsD}) = 1.390$. This ratio, together with the absence of any measurable shift in the carbonyl frequency, indicates the absence of a resonance coupling between ν(CO) and ν(MH).[35] The proton NMR spectrum of Va in CD_2Cl_2 showed the presence of a sharp 1:2:1 triplet from the hydride resonance at τ 19.51 with $J_{\mathrm{PH}} = 21$ Hz. The hydride resonance of VIa in deuteriobenzene was found at τ 18.97 with $J_{\mathrm{PH}} = 21$ Hz. The only stereochemical arrangements consistent with the spectral data are those which contain two chemically equivalent phosphine ligands both of which are cis to the hydride which in turn is not trans to the carbonyl. Excluding the square-pyramidal geometry with axial hydride and trans phosphine ligands as being unlikely, the only two remaining possibilities are B and C, the latter being the proposed geometry for the analogous nitrosyl complex suggested by Johnson and Segal.[36] Since the geometry in C is not frequently found in five-coordinate bis(triphenylphosphine) complexes, probably owing to the unfavorable steric interactions of the bulky phosphine ligands, we believe that B is the favored geometry for both the aryldiazo and nitrosyl complexes. If V is prepared at 20° according to reaction 7, it crystallizes out of solution as orange crystals in slightly lower yield. Unexpectedly, the "high-temperature" orange form is less stable and reverts to the brown form immediately upon dissolution in benzene; this transformation requires 10–20 hr in the solid state. Infrared (mulls) and NMR spectra of both forms are identical.

Infrared spectral data tend to support an earlier conclusion that the linear nitrosyl ligand is a better π acceptor than the singly bent phenyldiazo ligand.[37,38] Thus we find that the carbonyl stretching frequencies in $\mathrm{Ru(CO)_2(NNPh)(PPh_3)_2^+}$ (1978, 2064 cm^{-1}) and $\mathrm{Os(CO)_2(NNPh)(PPh_3)_2^+}$ (1967, 2051 cm^{-1}) are lower than those in $\mathrm{Ru(CO)_2(NO)(PPh_3)_2^+}$ (2014, 2065 cm^{-1}) and $\mathrm{Os(CO)_2(NO)(PPh_3)_2^+}$ (1998, 2055 cm^{-1}).[24,25] In contrast, however, we find the carbonyl stretching frequency in $\mathrm{OsH(CO)(NNPh)(PPh_3)_2}$ (1911 cm^{-1}) to be slightly higher than that in $\mathrm{OsH(CO)(NO)(PPh_3)_2}$ (1895 cm^{-1}).[24,25] One might expect the resonance (NMR) of the hydridic proton to appear at lower field when the electron density on the central metal is reduced, assuming that the paramagnetic shielding term is constant. On this basis, the nitrosyl ligand may be considered the better π acceptor since the hydridic resonance of $\mathrm{OsH(CO)(NO)(PPh_3)_2}$[25] ($\tau$ 15.0) appears at lower field than that of $\mathrm{OsH(CO)(NNPh)(PPh_3)_2}$ (τ 19.5). Of special interest is the chemical shift of the hydridic proton in $\mathrm{OsH(CO)_2(NNPh)(PPh_3)_2}$ at τ 12.8. The doubly bent form of the aryldiazo ligand is remarkably effective at removing electron density from the central metal by comparison with the singly bent form of the same ligand.

With the exception of $\mathrm{MX_3(NNPh)(PPh_3)_2}$ complexes, *all* of the complexes herein reported react with $HClO_4$, HCl, and HBr forming a variety of cis phenyldiazene complexes. Indeed, the reaction of V with HCl parallels the same reaction in the

$$\begin{tikzcd}
\mathrm{OsCl(NNPh)(CO)(PPh_3)_2} \arrow[r, "\mathrm{HCl}", "\mathrm{excess}"'] & \mathrm{OsCl_2(HN{=}NPh)(CO)(PPh_3)_2} \\
\mathrm{OsCl(NNPh)(CO)(PPh_3)_2} \arrow[r, "\mathrm{HCl}", "\mathrm{excess}"'] & \mathrm{OsCl_2(HN{=}NPh)(CO)(PPh_3)_2} \\
\mathrm{OsH(NNPh)(CO)(PPh_3)_2} \arrow[r, "\mathrm{HCl}", "\mathrm{1\ mol}"'] & \mathrm{OsHCl(HN{=}NPh)(CO)(PPh_3)_2} \arrow[u, "\Delta", "\mathrm{excess\ HCl}"']
\end{tikzcd} \tag{8}$$

analogous nitrosyl complex[39] which is only one of four nitrosyl complexes to react in this manner; $\mathrm{ReCl(NO)_2(PPh_3)_2}$,[40] $\mathrm{Re(CO)_2(NO)(PPh_3)_2}$,[40] and $\mathrm{CoBr(NO)(diars)_2^+}$ [41] are the other three such nitrosyl complexes. It is important to realize that the protonation of nitrosyl or aryldiazo ligands does *not necessarily* indicate that the respective ligands were bent or doubly bent prior to protonation. The preparative details and characterization of these phenyldiazene complexes will be reported elsewhere.

Table IV. ν(NN) and ν'(NN) for Os and Ru Aryldiazo Complexes

	Freq, cm^{-1}	
	M = Os	M = Ru
$\mathrm{MCl_3(NNPh)(PPh_3)_2}$	~1815 (~1815)	1882 (1852)
$\mathrm{[M(CO)_2(NNPh)(PPh_3)_2][PF_6]}$	1661 (1851)	1666 (1556), 1583 (1473)
$\mathrm{MH(CO)(NNPh)(PPh_3)_2}$	1543 (1563)	~1550 (~1540)
$\mathrm{MCl(CO)_2(NNPh)(PPh_3)_2}$	1455 (1455)	1462 (1432)
$\mathrm{MH(CO)_2(NNPh)(PPh_3)_2}$	1454 (1474)	~1460 (~1450)

Finally, $\mathrm{OsCl_3(NNPh)(PPh_3)_2{\cdot}CH_2Cl_2}$ (VIIa) and its bromo analog (VIIb) were prepared in the same manner as the analogous tolydiazo–bromo complex of osmium.[10] The

$$\mathrm{OsCl_2(PPh_3)_3 + [PhN_2][PF_6] + LiCl} \xrightarrow[-\mathrm{LiPF_6}]{\mathrm{acetone}} \mathrm{OsCl_3(NNPh)(PPh_3)_2 + PPh_3} \tag{9}$$

crude products were recrystallized from dichloromethane–methanol to yield yellow-brown crystals of the pure solvated complexes. The infrared spectra of $\mathrm{OsCl_3(NNPh)(PPh_3)_2{\cdot}CH_2Cl_2}$ contain two bands assignable to the Os–Cl stretching frequencies at 308 and 321 cm^{-1}, both of which are absent in the analogous bromo complex. These two bands correspond to the 323- and 332-cm^{-1} bands in $\mathrm{RuCl_3(NNPh)(PPh_3)_2{\cdot}CH_2Cl_2}$. Undoubtedly, the structures of the aryldiazo complexes of osmium are very similar to that of the ruthenium tolydiazo complex whose structure contains a singly bent *p*-tolydiazo ligand which possesses an unusually large N–N–C(phenyl) angle of 137°.[38,42] It is interesting to note that, for a wide range of aryl groups, these ruthenium– and osmium–aryldiazo complexes possess a characteristic brown color with one notable exception. The Ru complex containing $\mathrm{2,6\text{-}F_2C_6H_3NN}$ is ruby red, and its infrared spectrum in the N–N stretching region shows a complicated multiplet of four medium intense bands.

In light of recent studies dealing with the protonation of singly bent aryldiazo complexes, we attempted to protonate $\mathrm{OsCl_3(NNPh)(PPh_3)_2}$ using concentrated ethanolic solutions of HCl and $HClO_4$. Nothing was isolated but starting ma-

$$\mathrm{OsCl_3(NNPh)(PPh_3)_2 + H^+} \rightarrow \text{no reaction} \tag{10}$$

terial, and no reaction was apparent in solution (CH_2Cl_2). Both $\mathrm{ReCl_2(NH_3)(NNPh)(PMe_2Ph)_2}$[43] and $\mathrm{W(N_2)_2(diphos)_2}$[44] react with H^+ forming complexes containing PhNH=N=Re and $\mathrm{NH_2{=}N{=}W}$ moieties. The ready protonation of the tungsten–dinitrogen complex suggests that $\mathrm{WCl(NNPh)(diphos)_2}$ would also protonate in the presence of noncoordinating acids to form a PhNH=N=W group. In contrast, $\mathrm{ReCl_2(NNPh)(PMe_2Ph)_3}$[43] and $\mathrm{OsCl_3(NNPh)(PPh_3)_2}$ will not protonate. Thus, the ease of protonation of the nitrogen atom not attached to the metal in these d^6 aryldiazo complexes seems to follow the ordering Os(II) < Re(I) < W(0) which is the same sequence of reactivity of dinitrogen complexes observed by Chatt et al.[45]

N–N Stretching Frequencies. The N–N stretching frequencies of the aryldiazo complexes described in this paper span a range in excess of 400 cm^{-1}, as can be seen from Table IV. The values of the modified stretching frequencies, ν', appear in parentheses.[8,38] We have noted before that higher values of ν(NN) are indicative of singly bent aryldiazo ligands and lower values are indicative of doubly bent aryldiazo ligands. Two difficulties, however, were encountered: the N–N stretching vibration was often obscured by or confused with other vibrational modes in the complex and/or was vi-

Table V. Some Infrared Spectral Data (cm^{-1}) in the N=N Stretching Region for Some Phenyldiazo Complexes in Which Vibrational Coupling Is Found

Compd[a]	Obsd ν(NN)	$\Delta\nu$(NN)[b]	Intens ratios[c]	Coupl freq[c]	Calcd ν(NN)[c]	ν(NN)[c,f]
$[Os(CO)_2(L)(PPh_3)_2][PF_6]$						
$L = C_6H_5{}^{14}N_2$	1577, 1668	(28, 58)	10:109	1585	1660	1660
$L = C_6H_5{}^{14}N^{15}N$	1572, 1644	29	10:46	1585	1631	1659
$L = C_6H_5{}^{15}N^{14}N$	1572, 1647	26	10:55	1584	1635	1663
$L = C_6H_5{}^{15}N_2$	1560, 1625	60	10:20	1583	1602	1658
$L = C_6D_5{}^{14}N_2$	1663				1663	1663
$L = C_6D_5{}^{14}N^{15}N$	1633	30			1633	1661
$[Ru(CO)_2(L)(PPh_3)_2][PF_6]$[d]						
$L = C_6H_5{}^{14}N_2$	1592, 1680	(28, 58)	10:45	1607	1665	1665
$L = C_6H_5{}^{14}N^{15}N$	1591, 1655	26	10:27	1610	1636	1664
$L = C_6H_5{}^{15}N^{14}N$	1590, 1657	25	10:26	1609	1638	1666
$L = C_6H_5{}^{15}N_2$	1587, 1675	52	26:32	1608	1612	1668
$L = C_6D_5{}^{14}N_2$	1572, 1675		10:108	1581	1666	1666
$L = C_6D_5{}^{14}N^{15}N$	1571, 1650	26	10:53	1584	1637	1665
$[Ru(CO)_2(L)(PPh_3)_2][PF_6]$[e]						
$L = C_6H_5{}^{14}N_2$	1555, 1605	(27, 55)	25:30	1578	1582	1582
$L = C_6H_5{}^{14}N^{15}N$	1540, 1597	23	25:12	1580	1557	1583
$L = C_6H_5{}^{15}N^{14}N$	1539, 1597	24	26:10	1582	1555	1581
$L = C_6H_5{}^{15}N_2$	1518, 1590	52	48:10	1578	1530	1584
$L = C_6D_5{}^{14}N_2$	1530, 1595		17:101	1541	1584	1584
$L = C_6D_5{}^{14}N^{15}N$	1520, 1585	20	19:44	1545	1560	1586
$RuCl_3(L)(PPh_3)_2$						
$L = C_6H_5{}^{14}N_2$	1882	(32, 66)			1882	1882
$L = C_6H_5{}^{14}N^{15}N$	1850	32			1850	1881
$L = C_6H_5{}^{15}N^{14}N$	1852	30			1852	1883
$L = C_6H_5{}^{15}N_2$	1820	62			1820	1884
$L = C_6D_5{}^{14}N_2$	1853, 1886		10:53	1858	1881	1881
$L = C_6D_5{}^{14}N^{15}N$	1838, 1866	35	11:10	1853	1851	1882
$RuCl(CO)_2(L)(PPh_3)_2$[g]						
$L = C_6H_5{}^{15}N_2$	1404, 1446	(25, 51)	50:10	1439	1411	1460
$L = C_6D_5{}^{14}N_2$	1462				1462	1462
$L = C_6D_5{}^{14}N^{15}N$	1440	22			1440	1464
$OsCl(CO)_2(L)(PPh_3)_2$[g]						
$L = C_6H_5{}^{15}N_2$	1403, 1447	(25, 51)	100:10	1443	1407	1456
$L = C_6D_5{}^{14}N_2$	1455				1455	1455

[a] Ph = C_6H_5. [b] The sum of the differences for all bands which shift. In parentheses are the calculated shifts for one and two ^{15}N atoms, respectively. [c] See ref 4 for calculations. [d] Calculations based on bands 3 and 1; see text. [e] Calculations based on bands 6 and 2; see text. [f] Value calculated on the basis of two ^{14}N atoms. [g] Calculations could not be performed for complexes with other isotopic labels because some bands associated with ν(NN) seem to be completely hidden by other interfering bands.

brationally coupled with phenyl modes of the diazo phenyl group.[4] With the aid of ^{15}N and ^{2}H substitution we have conclusively identified ν(NN) or the bands associated with ν(NN) and have been able to estimate the true (decoupled) values of ν(NN) in many cases where vibrational coupling occurred.

The infrared spectra of $OsCl_3(NNPh)(PPh_3)_2{\cdot}CH_2Cl_2$ in the N–N stretching region (1800–1850 cm^{-1}) are rather complex. There are two strong bands near 1815 cm^{-1} and several other weak bands which change position and relative intensity upon ^{15}N substitution. The spectra change somewhat in solution, but they are still complicated and difficult to rationalize in terms of a simple resonance coupling model. Although the melting points and analytical data both point to the presence of only one pure compound, we are studying this problem further in order to determine if additional isomers or aryldiazo complexes might be present. We find the same behavior for the analogous bromo complex. However, Laing et al.[10] reported only one band for the tolydiazo–bromo complex of osmium near 1855 cm^{-1}. It is interesting to contrast these values of ν(NN) with ν(NO) for $OsCl_3(NO)(PPh_3)_2$[46] at 1850 cm^{-1} and with ν(NP) for $OsCl_3(NPPh_3)(PPh_3)_2$[47] at 1127 cm^{-1}.

The infrared spectra of the ruthenium–aryldiazo complexes $RuCl_3(NNAr)(PPh_3)_2$ show some interesting features. The value of ν(NN) is somewhat sensitive to substitution of the diazo phenyl group. The values range from 1850 to 1895 cm^{-1} for Ar = *p*-XC_6H_4, X = F, H, CH_3, and are consistent with the presence of singly bent aryldiazo ligands. For the complexes with Ar = C_6H_5, only one strong band associated with ν(NN) appears in the infrared spectra, and it shifts the expected amount upon single and double ^{15}N substitution. However, for the complexes with Ar = C_6D_5, the phenyl vibrational modes are shifted to lower energy and effective vibrational coupling with ν(NN) is established. The perdeuterated complex with two ^{14}N atoms shows two strong bands which change position and relative intensity upon ^{15}N substitution. When mathematically decoupled, the expected values of ν(NN) are obtained as well as the aryl coupling frequency, about 1855 cm^{-1} (see Table V). These observations represent the first carefully documented case of resonance interaction between ν(NN) and aryl vibrational modes in the region above 1850 cm^{-1}.

The spectra of $OsH(CO)(NNPh)(PPh_3)_2$ and its Ru analog contain three bands in the region 1470–1615 cm^{-1} which are associated with the N–N stretching vibration. The changes in the relative intensities and peak positions of the three bands show that all three are interacting and that multiple isomers are not present. Fortunately, except for the complexes without isotopic substitution, the high-energy band is low enough in intensity that it may be neglected when calculating the decoupled values of ν(NN). The spectra of the osmium complex have already been discussed in detail elsewhere.[4] Like the Os complex, the high- and low-energy bands in RuH(CO)-

$(NNPh)(PPh_3)_2$ are approximately equal in intensity and almost symmetrically disposed about the more intense band at 1550 cm^{-1}. Thus we estimate the uncoupled value of $\nu(NN)$ to be near in energy to this centrally located band; we did not prepare any ^{15}N-labeled complexes in this case. The spectra of $Os(CO)_2(NNPh)(PPh_3)_2^+$ contain two bands both of which shift upon isotopic substitution and are vibrationally coupled (see Table V). The uncoupled value of the N–N stretching frequency for the cationic osmium–carbonyl complex at 1661 cm^{-1} and those for the neutral ruthenium- and osmium-hydrido complexes near 1543–1550 cm^{-1} are all indicative of singly bent phenyldiazo ligands.[38]

The infrared spectrum of $[Ru(CO)_2(NNPh)(PPh_3)_2][PF_6]$ is much more complicated than that of its osmium analog. Careful inspection of the spectra revealed the presence of four bands in the 1500–1700-cm^{-1} region which change intensity and position upon isotopic substitution. The mull spectra of the unlabeled complex and of the complex with a single ^{15}N label ($Ph^{14}N^{15}N$) are shown in Figure 2. Six bands appear in both spectra in this region. The first three and the sixth (counting from left to right) are associated with $\nu(NN)$; the fourth and fifth bands near 1570 and 1585 cm^{-1} are associated with the triphenylphosphine ligands and do not shift upon isotopic substitution. The first and third bands seem to be vibrationally coupled as well as the second and sixth bands. In dichloromethane solution, three bands at 1556, 1607, and 1681 cm^{-1} are clearly visible in addition to the triphenylphosphine bands at 1568 and 1583 cm^{-1}. Careful inspection of the spectra shows the presence of a distinct shoulder near 1594 cm^{-1}. Indeed, it is this shoulder which sharply increases in intensity in the ^{15}N-labeled complexes, and the band associated with the 1607-cm^{-1} band shifts and decreases in intensity so that it becomes a shoulder on the neighboring stronger band. It was this which initially caused us to overlook one band in the solution spectra and to misinterpret the mull spectra. Only with the full complement of spectra for all the isotopically labeled compounds was the solution apparent.

The data in hand indicate that two different isomers of the ruthenium–dicarbonyl complex are present. The sum of the isotopic shifts is much too large for one compound and about right for two compounds. The apparent self-consistency of the intensity data is shown by the successful mathematical decoupling of two individual pairs of bands. The multiple bands do not arise from solid-state splitting. In solution and in the solid state, both isomers seem to be present in appreciable amounts; however, the solutions seem to favor slightly the isomer with lower frequencies and the solid state seems to favor slightly the isomer with higher frequencies. Changing solvents or recrystallization makes small but observable changes in isomer distribution in solution or in the solid. The elemental analyses are acceptable and do not directly indicate the presence of impurities. Reactions with X^-, HX, or $HClO_4$ often result in yields in excess of 80% of pure product formed. In the absence of other more conclusive data, we postulate the presence of a dynamic equilibrium between two isomers. The values of ν' of 1556 and 1473 cm^{-1} suggest that one form contains a singly bent phenyldiazo ligand and the other a doubly bent phenyldiazo ligand. We are still studying this problem further for several reasons. (1) Only *two* carbonyl stretching bands can be seen in the solid state and in solution. This observation would be unexpected if multiple isomers were present unless bands accidently overlapped. Although the N–N stretching bands change by only two or three wave numbers between mull and solution spectra, the C–O stretching bands change much more: 1995, 2051 cm^{-1} in CH_2Cl_2 solution and 1978, 2064 cm^{-1} in Nujol mulls. Previously we reported a band at 2080 cm^{-1} in solution which in fact is an impurity. Indeed, after 10 or 15 min in solution, bands from impurities begin to grow into the spectra. (2) Perdeuteration of the diazo phenyl group in the osmium complex removed the vibrational coupling interaction, but did not do so for either form of the ruthenium complex. (3) The coupling frequency for the osmium complex (1584 cm^{-1}) and those for the lower energy form of the ruthenium complex (1580 cm^{-1}, C_6H_5; 1543 cm^{-1}, C_6D_5) are virtually the same as those which have been observed before;[4,29] this adds credence to our analysis of the data. However, coupling frequencies of the higher energy form of the ruthenium complex (1609 cm^{-1}, C_6H_5; 1583 cm^{-1}, C_6D_5) seem to be somewhat high in light of our experience. The highest frequencies in this region heretofore observed are for $OsH(CO)(NNPh)(PPh_3)_2$ which appear at ca. 1595 cm^{-1} for C_6H_5 and 1556 cm^{-1} for C_6D_5.

Figure 2. Infrared spectra of $[Ru(CO)_2(NNPh)(PPh_3)_2][PF_6]$ in the 1500–1700-cm^{-1} region measured in Nujol mulls; energy increases to the left. The transmittance scale is arbitrary and varies with mull thickness and concentration. Four of the six bands visible in each spectrum are associated with $\nu(NN)$. On the left is the spectrum of the complex containing $Ru^{14}N_2Ph$. On the right is the spectrum of the complex containing $Ru^{15}N^{14}NPh$.

The infrared spectra of $OsX(CO)_2(NNPh)(PPh_3)_2$, $OsH(CO)_2(NNPh)(PPh_3)_2$, and their Ru analogs all contain bands associated with the N–N stretching vibration in the 1400–1500 cm^{-1} region. Because the intensities of $\nu(NN)$ in these Os and Ru complexes are smaller (weak to medium intensity) as compared with those of other phenyldiazo complexes and because two strong phosphine bands near 1435 and 1480 cm^{-1} obscure others nearby, the bands associated with $\nu(NN)$ are harder to identify. It appears that all bands are visible in complexes which contain $C_6H_5{}^{15}N_2$ and $C_6D_5{}^{14}N_2$. All bands also seem to be visible in several of the ruthenium complexes which contain $C_6D_5{}^{14}N^{15}N$. To the extent that the spectra of the complexes which contain these two or three isotopic labels are self-consistent, we are able to estimate the uncoupled values of $\nu(NN)$ (see Table V). The N–N stretching frequency does not appear to be sensitive to changes in the anionic ligand, X. As was found in the iridium complex $IrCl_2(CO)(NNPh)(PPh_3)_2$,[4] vibrational coupling is not observed when the diazo phenyl ring is perdeuterated. With such low values of $\nu(NN)$, the phenyldiazo ligands must be doubly bent. Certainly the reaction chemistry is consistent with this proposal, since all three readily protonate on the nitrogen atom which is bonded to the metal forming cis phenyldiazene complexes. It is interesting that both the positions and intensities of the N–N stretching vibrations follow the sequence

$$\underset{1470\ \mathrm{cm}^{-1}}{\mathrm{IrCl_2(CO)(NNPh)(PPh_3)_2}} > \underset{1462\ \mathrm{cm}^{-1}}{\mathrm{RuCl(CO)_2(NNPh)(PPh_3)_2}} > \underset{1455\ \mathrm{cm}^{-1}}{\mathrm{OsCl(CO)_2(NNPh)(PPh_3)_2}}$$

Furthermore, the relative basicities of the coordinated phenyldiazenide (PhN_2^-) follow the reverse ordering. The value of ν(NN) at 1455 cm^{-1} for the osmium complex is the lowest yet recorded for a nonbridging aryldiazo ligand. A comparison of the $MX_3(NNPh)(PPh_3)_2$ and $MX(CO)_2(NNPh)(PPh_3)_2$ complexes of Ru and Os vividly illustrates the effects of replacing two one-electron donors (X) by two two-electron donors (CO). In the dicarbonyl complexes, it was anticipated that the phenyldiazo ligands would act as one-electron donors in order to avoid an unfavorable 20-electron configuration. Thus, two electrons are removed from the system by reducing the easily reduced PhN_2^+ to PhN_2^- with a concomitant change in chemical reactivity, geometry, and N–N stretching frequency (~400 cm^{-1}) of the phenyldiazo moiety. Clearly, the aryldiazo group is a versatile ligand which is very useful as a precursor to other interesting ligands and complexes.

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Registry No. I, 56335-36-5; II, 56389-71-0; IIIa, 56335-37-6; IIIb, 56335-38-7; IIIc, 56335-39-8; IIId, 56363-47-4; IIIe, 56335-40-1; IIIf, 56335-41-2; IIIg, 56335-42-3; IIIh, 56335-55-8; IIIi, 56335-43-4; IIIj, 56335-44-5; IIIk, 56335-45-6; IVa, 56335-46-7; IVb, 56335-47-8; IVc, 56335-48-9; IVd, 56335-49-0; IVe, 56335-50-3; IVf, 56335-51-4; Va, 53608-71-2; Vb, 56335-52-5; VIa, 56335-53-6; VIb, 56335-54-7; VIIa, 56335-56-9; VIIb, 56335-57-0; $RuCl_3(4\text{-}FC_6H_4NN)(PPh_3)_2$, 56335-58-1; $RuCl_3(2,6\text{-}F_2C_6H_3NN)(PPh_3)_2$, 56335-59-2; $RuCl_3(NNPh)(PPh_3)_2$, 56389-72-1; $RuCl_3(4\text{-}CH_3C_6H_4NN)(PPh_3)_2$, 39556-32-6; $Os(CO)_3(PPh_3)_2$, 20332-51-8; $Ru(CO)_3(PPh_3)_2$, 20332-49-4; $[PhN_2][PF_6]$, 369-58-4; $NaBH_4$, 16940-66-2; $OsH_2(CO)(PPh_3)_3$, 12104-84-6; $OsH_2(CO)_2(PPh_3)_2$, 18974-23-7; $RuH_2(CO)(PPh_3)_3$, 25360-32-1.

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(9) Abbreviations: Ar, aryl; To, *p*-tolyl; Ph, phenyl; Et, ethyl; Me, methyl; Bu, *n*-butyl; R, organic group.
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