Contribution from the Department of Chemistry and
Materials Research Center, Northwestern University, Evanston, Illinois 60201

Linear vs. Bent Nitrosyl Ligands in Four-Coordinate Transition Metal Complexes. Structure of Dinitrosylbis(triphenylphosphine)osmium(–II) Hemibenzene, $Os(NO)_2(P(C_6H_5)_3)_2 \cdot {}^1/_2C_6H_6$

BARRY L. HAYMORE and JAMES A. IBERS*

Received December 26, 1974 AIC40847I

The structure of dinitrosylbis(triphenylphosphine)osmium(–II) hemibenzene, $Os(NO)_2(P(C_6H_5)_3)_2 \cdot {}^1/_2C_6H_6$, has been determined using three-dimensional X-ray diffraction techniques. This structure completes those of $M(NO)_2(P(C_6H_5)_3)_2$ of the Fe triad. The conditions and requirements leading to bent and linear nitrosyl ligands in four-coordinate complexes are discussed and compared with those for similar five- and six-coordinate complexes. A set of empirical rules is presented which allows the a priori prediction in many cases of whether the bent or linear form of the nitrosyl ligand will be present. The Os compound crystallizes from benzene–hexane as hemisolvated crystals in space group $C_{2h}{}^5$-$P2_1/n$ with four formula units in a cell of dimensions a = 17.034 (5) Å, b = 18.735 (5) Å, c = 10.799 (3) Å, and β = 96.81 (1)°. Based on 3455 unique reflections with $F_o{}^2 > 3\sigma(F_o{}^2)$, the structure was solved and refined by full-matrix, least-squares methods to values of R of 0.031 and R_w of 0.039. The structure consists of discrete molecules of the complex and of benzene, the latter being located on centers of inversion. The osmium complex is four-coordinate with pseudotetrahedral geometry and linear nitrosyl ligands. Although ESCA spectra show that the nitrosyl ligands are very effective at removing electron density from the metal, the coordination geometry is best rationalized on the basis of Os(–II), which is a d^{10} system. This structure is remarkably similar to its Ru analog. The short Os–N and N–O distances point to the extensive metal–nitrogen and nitrogen–oxygen multiple bonding. Important angles and distances are Os–N(1) = 1.771 (6) Å, Os–N(2) = 1.776 (7) Å, N(1)–O(1) = 1.195 (8) Å, N(2)–O(2) = 1.211 (7) Å, N(1)–Os–N(2) = 139.1 (3)°, Os–N(1)–O(1) = 178.7 (7)°, Os–N(2)–O(2) = 174.1 (6)°, and P(1)–Os–P(2) = 103.51 (6)°.

Introduction

The presence of two powerful π-acceptor ligands in dinitrosyl complexes of transition metals stabilizes uncommon, low oxidation states and imparts other unusual properties to such complexes. Especially interesting in this regard are the four-coordinate, pseudotetrahedral dinitrosyl complexes. Several of these complexes have been shown to be effective catalysts in the reduction of nitric oxide by carbon monoxide forming nitrous oxide and carbon dioxide.[1,2]

$$2NO + CO \xrightarrow[\text{“}M(NO)_2\text{”}]{} N_2O + CO_2$$

Many of these complexes can undergo two-electron and four-electron oxidations thereby allowing two successive oxidative addition reactions to take place.[3-5]

Until recently only two of the four-coordinate dinitrosyl phosphine complexes had been studied structurally.[6,7] In the last year or so, five more have been studied, two of which are iron and ruthenium complexes of the type $M(NO)_2(PPh_3)_2$.[8-12] We now report the structure of the osmium analog which completes this isoelectronic and isostructural series.

Of special interest in nitrosyl coordination chemistry is the amphoteric nature of the ligand.[13] It can act as a three-electron donor (linear NO^+) in its usual coordination mode, but it can also act as a one-electron donor (bent NO^-) under certain conditions. Complexes containing bent nitrosyl ligands are often considered to be electron deficient and coordinatively unsaturated. These conditions are frequently cited as reasons for the increased reactivity and catalytic activity of certain nitrosyl complexes.[5,6,14] The linear-to-bent transition in nitrosyl complexes has consequently received much attention since the first well-documented report of a bent nitrosyl[13] and has prompted several groups of authors to propose molecular orbital schemes which they believe rationalize the behavior of five-coordinate nitrosyl complexes.[15-18] Four-coordinate nitrosyl complexes have received some, but much less, attention.[16-18]

We believe that this bent-to-linear transition requires relatively little energy. Consequently, the mode of NO coordination is strongly dependent on the nature and disposition of the remaining ligands in the complex. With this in mind, we have developed a set of empirical generalizations which allow the coordination geometries of many nitrosyl complexes to be predicted a priori without the encumbrance of knowing or estimating relative energies of molecular orbitals. Although well-documented for five-coordinate complexes, a bent nitrosyl ligand in a four-coordinate complex has yet to be observed. Notwithstanding, we present evidence that such a four-coordinate complex could exist but that it will be less frequently observed because few complexes have the requisite ligand environments.

Experimental Section

Crystal Preparation. Initial attempts to prepare $Os(NO)_2(PPh_3)_2$ by treating $Os(CO)_3(PPh_3)_2$ with NO gas in refluxing toluene or by treating $OsH(NO)(PPh_3)_3$ with MNTS[8] in refluxing toluene proved unsuccessful. Finally, the desired product was isolated from the second reaction in low yield (~10%) and recrystallized from benzene–hexane as deep red prisms of the hemisolvate of benzene, ν(NO) 1605, 1650 cm^{-1} (Nujol mull); literature values are 1615 and 1665 cm^{-1}.[3] Anal. Calcd for $C_{39}H_{33}N_2O_2OsP_2$: C, 57.56; H, 4.09; N, 3.44. Found: C, 57.50; H, 4.18; N, 3.26. Because no crystals of acceptable size or quality were obtained, a larger amount of the osmium dinitrosyl was obtained by a modification[19] of the published procedure.[3] From this material, suitable crystals were obtained by recrystallization from benzene–hexane. Elemental analyses were performed by H. Beck of Northwestern's Analytical Services Laboratory. Infrared spectra were obtained using a Perkin-Elmer 337 double-beam infrared spectrometer with a scale-expanding unit attached. The spectra were calibrated using a polystyrene film. ESCA spectra were obtained using an AEI ES200A spectrometer and Al Kα X-radiation. The carbon 1s peak of the triphenylphosphine ligands was used as an internal reference (283.0 eV). Spectra were taken of pressed pellets of freshly prepared compounds which were handled under vacuum or under nitrogen.

Crystallographic Data and Structure Refinement. Preliminary film data showed the crystal to belong to the monoclinic system with extinctions ($h0l$, $h + l$ odd; $0k0$, k odd) characteristic of the centrosymmetric space group $C_{2h}{}^5$-$P2_1/n$. Using a least-squares procedure[20] based on the angular positions of 21 hand-centered reflections in diverse regions of reciprocal space, accurate unit cell dimensions were determined. See Table I for pertinent crystal information and details of data collection. The mosaicity of the crystal was acceptable for the θ–2θ scan technique.

Data collection was carried out exactly as described before except that monochromatized Mo Kα radiation was used.[12] Six standard reflections remained constant during data collection; there was no

Table I. Summary of Crystal Data and Intensity Collection

Compd	$Os(NO)_2(P(C_6H_5)_3)_2 \cdot {}^1/_2 C_6H_6$
Formula wt	813.858
Formula	$C_{39}H_{33}N_2O_2OsP_2$
a	17.034 (5) Å
b	18.735 (5) Å
c	10.799 (3) Å
β	96.81 (1)°
V	3422 Å^3
Z	4
Density	1.580 g/cm^3 (calcd) 1.60 (1) g/cm^3 (exptl)
Space group	$C_{2h}{}^5$-$P2_1/n$
Crystal dimensions	0.38 × 0.34 × 0.34 mm
Crystal shape	Parallelepiped along [101]; octagonal cross section with faces $\{010\}$, $\{10\bar{1}\}$, and $\{11\bar{1}\}$
Crystal vol	0.0524 mm^3
Temp	20°
Radiation	Mo Kα_1 (λ 0.709300 Å), monochromatized from (002) face of mosaic graphite
Transmission factors	0.24–0.40
μ	38.59 cm^{-1}
Receiving aperture	5.5 mm wide by 5.5 mm high, 32 cm from crystal
Scan range	1.0° below Kα_1 to 1.0° above Kα_2
Background counts	10 sec 2$\theta \leqslant 35°$; 20 sec thereafter
2θ limits	3.8–47.0°
Final no. of variables	143
Unique data used, $F_o{}^2 > 3\sigma(F_o{}^2)$	3455
Error in observation of unit wt	1.37 e

evidence for crystal decomposition. The intensities of 5320 unique reflections were measured, of which 3455 satisfied the condition $F_o{}^2 > 3\sigma(F_o{}^2)$ and were used subsequently. The data were processed in the usual way with $\sigma(F_o{}^2)$ calculated using a value of 0.04 for p.[20] An absorption correction was applied to the data.[21] The R index for averaging 137 pairs of symmetry-related reflections was 2.5% before the absorption correction was applied and 1.9% afterward.

The structure was solved and refined with ease. A Patterson synthesis showed the osmium atom to be located in the same relative position as the ruthenium atom in the analogous Ru structure. Thus, the positional coordinates of all nonhydrogen atoms from the ruthenium structure were used as starting values,[12] and the first cycle of refinement (isotropic atoms) almost converged, resulting in agreement indices of $R = 0.092$ and $R_w = 0.115$. The structure was subsequently refined exactly as before yielding final values of $R = 0.031$ and $R_w = 0.039$ for the converged anisotropic model.[12] Atomic scattering factors were taken from Cromer and Waber's tabulation.[22] The anomalous dispersion terms for Os and P were included in F_c.[23] The value of the isotropic extinction parameter, 1×10^{-8} e^{-2}, is less than its error; the error in the observation of unit weight is 1.37 e.

A final difference Fourier synthesis revealed nothing interesting. Of the ten strongest peaks, the largest (0.8 e/Å^3) is an osmium residual, and the remaining nine peaks belong to residuals near various phenyl groups (0.4–0.6 e/Å^3). All but one unobserved reflection obeys the relation $|F_c{}^2 - F_o{}^2| < 4\sigma(F_o{}^2)$. There are no trends of the quantity $\sum w(|F_o| - |F_c|)^2$ as a function of $|F_o|$, diffractometer setting angles or Miller indices. The final positional and thermal parameters of atoms and groups appear in Tables II and III, and root-mean-square amplitudes of vibration are given in Table IV. A listing of the observed and calculated structure amplitudes for those data used in the refinement is available.[24]

Description of the Structure

In light of previous structural results, undoubtedly the most striking feature of this osmium structure is its uncanny similarity to its ruthenium analog.[12] Both structures are of good quality and well behaved, but there are only four bond angles and distances which differ by more than 2σ. Indeed, our first inclination was that we had accidentally redetermined the structure of the Ru complex. Subsequent experiments have shown that the osmium complex contains no ruthenium and vice versa and that the two structural studies were performed on different compounds. (1) Carbon analyses reproducibly yield 64.6 (2)% for the Ru complex and 57.6 (2)% for the Os complex. (2) ESCA spectra of the Ru complex show a moderately intense Ru 3d peak and no measurable Os 4f peak (less than 5% Os) while spectra of the Os complex show a strong Os 4f peak and no measurable Ru 3d peak (less than 20% Ru). (3) Experimental density measurements reproducibly yield 1.60 (1) g/cm^3 for the Os complex and 1.41 (1) g/cm^3 for the Ru complex. The density of the crystal used to collect intensity data was 1.61 g/cm^3. (4) Attempts to refine the osmium diffraction data using ruthenium scattering factors yielded unreasonable thermal parameters for the metal and much poorer agreement indices ($R = 0.064$). Despite a moderately high correlation (−0.84) between the scale factor and the occupancy factor, two cycles of refinement with an occupancy factor (α) for the osmium atom converged with $R = 0.031$, $R_w = 0.038$, and $\alpha = 0.976$ (3). The largest shift in a positional parameter was 0.5σ and the largest shift in a thermal parameter was 2σ. If one assumes that the Ru and Os scattering factors are approximately related by a constant multiplicative factor, then the maximum Ru impurity would be 7% on the basis of the derived value of α. However, because of inherent errors in the calculated scattering factors coupled with our ignorance of the true effective oxidation state of the

Table II. Final Parameters for $Os(NO)_2(PPh_3)_2 \cdot {}^1/_2 C_6H_6$

Atom	x^a	y	z	$\beta_{11}{}^b$	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Os	0.19249 (1)	0.24675 (1)	0.2534 (2)	26.85 (12)	20.22 (9)	70.23 (29)	1.92 (9)	−2.11 (11)	−7.56 (15)
P(1)	0.14102 (10)	0.17438 (9)	−0.13936 (16)	25.6 (7)	20.3 (5)	66.1 (17)	−1.2 (5)	6.9 (9)	−5.7 (8)
P(2)	0.10788 (10)	0.34555 (9)	0.00986 (16)	25.6 (7)	21.2 (5)	62.7 (17)	0.5 (5)	3.5 (9)	−3.5 (8)
O(1)	0.3437 (4)	0.3071 (4)	−0.0391 (8)	45 (3)	82 (4)	289 (13)	−33 (3)	57 (5)	−70 (6)
O(2)	0.1306 (4)	0.1514 (3)	0.2119 (5)	91 (4)	43 (2)	92 (6)	2 (2)	21 (4)	24 (3)
N(1)	0.2825 (4)	0.2836 (4)	−0.0135 (7)	31 (3)	40 (2)	149 (9)	−4 (2)	9 (4)	−32 (4)
N(2)	0.1586 (4)	0.1917 (3)	0.1412 (5)	54 (3)	28 (2)	60 (6)	5 (2)	−2 (4)	−2 (3)

Group	$x_c{}^c$	y_c	z_c	δ	ϵ	η
11	−0.0431 (2)	0.1440 (2)	−0.1185 (3)	0.360 (3)	2.468 (3)	−0.319 (3)
12	0.1715 (2)	0.2233 (1)	−0.4148 (3)	1.910 (3)	2.848 (3)	1.778 (3)
13	0.2210 (2)	0.0179 (2)	−0.1270 (3)	−1.153 (5)	−2.150 (3)	3.123 (5)
21	−0.0017 (2)	0.3780 (1)	−0.2466 (3)	1.441 (4)	−2.520 (3)	1.676 (3)
22	0.2082 (2)	0.4904 (2)	0.0640 (3)	0.832 (4)	2.253 (3)	−2.949 (4)
23	−0.0152 (2)	0.3406 (2)	0.2137 (3)	2.954 (3)	2.924 (3)	−2.258 (3)
$C_6H_6{}^d$	$^1/_2$	$^1/_2$	0	2.537 (5)	3.153 (6)	1.126 (6)

[a] Estimated standard deviations of the least significant figure(s) are given in parentheses in this and all subsequent tables. [b] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. The quantities given in the table are the thermal coefficients × 10^4. [c] x_c, y_c, and z_c are the fractional coordinates of the rigid-group centers. The angles δ, ϵ, and η (radians) have been defined previously: R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **4**, 793 (1965). [d] The rigid-group center of the benzene solvate is constrained to a crystallographic center of symmetry.

Table III. Derived Positional and Thermal Parameters for Ring Atoms

	Carbon				Hydrogen		
Atom[a]	*x*	*y*	*z*	*B*,[b] Å^2	*x*	*y*	*z*
C(111)	0.0357 (2)	0.1553 (2)	−0.1354 (4)	3.10 (12)			
C(112)	0.0159 (2)	0.1026 (2)	−0.0537 (4)	4.11 (15)	0.056	0.075	−0.009
C(113)	−0.0629 (3)	0.0913 (2)	−0.0368 (4)	4.88 (17)	−0.077	0.055	0.018
C(114)	−0.1219 (2)	0.1327 (3)	−0.1017 (5)	4.78 (17)	−0.176	0.124	−0.091
C(115)	−0.1022 (2)	0.1854 (2)	−0.1833 (4)	4.52 (16)	−0.143	0.213	−0.228
C(116)	−0.0234 (3)	0.1967 (2)	−0.2002 (4)	3.72 (14)	−0.010	0.233	−0.255
C(121)	0.1552 (3)	0.2019 (2)	−0.2971 (3)	3.05 (12)			
C(122)	0.2277 (2)	0.2331 (2)	−0.3116 (4)	3.82 (14)	0.265	0.240	−0.242
C(123)	0.2440 (2)	0.2545 (2)	−0.4293 (4)	5.13 (16)	0.293	0.277	−0.440
C(124)	0.1879 (3)	0.2447 (3)	−0.5325 (3)	5.14 (16)	0.198	0.261	−0.613
C(125)	0.1154 (3)	0.2135 (3)	−0.5180 (4)	5.54 (18)	0.077	0.208	−0.589
C(126)	0.0991 (2)	0.1921 (3)	−0.4003 (5)	4.99 (17)	0.050	0.170	−0.391
C(131)	0.1864 (3)	0.0854 (2)	−0.1322 (4)	3.20 (13)			
C(132)	0.1680 (3)	0.0374 (3)	−0.2297 (4)	4.86 (17)	0.132	0.051	−0.300
C(133)	0.2026 (3)	−0.0301 (2)	−0.2245 (4)	5.53 (19)	0.191	−0.063	−0.291
C(134)	0.2555 (3)	−0.0495 (2)	−0.1218 (5)	5.14 (18)	0.279	−0.095	−0.118
C(135)	0.2739 (3)	−0.0015 (3)	−0.0244 (4)	5.39 (18)	0.309	−0.015	0.046
C(136)	0.2393 (3)	0.0660 (2)	−0.0295 (4)	4.67 (16)	0.251	0.099	0.037
C(211)	0.0444 (2)	0.3647 (2)	−0.1338 (3)	3.14 (13)			
C(212)	0.0788 (2)	0.3646 (2)	−0.2445 (4)	3.53 (13)	0.134	0.355	−0.243
C(213)	0.0326 (3)	0.3780 (3)	−0.3573 (3)	4.73 (17)	0.056	0.378	−0.433
C(214)	−0.0479 (3)	0.3914 (4)	−0.3594 (4)	5.50 (19)	−0.079	0.401	−0.437
C(215)	−0.0822 (2)	0.3915 (3)	−0.2488 (4)	5.41 (18)	−0.137	0.401	−0.252
C(216)	−0.0361 (3)	0.3781 (3)	−0.1359 (4)	4.14 (15)	−0.060	0.378	−0.061
C(221)	0.1628 (3)	0.4291 (2)	0.0399 (4)	3.29 (13)			
C(222)	0.2187 (3)	0.4324 (2)	0.1448 (4)	4.20 (15)	0.226	0.393	0.199
C(223)	0.2641 (3)	0.4938 (3)	0.1688 (4)	4.96 (17)	0.302	0.497	0.240
C(224)	0.2536 (3)	0.5518 (2)	0.0880 (5)	5.05 (17)	0.284	0.594	0.104
C(225)	0.1977 (3)	0.5484 (2)	−0.0169 (4)	4.84 (17)	0.191	0.588	−0.072
C(226)	0.1523 (3)	0.4871 (2)	−0.0409 (4)	4.23 (15)	0.115	0.485	−0.113
C(231)	0.0386 (3)	0.3440 (2)	0.1265 (4)	3.32 (13)			
C(232)	0.0247 (3)	0.4040 (2)	0.1966 (5)	4.24 (15)	0.052	0.447	0.184
C(233)	−0.0291 (3)	0.4007 (2)	0.2839 (4)	5.24 (18)	−0.039	0.442	0.332
C(234)	−0.0690 (3)	0.3373 (3)	0.3010 (4)	5.22 (18)	−0.106	0.335	0.360
C(235)	−0.0551 (3)	0.2773 (2)	0.2309 (5)	4.83 (17)	−0.082	0.234	0.243
C(236)	−0.0013 (3)	0.2806 (2)	0.1436 (4)	3.98 (14)	0.009	0.240	0.096
C(1)	0.4452 (3)	0.4565 (3)	0.0492 (7)	7.11 (24)	0.406	0.427	0.081
C(2)	0.4739 (4)	0.4377 (2)	−0.0618 (6)	7.15 (24)	0.456	0.396	−0.105
C(3)	0.5287 (5)	0.4812 (4)	−0.1110 (4)	7.50 (25)	0.549	0.468	−0.186

[a] C(*xx*1) is attached to P, and the atoms in the ring are sequentially numbered around the ring. [b] Isotropic thermal parameters of the hydrogen atoms are taken as the same as those of the respective carbon atoms to which they are bonded.

Table IV. Root-Mean-Square Amplitudes of Vibration (Å)

Atom	Min	Intermed	Max
Os	0.1739 (5)	0.1875 (5)	0.2280 (5)
P(1)	0.177 (3)	0.190 (3)	0.209 (3)
P(2)	0.183 (3)	0.192 (3)	0.204 (3)
O(1)	0.195 (10)	0.297 (9)	0.494 (10)
O(2)	0.193 (9)	0.300 (8)	0.363 (8)
N(1)	0.206 (10)	0.221 (9)	0.335 (9)
N(2)	0.185 (10)	0.219 (8)	0.290 (9)

metal, the refined value of α can be used only as a qualitative indicator of possible Ru impurities. That data collected on two closely related structures at different times with different radiations yield such similar results indicates that our current methods used to refine structures and derive errors are reliable.

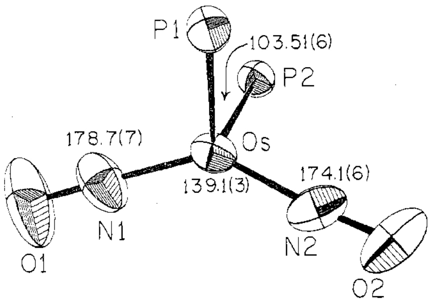


Figure 1. The coordinate sphere with some bond angles for $Os(NO)_2(PPh_3)_2 \cdot {}^1/_2\, C_6H_6$. Vibrational ellipsoids are drawn at 50% probability level. Some pertinent bond distances and angles: Os–N(1), 1.771 (6) Å; Os–N(2), 1.776 (7) Å; Os–P(1), 2.324 (2) Å; Os–P(2), 2.340 (2) Å; N(1)–O(1), 1.195 (8) Å; N(2)–O(2), 1.211 (7) Å; P(1)–Os–N(1), 107.7 (2)°; P(1)–Os–N(2), 94.3 (2)°; P(2)–Os–N(1), 102.6 (2)°; P(2)–Os–N(2), 105.2 (2)°.

The osmium dinitrosyl complex possesses a distinct but distorted pseudotetrahedral coordination geometry which was also found for the Ru and Fe analogs.[9,12] Figure 1 shows the coordination sphere of the osmium complex. Other drawings have been omitted owing to their similarity to those presented earlier for the ruthenium analog. Conceivably, the complex could have C_{2v} symmetry, but in the solid state two factors cause significant deviation from this geometry. (1) The phenyl rings of the two phosphine groups are oriented very differently and are not related by a C_2 axis. (2) The distinct nonequivalence of the P–Os–N angles causes the two nitrosyl ligands to be nonequivalent. The nitrosyl ligands are essentially linear, being bent by only 1–6°. However though bent by slightly different amounts, they both bend in a particular manner: O(1) bends toward P(2) along the O(1)–P(2) vector; O(2) moves toward P(1) in the same manner. The Os–N distances at 1.771 (6) and 1.776 (7) Å are typical of osmium- or ruthenium-to-nitrogen double bonds found in nitrosyl complexes (near 1.75 (3) Å[25]). The N–O distances at 1.195 (8) and 1.211 (7) Å are typical of those belonging to second- and third-row transition metal complexes containing linear nitrosyl ligands and are near the expected N=O double-bond distance of 1.21 Å.[26]

The similarity of the Os and Ru structures eliminates the

Table V. Distances (Å) and Angles (deg) in Selected Four-Coordinate Nitrosyl Complexes

Compd[a]	M-N	M-P	N-O	MNO	NMN	XMX
$Fe(CO)(NO)_2(PPh_3)$[e,f]	1.69-1.73	2.260 (3)	1.15	177-179	113-117	104
$Fe(NO)_2(PP)$[g]	1.661 (7)	2.240 (2)	1.184 (10)	177.8 (7)	125.4 (4)	86.8 (1)
	1.645 (7)	2.248 (2)	1.177 (10)	176.9 (7)		
$Fe(NO)_2(PPh_3)_2$[f]	1.650 (7)	2.267 (2)	1.190 (10)	178.2 (7)	123.8 (4)	111.9 (1)
$Ru(NO)_2(PPh_3)_2$[h]	1.762 (6)	2.337 (2)	1.190 (7)	177.7 (6)	139.2 (3)	103.85 (6)
	1.776 (6)	2.353 (2)	1.194 (7)	170.6 (5)		
$Os(NO)_2(PPh_3)_2$[i]	1.776 (7)	2.324 (2)	1.195 (8)	178.7 (7)	139.1 (3)	103.51 (6)
	1.771 (6)	2.340 (2)	1.211 (7)	174.1 (6)		
$[Ir(NO)_2(PPh_3)_2][ClO_4]$[j]	1.771 (12)	2.339 (3)	1.213 (13)	163.5 (10)	154.2 (7)	116.3 (2)
$[Ir(NO)_2(PPh_3)]_2$[k]	1.787	2.270	1.19	167	156	105[c]
$Ir(CO)(NO)(PPh_3)_2$[l]	1.787 (8)	2.324 (2)	1.180 (9)	174.1 (7)	128.7 (4)[b]	103.9 (1)[d]
		2.323 (2)				
$Co(CO)(NO)(PPh_3)_2$[e,m]	1.72	2.230 (3)	1.15	177	120[b]	114.1 (2)[d]
$CoI(NO)_2L$[n]	1.67	2.260 (4)	1.05	120-166	119.9 (11)	97.1 (2)
				149-155		
$[CoI(NO)_2]_x$[o]	1.61 (4)		1.16 (5)	168 (4)	118.3 (18)	96.2 (1)
			1.19 (5)	173 (4)		

[a] Abbreviations used: Ph, C_6H_5; X, nonnitrosyl ligand; M, metal; PP, $Ph_2\overline{C{=}C(PPh_2)CF_2CF_2C}F_2$; L′, $Ph_2PCH_2CH_2P(O)Ph_2$. The structures of $Fe(NO)_2(CO)_2$, $[CoCl(NO)_2]_2$ and $[Co(NO_2)(NO)_2]_x$ have been omitted. See L. O. Brockway and J. S. Anderson, *Trans. Faraday Soc.*, 33, 1233 (1937); S. Jagner and N. Vannerberg, *Acta Chem. Scand.*, 21, 1183 (1967); C. E. Strouse and B. I. Swanson, *Chem. Commun.*, 55 (1971). [b] N-M-C angle. [c] P-Ir-Ir′ angle. [d] P-M-P angle. [e] Disordered CO and NO ligands. [f] Reference 9. [g] Reference 7. [h] Reference 12. [i] This work. [j] Reference 6. [k] Reference 10. [l] Reference 34. [m] Reference 35. [n] Reference 11. [o] L. F. Dahl, E. R. deGil, and R. D. Feltham, *J. Am. Chem. Soc.*, **91**, 1653 (1969).

need for a detailed comparison of the two structures. Only two angles and two distances differ by amounts greater than 2σ: Os-P(1) and Os-P(2) are both longer by 0.013 (3) Å, and the P(1)-Os-P(2) angle is smaller by 0.34 (8)°. In addition, the Os-N(2)-O(2) angle opens up by 3.5 (8)°. The Ru and Fe structures have been compared and discussed previously.[12] Certainly, one would expect the Os and Ru complexes to have similar structures, but that these structures are virtually identical is surprising. It is conceivable that small but significant differences between the two molecular structures might be masked by the effects of crystal packing forces. This seems unlikely since statistically and chemically significant differences in angles and distances have been observed in other structures of similar pairs of compounds containing complexes of second- and third-row metals in similar coordination and lattice environments, e.g., $[Rh/Ir(diphos)_2(O_2)][PF_6]$,[8,27] $Ru/OsH(C_{10}H_7)(dmpe)_2$,[8,28] $Pd/PtI_2(diars)_2$,[8,29] and $Pd/Pt(PPh_3)_2(CS_2)$.[30] In this regard, it is important to note that $[Rh(NO)_2(PPh_3)_2][ClO_4]$ has the same space group and unit cell dimensions as its iridium analog while the cobalt analog does not.[31] For a further discussion of other intra- and intermolecular features of the osmium structure, the reader is referred to the previous description for the ruthenium complex.[12]

There are only three short communications reporting structures of osmium nitrosyl complexes: $Os(OH)(NO)_2(PPh_3)_2^+$,[32] $OsCl_2(HgCl)(NO)(PPh_3)_2$,[32] and $Os(CO)_2(NO)(PPh_3)_2^+$.[33] The first compound has both linear and bent nitrosyl ligands. Despite the difference in Os-N distances of 1.71 (4) and 1.79 (4) Å for the linear nitrosyl ligands in the first two complexes, the large magnitudes of the errors precludes any exact comparison of them with the present four-coordinate structure. Although the errors are much smaller in the structure of the nitrosyl dicarbonyl complex, a very long Os-N distance of 1.89 (1) Å is found to the linear nitrosyl group. Although the structure of $Ir(CO)(NO)(PPh_3)_2$[34] seems to be straightforward, the structural results from the osmium nitrosyl dicarbonyl cation must be viewed with caution in light of the CO-NO disorder problems in $Fe(CO)(NO)_2(PPh_3)$,[9] $Co(CO)_2(NO)(PPh_3)$,[35] $Co(CO)(NO)(PPh_3)_2$,[35] $Co(CO)_2(NO)(AsPh_3)$,[36] $Mo(HB(pz)_3)(CO)_2(NO)$,[37] and $RuI(CO)(NO)(PPh_3)_2$.[38]

Discussion

Four-Coordinate Nitrosyl Structures. To date, all four-coordinate dinitrosyl complexes whose structures are known have pseudotetrahedral geometry (see Table V). The distortions from an idealized geometry in these d^{10} dinitrosyl complexes have been interpreted in terms of the extent of the metal-to-ligand π back-bonding.[6,9,12] Increased back-bonding is then expected to cause the nitrosyl ligands to bend more and the N-M-N angle to open up owing to increased repulsion between the nitrosyl ligands. A neutral Os(-II) complex would be expected to be a better π back-bonder than either a neutral Ru(-II) complex or a cationic Ir(-I) complex. However, the osmium nitrosyls are *less* bent and the N-M-N angle is either the *same or smaller* than in the ruthenium and iridium analogs. Either our intuitive notion is wrong and Os(-II) is a poorer π back-bonder than Ru(-II) or other additional factors also influence the geometries of these complexes.

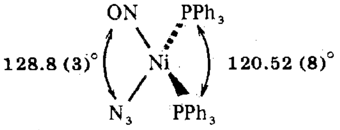
If one assumes that linear NO ligands are capable of greatly reducing the electron density on the metal to which they are attached by virtue of their very effective π-accepting characteristics, perhaps even more so than bent nitrosyls, and if one also assumes that, as in the 16-18-electron (NO = 1-3-electron donor) five-coordinate complexes, the bending of the nitrosyl is accompanied by a distinct change in coordination geometry (see eq 1), then a highly basic metal such as Os(-II)

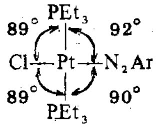
$$\underset{\text{tetrahedral}}{L_3(NO^+)M^n} \rightarrow \underset{\text{square planar}}{L_3(NO^-)M^{n+2}} \quad (1)$$

could very effectively dispense its electron density to two linear nitrosyl ligands which would be less inclined to bend (MNO angle) and distort (NMN angle) toward a square-planar geometry. Unfortunately the iron and cobalt structural results are not conveniently rationalized on this basis. A molecular orbital scheme for pseudotetrahedral dinitrosyl complexes has been proposed, but we fail to see how such a scheme assists in rationalizing the details of our structural results.[17]

It has been suggested that the trigonal-bipyramidal-linear NO to square-pyramidal-bent NO conversion in 18-16-electron systems is also accompanied by a simultaneous interchange of relative molecular orbital energy levels.[6,15-18] Although there are many fewer experimental data documenting the similar transition (see eq 1) in four-coordinate systems, there are indications that it might occur. Indeed, others have also suggested the possibility.[16-18] When would a square-planar nitrosyl complex be observed, and why has not one been discovered yet? If we apply rules I-III (vide infra), which were originally developed for five-coordinate complexes, to four-coordinate complexes, we see that all of the following should be pseudotetrahedral: $M(NO)_2P_2$, $M(CO)(NO)_2P$, $M(CO)_2(NO)_2$, $M'(NO)P_3$, $M'(CO)(NO)P_2$, $M'(CO)_2(NO)P$, $M'(CO)_3(NO)$, $M'(NO)_2P_2^+$, $M'(CO)(NO)_2P^+$, $M'(CO)_2(NO)_2^+$, $M''(NO)P_3^+$, $M''(CO)(NO)P_2^+$, $M''(CO)_2(NO)P^+$, $M''(CO)_3(NO)^+$, $M''Cl(CO)_2(NO)$, $NiCl(NO)P_2$, and $NiCl(CO)NO)P$ (M = Fe, Ru, Os; M' = Co, Rh, Ir; M'' = Ni, Pd, Pt; P = Ph_3). However, $PtCl(NO)P_2$ and probably its Pd analog are expected to be square-planar complexes. These considerations coupled with the knowledge that Pd and Pt have a pronounced tendency to form unusually stable 16-electron square-planar complexes give credence to the prediction. Regretfully, *trans*-$PtX(NO)P_2$ complexes (X = halogen) and the Pd analogs are as yet unknown. There is a report of an unstable, paramagnetic, purple crystalline material which was formulated as $Pt(CF_3)(NO)(PPh_3)_2$ with ν(NO) 1660 cm^{-1}. If this compound is correctly formulated, the relatively high value of ν(NO) suggests a linear nitrosyl ligand with pseudotetrahedral geometry.[39] Thus, because of the considerations above and the requirements of the 16–18-electron rule, few complexes can be expected to exhibit the square-planar geometry with a bent nitrosyl ligand. We expect, then, that a square-planar structure for the osmium dinitrosyl with trans phosphines and trans nitrosyl ligands would be unfavorable. A square-planar cis structure cannot be completely ruled out on this basis alone, but the cis disposition of the triphenylphosphine ligands is probably unfavorable; furthermore, there are no known compounds where NO is trans to a phosphine.

There are, however, strong indications from two recent structural studies that such transitions to a square-planar geometry can and do occur. First, although pseudotetrahedral, $Ni(N_3)(NO)(PPh_3)_2$ (ν(NO) 1710 cm^{-1})[39] is distinctly distorted toward the trans square-planar geometry and has a partially bent nitrosyl ligand, Ni–N–O = 152.7 (7)°. The P–Ni–P and N(nitrosyl)–Ni–N(azide) angles distinctly open up, and the P–Ni–N angles all become smaller than the tetrahedral value all the while maintaining the orthogonality of the N–Ni–N and P–Ni–P planes (85.1 (2)°). The tendency of tetrahedral Ni(0) to go to square-planar Ni(II) is certainly perceptible in this case. Second, $PtCl(NNAr)(PEt_3)_2$ (Ar = *p*-FC_6H_4) is definitely square planar with trans phosphines and a doubly bent aryldiazo (Pt–N–N = 118°) ligand which is bent toward one of the vacant coordination sites;[40] NNAr is isoelectronic with NO. Since the Ni–N–O and P–Ni–P planes are almost perpendicular (73.0 (6)°) in the nickel structure, the NO bends in the same manner as does the diazo group. The strong trans effect of the NO^- ligand, which is greater than that of ArN_2^-, coupled with the tendency of NO^- to be oxidized to NO_2^-, suggests that the corresponding nitrosyls of Pt and Pd may be difficult to prepare. We have recently shown that the following complexes which contain doubly bent aryldiazo ligands behave spectroscopically and chemically in a similar manner: $PtCl(N_2Ph)(PEt_3)_2$, $IrCl_2(CO)(N_2Ph)(PPh_3)_2$, and $OsCl(CO)_2(N_2Ph)(PPh_3)_2$.[41] It is noteworthy that no nitrosyl analog of any of these compounds has yet been reported. Although the structure of $CoI(NO)_2L'$ (L' = $Ph_2PCH_2CH_2P(O)Ph_2$)[11] has been interpreted to suggest the presence of bent NO ligands, the apparent disorder of the nitrosyls and the artificial constraints placed on them require that the structural results be viewed with caution.[11] Certainly, better structures of $CoX(NO)_2P$ (X = Cl, Br, I; P = PPh_3, PPh_2Me, etc.) would clarify this point. Indeed, the oxidation of one of the phosphine ligands to a phosphine oxide suggests that a nitrosyl ligand may have been similarly affected and that $CoI(NO_2)(NO)L'$ may be present in the crystal.





The assignment of an oxidation state to the osmium atom in $Os(NO)_2P_2$ presents an interesting problem. ESCA spectra of some osmium triphenylphosphine complexes are pertinent to this problem. The Os $4f_{7/2}$ binding energies of $OsCl_4P_2$ (51.8 eV), $OsCl_2(CO)_2P_2$ (50.6 eV), and $Os(CO)_3P_2$ (49.4 eV) show a progressive decrease of 1.2 eV between Os(IV) and Os(II) and also between Os(II) and Os(0). The respective Os $4f_{7/2}$, N 1s, and O 1s binding energies for $OsCl_3(NO)P_2$ are 51.5, 400.1, and 531.8 eV; for $Os(NO)_2P_2$ the values are 50.2, 399.0, and 531.1 eV. The osmium 4f binding energy of the mononitrosyl is between Os(II) and Os(IV) on the above scale, and that of the dinitrosyl is between Os(0) and Os(II). Apparently the effective electron density on the osmium atom in the dinitrosyl complex as measured by this technique is closer to that for Os(0) or Os(II) than to that expected for Os(–II).

The ESCA data tend to support the suggestion that linear nitrosyl ligands are extremely effective at removing electron density from the metal.[42] Indeed, one might be tempted on this basis to suggest that the complex be described formally as Os(II) or Os(0) with two linear anionic or neutral NO ligands. However, although we know of no four-coordinate, low-spin, d^6 transition metal complexes, we would expect them to be square planar, not tetrahedral. Pearson, using symmetry arguments and an assumed molecular orbital scheme, has predicted that such complexes would indeed be square planar.[43] Whether such a molecular orbital scheme would be valid with two strong π-acceptor ligands present is not known. Furthermore, to describe the dinitrosyl complex as Os(0) with two neutral NO ligands also presents the same problem, namely, that low-spin, four-coordinate d^8 complexes are known to be square planar. Thus, we prefer the descriptions used previously[6,12] with the conditional understanding that linear nitrosyl ligands can be especially effective at removing the π-electron density from the Os(–II). On the basis of its filled d shell, an Os(–II) d^{10} complex with two NO^+ ligands is predicted to have a tetrahedral geometry with linear NO ligands. Although a ligand and a metal tend to distribute electron density so as to reduce the charges on each of them (Pauling's principle of electroneutrality), we do not feel that nitrosyl ligands should be arbitrarily assigned a formal charge of zero[44] because this practice often leads to unusual oxidation states for the metal. Furthermore, the NO^+ or NO^- formulation is very useful in predicting and understanding the reaction chemistry and stereochemistry of nitrosyl complexes.[45] Apparently the electron density on the linear NO ligands can be readily transferred back onto the metal since much of the reaction chemistry for these ruthenium and osmium dinitrosyl complexes is readily understood on the basis that the metal is the site of greatest electron density.[3,46]

Predictions of Coordination Geometries in Nitrosyl Complexes. This section contains eight rules of thumb for predicting the general coordination geometries in many nitrosyl complexes. Rules I, II, V, VI, VII, and VIII have been discussed before either directly or indirectly; we explicitly reformulate them here for the sake of clarity and completeness. Although the nitrosyl ligand is amphoteric in nature and can act either as a one-electron (bent NO) or as a three-electron (linear NO) donor ligand, we will consider NO to be a three-electron donor in this section for the sake of bookkeeping purposes only. Rules I–VII were developed primarily for 18-electron, five-coordinate nitrosyl complexes, since extensive structural data are available for these complexes. We include these rules in this paper because we believe that they will be useful for 18-electron, four-coordinate complexes too. Rule

VIII is more general in scope, as discussed later. One experimental observation for 18-electron, five-coordinate complexes seems to reoccur, namely, that the axial, bent nitrosyl ligand is associated with the square-pyramidal (SP) geometry (often d^6 metals), and the axial or equatorial, linear nitrosyl ligand is associated with the trigonal-bipyramidal (TBP) geometry (often d^8 metals).[47] We must not forget the possibility of intermediate coordination geometries in even-electron complexes which contain partially bent nitrosyl ligands, but for the sake of brevity we will not consider them in detail here.

(I) Without the assistance of special ligands (see below) first-row transition metals usually do not have enough reducing power by themselves to bend the nitrosyl ligand; second-row metals often do and third-row metals usually do. We expect $Mn(CO)_2(NO)(PPh_3)_2$, $FeCl(CO)(NO)(PPh_3)_2$,[49] and $CoCl_2(NO)(PPh_3)_2$[50] to be TBP and the Os and Ir analog of the last two to be SP. As a first guess, we would expect the Ru and Rh analogs to be SP. However, $RuI(CO)(NO)(PPh_3)_2$ appears to be an exception. Although the complex is distinctly disordered, the diffraction data have been interpreted to suggest that this compound is TBP.[38] Indeed, the value of ν(NO) is greatly (and anomalously) dependent on X in the complexes $RuX(CO)(NO)(PPh_3)_2$ suggesting that these complexes may contain a range of different geometries.[8,51]

(II) The number and size of bulky ligands play an important role; they usually go in the least sterically hindered positions. With one such ligand present, it usually occupies the nonaxial position. With two present, both are usually trans to each other and occupy the axial sites in TBP and nonaxial sites in SP. With three present, the SP geometry is usually not found, and all three would occupy the nonaxial sites in TBP. Thus we would expect that the phosphine ligands would occupy equatorial, axial–axial, and equatorial–equatorial–equatorial sites in the respective TBP complexes $FeCl(CO)_2(NO)(PPh_3)$,[52] $FeCl(CO)(NO)PPh_3)_2$,[53] and $FeCl(NO)(PPh_3)_3$.[52] We expect $OsCl(CO)(NO)(PPh_3)_2$[46,51] to be SP with trans nonaxial phosphines, $OsCl(NO)(PPh_3)_3$[52] to be TBP with equatorial phosphine ligands, and $OsCl(NO)(PMe_2Ph)_3$[52] to have an intermediate geometry.

(III) Strong π-acceptor ligands such as CO and NO (linear) and also σ-donor ligands with large trans effects, such as H and NO (bent), prefer not to be trans to each other in any combination if possible. Nitrosyl complexes which contain isocyanides have not been studied in any detail, but it is assumed that they would behave in a fashion similar to that of a less bulky phosphine ligand. Although H prefers being trans to P in preference to NO, the steric bulk of the three triphenylphosphines controls the stereochemistry in $RuH(NO)(PPh_3)_3$,[54] $Os(CO)(NO)(PPh_3)_3^+$,[33] and $IrH(NO)(PPh_3)_3^+$,[55] which should have TBP geometries with trans axial H, CO, and NO ligands. Interestingly, the iridium cation has another lattice-stabilized isomer in which the H is no longer trans to NO but in which there is also a distorted TBP geometry with linear NO.[56] By this rule we expect $Os(CO)_2(NO)(PPh_3)_2^+$ [33] and $OsH(NO)_2(PPh_3)_2^+$ [3] to be TBP, while $Os(NH_3)(CO)(NO)(PPh_3)_2^+$ [52] and $OsCl(NO)_2(PPh_3)_2^+$ [52,57] would be SP. The whole iron series would be expected to be TBP. The compound $IrCl(CO)(NO)P_2^+$ [6] is SP, but $IrH(CO)(NO)P_2^+$ is predicted to be TBP. Although the hydrido complex is not known, the corresponding methyl complex $Ir(CH_3)(CO)(NO)P_2^+$ [58] is known and might be expected to have the same geometry as the hydrido complex. Although ν(NO) is the same (1680 cm^{-1}) for the chloro and methyl complexes, it is not clear whether their geometries are similar or not.

(IV) Re and probably W and Mo, which form strong metal–nitrogen multiple bonds and prefer ligands which are good π acceptors, retard the bending of the attached nitrosyl ligands. Thus, by rule III, $Re(CO)_2(NO)(PPh_3)_2$[59] and $ReH(NO)_2(PPh_3)_2$[59] are TBP, but so is $ReCl(NO)_2(PPh_3)_2$[60] by this rule. There are no known five-coordinate complexes of W (C_5H_5 is considered tridentate); should $W(CO)(NO)_2P_2$[52] be prepared, it would be TBP.

(V) Bidentate ligands such as tetramethylethylenediamine, 1,10-phenanthroline, 2,2′-bipyridine, *o*-phenylenebis(dimethylarsine), and 1,2-bis(diphenylphosphino)ethane usually favor TBP geometry with equatorial NO when two such ligands are present. Because of their small bite angles (about 80–90°) they prefer to span axial–equatorial sites rather than equatorial–equatorial sites. Furthermore, because of unfavorably close ligand–ligand contacts if the two ligands were to occupy the four coordination positions in a square plane, TBP geometries are favored over SP. This may not apply to xanthates, dithiocarbamates, or ligands such as $CH_3SCH_2CH_2S^-$ which are sterically less bulky. Thus, $Ru(NO)(diphos)_2^+$,[61] $Ir(NO)(diphos)_2^{2+}$,[62] and $Co(NO)(diars)_2^{2+}$ [63] are expected to be TBP with equatorial nitrosyl ligands.

(VI) Special multidentate ligands can promote one geometry over another. $HC(CH_2PPh_2)_3$ stabilizes the TBP geometry while tetraphenylporphyrin (tpp) stabilizes the SP geometry. Similarly, $PhP(CH_2CH_2CH_2PPh_2)_2$ (ppp) can stabilize SP geometries or axial–equatorial–axial TBP geometries. We could expect $CoCl_2(NO)L_2$ (L = neutral ligand) to be TBP, but Co(tpp)(NO)[64] would be SP. Similarly, $RhCl(ppp)(NO)^+$ [65] would be SP, but $RhCl(NO)(PPh_3)_3^+$ [66] would be expected to be TBP.

(VII) Ligands which deactivate the metal by removing electron density from it, thereby decreasing its reducing power, favor the TBP geometry and conversely. An excessive number of carbonyl or olefin ligands without the presence of strong σ donors will deactivate the metal. Replacing Cl^- by $R_fCO_2^-$ (R_f = perfluoroalkyl or -aryl) could shift the electronic balance and also sufficiently deactivate the metal. While $IrCl_2(NO)P_2$[67] is SP, $Ir(R_fCO_2)(NO)P_2$ and $IrCl_2(CO)_2(NO)$[52] may well adopt the TBP geometry.

(VIII) The 16–18-electron rule is almost an infallible guide for all common coordination numbers, except for 17-electron and 18-electron complexes with four- or five-coordination. If the integrity of the nitrosyl ligand is maintained, all 20-electron systems must have bent nitrosyls (e.g., $CoCl(NO)(en)_2^+$,[68] $Co(NCS)(NO)(diars)_2^+$,[63] and $Co(NO)(NH_3)_5^{2+}$ [69]). Fewer six-coordinate, 20-electron complexes are known because of the strong trans-weakening effect of the bent nitrosyl ligand. Six-coordinate, 18- and 17-electron nitrosyl complexes all have linear nitrosyl ligands (e.g., $OsCl_3(NO)P_2$[70] and $ReCl_3(NO)P_2$[59,60]). Six-coordinate, 19-electron systems probably have "partially" bent NO ligands with M–N–O angles distinctly larger than 120° (e.g., $ReCl_2(NO)_2P_2$,[59,60] $FeCl(NO)(diars)_2^+$,[71] and $IrCl_3(NO)P_2$[1,4]). All 16-electron systems have linear nitrosyl ligands, e.g., $WCl_3(NO)(OPPh_3)_2$[72] (d^4 octahedral), $ReCl_2(NO)P_2$[73] (d^6, square-pyramidal, probably nonaxial NO), and $OsCl(NO)P_2$[52] or $IrCl(NO)P_2^+$ [58,74] (d^8, square planar).

Concluding Remarks

Why do the above generalizations seem to be useful in predicting the coordination geometry of the nitrosyl ligand? These empirical generalizations certainly have little value as ex post facto rationalizations since they are not inherently fundamental in nature as, for example, are energy and symmetry considerations in molecular orbital arguments. If one makes some simple and perhaps naive assumptions about the behavior of the nitrosyl ligand, then perhaps the generalizations can be understood. (1) The "normal" coordination geometry is linear. (2) In five-coordinate, 18-electron systems TBP geometry is associated with linear NO and SP geometry is associated with bent NO. (3) There is relatively little energy difference between the TBP and SP forms. Consequently, other subtle influences within a given complex which favor either TBP or SP geometries may well govern whether the NO is linear or bent. This idea has been discussed before, most recently and explicitly by Enemark and Feltham, who have named it stereochemical control of valence (SCV).[17] (4) The last generalization is simply an extension of the 16–18-electron rule, namely, that any electrons beyond the magic number of 18 must be located on easily reduced ligands. Part of the utility of these generalizations is that there are relatively few diamagnetic nitrosyl complexes known with intermediate geometries and "partially bent" (between 135 and 165°) nitrosyl ligands. It has been suggested that the reversal of the ordering of the d_{z^2} orbital and π^* orbital at the NO during the SP to TBP conversion would result in an effective level crossing along this conversion coordinate, a distinct barrier for this conversion, and a distinctly different charge separation on either side of the barrier.[18] On this basis one would expect nitrosyl complexes with intermediate geometries to occur less frequently.

Although Bruce[75] and Connelly[76] both suggested that the then current theories concerning the preferred geometry of the M–N–O system in any specific situation had little predictive power, we believe that the above considerations and generalizations will be very useful in predicting the general stereochemistry of nitrosyl complexes and in designing coordination compounds with specific stereochemistries and properties. It is possible that exceptions to the rules will be found and that some of the generalizations may have to be modified, expanded, or discarded. Notwithstanding, their current usefulness is apparent; it will be the exceptions which will yield new chemical insights into nitrosyl complexes.

Acknowledgment. This work was kindly supported by the National Science Foundation through the Northwestern University Materials Research Center. We are indebted to Matthey-Bishop, Inc., for the loan of precious metal used in this study. For supplying us with samples of the osmium complex, we wish to thank Dr. W. R. Roper and Dr. S. D. Robinson from whose (SDR) sample the final data crystal was grown. We are indebted to Dr. R. Bastasz for assistance in obtaining ESCA spectra.

Registry No. $Os(NO)_2(PPh_3)_2 \cdot {}^1/_2C_6H_6$, 55954-46-6.

Supplementary Material Available. A listing of structure amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Business Office, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number AIC40847I-11-75.

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(8) Abbreviations: Ph, C_6H_5; Et, C_2H_5; Me, CH_3; Ar, aryl; P, mono(tertiary phosphine); diphos, $Ph_2PCH_2CH_2PPh_3$; MNTS, *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide; ppp, $PhP(CH_2CH_2CH_2PPh_2)_2$; dmpe, $Me_2PCH_2CH_2PMe_2$; diars, *o*-$(Me_2As)_2C_6H_4$; X, anionic ligand; pz, pyrazolyl.

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Contribution from the Department of Chemistry and Materials Research Center,
Northwestern University, Evanston, Illinois 60201

Aryldiazo Complexes. Structure of a Hydrido–Aryldiazo Complex of Osmium, $OsH(CO)(N_2C_6H_5)(P(C_6H_5)_3)_2 \cdot CH_2Cl_2$

MARTIN COWIE, BARRY L. HAYMORE, and JAMES A. IBERS*

Received June 3, 1975 AIC50374V

The structure of $OsH(CO)(N_2C_6H_5)(P(C_6H_5)_3)_2 \cdot CH_2Cl_2$ has been determined crystallographically and consists of discrete molecules of the aryldiazo complex and solvent. This complex of Os(0) is five-coordinate and has a distorted trigonal-bipyramidal coordination geometry about the osmium atom. Owing to the reduced steric requirements of the hydrido ligand, the P(1)–Os–P(2) and N(1)–Os–C(1) angles change from the respective idealized values of 180 and 120° to 164.37 (6) and 138.0 (3)° indicating a distortion toward a quasitetrahedral geometry. The singly bent, phenyldiazo ligand occupies an equatorial coordination site and possesses an unusually long osmium–nitrogen bond length with Os–N = 1.867 (6) Å, N–N = 1.211 (8) Å, N–C = 1.460 (10) Å, Os–N–N = 171.1 (6)°, and N–N–C = 118.5 (7)°. The compound crystallizes from dichloromethane as solvated crystals in space group C_i^1-$P\bar{1}$ of the triclinic system with $a = 13.440$ (2) Å, $b = 13.481$ (1) Å, $c = 12.528$ (2) Å, $\alpha = 114.30$ (1)°, $\beta = 101.82$ (1)°, $\gamma = 81.43$ (1)°, and $Z = 2$. Based upon 5340 unique reflections with $F_o^2 > 3\sigma(F_o^2)$ the structural data were refined by full-matrix, least-squares methods to $R = 0.046$ and $R_w = 0.057$.

Introduction

Much current interest has been stimulated in aryldiazo ligands, not only because of their close relationship to nitrosyl and dinitrogen ligands but also because of their varied modes of bonding and their utility as intermediates in the syntheses of aryldiazene and arylhydrazine ligands.[1-9] Structural studies have shown that the aryldiazo ligand can adopt a doubly bent geometry[10,11] or a singly bent geometry[12] or that it can bridge two metal atoms.[13] In this regard, it is similar to the isoelectronic nitrosyl ligand; indeed, nitrosyl and aryldiazo ligands have been compared structurally in almost identical coordination environments in $[RhCl(L)(PhP(CH_2CH_2CH_2PPh_2)_2)][PF_6]$[10,14,15] (bent Rh–N–N) and in $RuCl_3(L)(PPh_3)_2$[16,17] (linear Ru–N–N) where L = NNAr, NO. The geometry and chemical reactivity seem to be very sensitive to the electronic characteristics of the central metal and especially to the coordination geometry about it. For this reason, structural studies are especially useful in understanding the types of reactions which aryldiazo ligands undergo.

Recently, acyl-, aroyl-, and alkyldiazo ligands have been prepared starting with dinitrogen complexes of rhenium, molybdenum, and tungsten.[18] Many aryldiazo ligands, especially those attached to Ru, Os, Rh, Ir, and Pt, react with coordinating and noncoordinating protonic acids to form complexes of *cis*-aryldiazene.[2-4,19] A rhenium complex containing a singly bent aryldiazo ligand has been observed to react with H^+ at the nitrogen atom which is attached to the aryl group, thus forming an unsymmetrical form of phenyldiazene, Re=N=NHPh.[20] In an aryldiazo complex the value of ν(NN), when not vibrationally coupled with other ligand modes, is indicative of the mode of coordination of the aryldiazo group.[10,16] Despite the relatively low value of ν(NN) at 1543 cm^{-1} for $OsH(CO)(NNPh)(PPh_3)_2$, we felt that it was indicative of a singly bent mode of coordination for the diazo ligand.[21]

For this reason and because this reactive complex is the first hydrido–aryldiazo complex to be synthesized we have determined its solid-state structure crystallographically and report it here. This is the third five-coordinate, aryldiazo complex to be studied crystallographically and the second one found to possess a trigonal-bipyramidal coordination geometry about the metal.[22]

Experimental Section

Crystal Preparation. The title complex was prepared according