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Structure of Dinitrosyl(1,2-bis(diphenylphosphino)ethane)cobalt Hexafluorophosphate, $[Co(NO)_2((C_6H_5)_2PC_2H_4P(C_6H_5)_2)][PF_6]$

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The structure of dinitrosyl(1,2-bis(diphenylphosphino)ethane)cobalt hexafluorophosphate, $[Co(NO)_2((C_6H_5)_2PC_2H_4P(C_6H_5)_2)][PF_6]$, has been determined from three-dimensional x-ray data. The compound crystallizes in the space group C_s^4-Cc with four molecules in a unit cell of dimensions a = 13.510 (8) Å, b = 17.075 (9) Å, c = 13.532 (7) Å, and β = 115.42 (2)°. Least-squares refinement of the 191 variables has led to the value of the conventional R index (on F) of 0.068 for the 2663 independent reflections for which $F_o^2 > 3\sigma(F_o^2)$. The complex may be described as a tetrahedral Co(–I) complex of approximate C_{2v} symmetry. Structural parameters: Co–P(1) = 2.249 (3), Co–P(2) = 2.244 (3), Co–N(1) = 1.656 (10), Co–N(2) = 1.671 (11) Å; P(1)–Co–P(2) = 87.87 (9), N(1)–Co–N(2) = 131.7 (5), Co–N(1)–O(1) = 176.6 (14), Co–N(2)–O(2) = 172.3 (11)°. The angle between the $Co(NO)_2$ and CoP_2 planes is 92°. Comparisons are made between the structures and infrared and visible spectra of the title compound, $[Co(NO)_2(PPh_3)_2][PF_6]$, and $Co(NO)_2$(SacSac). These structures generally conform to the trends previously observed in $M(NO)_2L_2$ complexes, and the partial success of molecular orbital theory in rationalizing these trends is discussed.

Introduction

The structures of a number of isoelectronic $M(NO)_2(PPh_3)_2$ (M = Fe,[1] Ru,[2] Os,[3] Co^+,[4] Rh^+,[5] Ir^+,[6] Ph = C_6H_5 = phenyl) complexes have been reported. In this series of complexes the P–M–P angles span a relatively narrow range (104–116°) despite considerable variations in the N–M–N and M–N–O angles (124–158 and 159–179°, respectively). Moody and Ryan[7] recently reported the structure of the related complex $Pt(SO_2)_2(PPh_3)_2$. In this complex the P–Pt–P angle is 158.58 (6)° and both SO_2 ligands are pyramidal (the geometry analogous to a bent nitrosyl group, if one accepts the notion that bonding in complexes containing coordinated SO_2 is similar to that in the analogous nitrosyl complexes). This structure, discussion of structural effects on the electronic properties of nitrosyl complexes,[8] and our observation of a possible correlation between the P–M–P and N–M–N angles in the series $M(NO)_2(PPh_3)_2$[5] prompted us to ask what would be the effects on the geometries of the nitrosyl groups in an $M(NO)_2L_2$ (L = PR_3) complex if the P–M–P angle were constrained to a value outside the 104–116° range. Attempts to synthesize such complexes with either larger or smaller P–M–P angles were frustrated by the difficulty of isolating pure complexes. The complex $[Co(NO)_2diphos][PF_6]$ (diphos = 1,2-bis(diphenylphosphino)ethane) is known[9] and can be crystallized. The P–M–P angle in complexes containing this chelating phosphine ligand is generally about 90°. This large change from the geometry of the bis(triphenylphosphine) complexes might have some observable effect on the nitrosyl groups. In fact, there are differences in certain properties of $[Co(NO)_2diphos][PF_6]$ and $[Co(NO)_2(PPh_3)_2][PF_6]$.[9] The visible spectra differ (λ_{max}(diphos) 450 (sh) nm and $\lambda_{max}(PPh_3)$ 590 (sh) nm), as do the infrared spectra (ν(NO, diphos) 1860 and 1790 cm^{-1} and $\nu(NO, PPh_3)$ 1836 and 1784 cm^{-1} (Nujol mulls)). These frequencies are those expected for linear or nearly linear Co–N–O groups.[10] The catalytic properties of these two compounds also differ. Both complexes catalyze reaction 1. The diphos complex is a slightly better catalyst

$$2NO + CO \rightarrow N_2O + CO_2 \quad (1)$$

than the bis(triphenylphosphine) complex. From the possible correlation between catalytic activity and solid-state structure for $M(NO)_2L_2$ complexes,[5,11] we expected the Co–N–O angle to be slightly smaller in $[Co(NO)_2diphos][PF_6]$ than in $[Co(NO)_2(PPh_3)_2][PF_6]$.

For comparison with the structures of $[Co(NO)_2(PPh_3)_2][PF_6]$ and of $Co(NO)_2$(SacSac) (SacSac = dithioacetylacetonato),[12] the structure of $[Co(NO)_2(diphos)][PF_6]$ is of interest and is reported here.

Experimental Section

The complex $[Co(NO)_2diphos][PF_6]$ was prepared by the method of Gwost and Caulton.[9] The infrared spectrum (Nujol mull, taken on a Perkin-Elmer 337 spectrometer) exhibits nitrosyl stretching frequencies at 1860 and 1790 cm^{-1}. Visible spectra of $[Co(NO)_2diphos][PF_6]$ and $[Co(NO)_2(PPh_3)_2][PF_6]$[9] were measured for solutions (~5 × 10^{-4} M) in CH_2Cl_2; a $[Co(NO)_2(PPh_3)_2][PF_6]$ solution is stable in air for a few hours, decomposing to $CoCl_2(PPh_3)_2$; a $[Co(NO)_2diphos][PF_6]$ solution is stable in air for several days. The brown bis(triphenylphosphine) complex exhibits a prominent broad shoulder at 590 nm, while the orange diphos complex exhibits a less prominent one at about 450 nm.

Crystals of $[Co(NO)_2diphos][PF_6]$ were grown by layering a solution of the complex in *N*,*N*-dimethylformamide (DMF) with ethanol. One of the deep red rhombs, of approximate dimensions 0.22 × 0.60 × 0.66 mm, was mounted on a glass fiber. On the basis of optical goniometry and x-ray measurements, we established that the crystal belongs to the monoclinic system and that the principal faces belong to the forms {010}, $\{11\bar{1}\}$, and {110}. From Weissenberg photography taken with Cu Kα radiation, the space group was determined to be either C_{2h}^6-$C2/c$ or C_s^4-Cc. The lattice constants at 20 °C, determined[13] from the setting angles of 12 strong reflections which had been centered manually on a Picker FACS-I diffractometer using Mo Kα radiation (λ 0.709 300 Å) are a = 13.510 (8) Å, b = 17.075 (9) Å, c = 13.532 (7) Å, and β = 115.42 (2)°. With four formula weights per unit cell, the calculated density is 1.56 g cm^{-3}, in excellent agreement with the measured density of 1.57 (1) g cm^{-3}, measured by flotation of the crystals in a mixture of dibromomethane and hexane.

For data collection Mo Kα radiation was used. The intensities were measured by the θ–2θ technique at a takeoff angle of 3.0°. At this angle the intensity of a reflection was about 90% of its maximum value. A receiving counter aperture 5 mm high and 5 mm wide was positioned 35 cm from the crystal. Symmetric scans in 2θ, 0.9° below the Kα_1 peak to 0.9° above the Kα_2 peak, were used. Stationary-counter, stationary-crystal background counts of 10 s were measured at the beginning and end of each scan. For reflections having $I < 3\sigma(I)$, the scan was repeated once with background counting times of 20 s and added to the results of the first scan. Attenuators were inserted automatically if the intensity of the diffracted beam exceeded about 7000 counts s^{-1}.

The data set for which $k \geq 0$, $l \geq 0$, and $2\theta \leq 54°$ was gathered; the intensities of 3093 reflections were recorded. The reflections for which $k \leq 0$, $l \leq 0$, and $2\theta \leq 22°$ were also collected to provide a set of Friedel pairs. The intensities of the six standard reflections remained constant within counting statistics.

All data processing was carried out as previously described.[13] The value of p was selected as 0.04. The values of I and $\sigma(I)$ were corrected for Lorentz and polarization effects. The 2663 unique reflections for which $F_o^2 > 3\sigma(F_o^2)$ were used in subsequent calculations. The linear absorption coefficient, μ, for this compound using Mo Kα radiation is 8.39 cm^{-1}. An absorption correction was made,[14] and transmission coefficients ranged from 0.714 to 0.850.

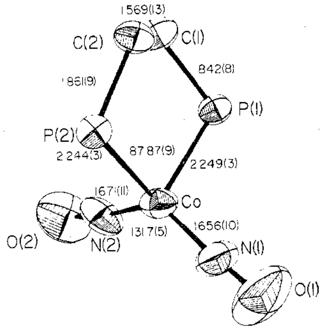

Figure 1. A perspective view of the coordination sphere of the $Co(NO)_2diphos^+$ ion. The shapes of the atoms in this and the following drawing represent 50% probability contours of thermal motion.

The intensity statistics strongly favored the acentric space group. A Patterson synthesis did not reveal the Co–Co Harker vectors expected for the space group $C2/c$. Therefore the space group was assumed to be C_s^4-Cc, and this was confirmed by the successful solution and refinement of the structure. The sharpened Patterson synthesis revealed the positions of the Co atom and of one of the P atoms of the coordination sphere. The Co atom was fixed at 0, y, $^1/_4$, and a least-squares refinement on F was computed. The function $\sum w(|F_o| - |F_c|)^2$ was minimized, in which $w = 4F_o^2/\sigma^2(F_o^2)$ and $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes. Values of the atomic scattering factors and anomalous terms were taken from the usual source.[15] Only the overall scale factor and the positional parameters of the Co and P atoms were varied. This refinement led to the agreement indices $R = 0.39$ and $R_w = 0.47$, where $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum F_o^2)^{1/2}$. Subsequent difference Fourier maps revealed the positions of all of the remaining atoms. The Co, P, F, N, O, and methylene C atoms were refined isotropically as individual atoms; the phenyl rings were treated as rigid groups[16] and restricted to their known geometry ($6/mmm$ symmetry, d(C–C) = 1.392 Å). Each ring carbon atom was assigned an individual isotropic thermal parameter.

In an attempt to establish the correct enantiomer for the crystal chosen, two models of the structure were refined: one (A) with the indices as assigned and the second (B) in which hkl was changed to $\bar{h}\bar{k}\bar{l}$. Refinement of model A converged at $R = 0.0931$ and $R_w = 0.1221$; model B converged at $R = 0.0930$ and $R_w = 0.1213$. This difference is not significant, according to Hamilton's ratio test.[17] Based on trends in the structure amplitudes of Friedel pairs and the slightly smaller standard deviations, model B was chosen for further refinement. Clearly in the present instance any errors resulting from an incorrect choice of enantiomer in this space group are negligible.

In later refinements the Co, P, F, N, O, and methylene C atoms were refined anisotropically. A difference Fourier map revealed the positions of all 24 unique hydrogen atoms. They were included in later structure factor calculations in calculated idealized positions (d(C–H) = 0.95 Å) which were not refined.

The final refinement of 191 variables using 2663 observations resulted in the values $R = 0.068$ and $R_w = 0.086$. A structure factor calculation for the 430 reflections omitted from the refinements because $F_o^2 < 3\sigma(F_o^2)$ revealed that in no case was $|F_o^2 - F_c^2| > 3\sigma(F_o^2)$. There are no significant trends in $\sum w(|F_o| - |F_c|)^2$ as a function of $|F_o|$, setting angle, or Miller indices. The largest peak in the final difference Fourier map is 0.40 (6) e Å^{-3}, in the vicinity of the hexafluorophosphate ion. The error in an observation of unit weight is 2.69 electrons.

The positional, thermal, and group parameters derived from the last cycle of least-squares refinement are given in Table I, along with the standard deviations as estimated from the inverse matrix. The positional parameters of the ring carbon atoms which may be derived from the data in Table I are presented in Table II, together with their thermal parameters. The final values of $10|F_o|$ and $10|F_c|$ in electrons are given in Table III.[18] Table IV presents the root-mean-square amplitudes of vibration.[18] Table V gives the idealized positions of the hydrogen atoms.[18]

Description of the Structure and Discussion

The crystal structure consists of discrete, monomeric ions occupying general positions in the space group Cc. The inner-coordination geometry of the cation is shown in Figure 1, a stereoview of the cation is presented in Figure 2, and a

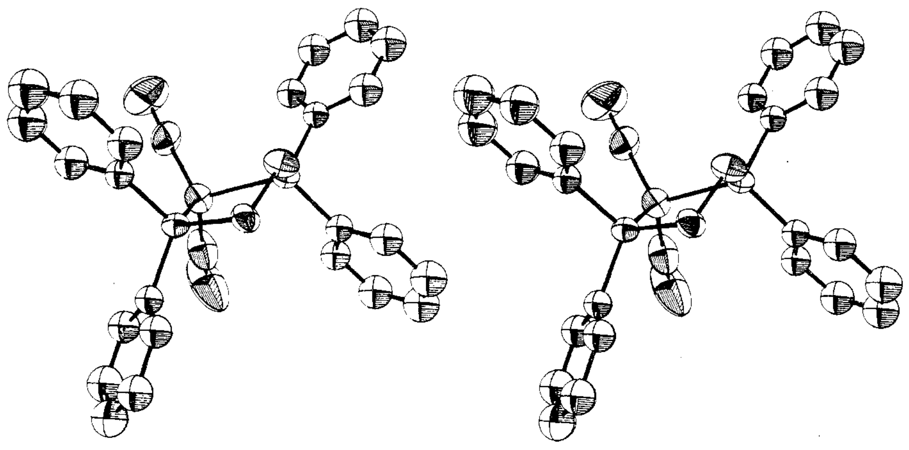

Figure 2. A stereoview of the cation. The view is approximately down the y axis, with the x axis horizontal and to the right. Hydrogen atoms are omitted for clarity.

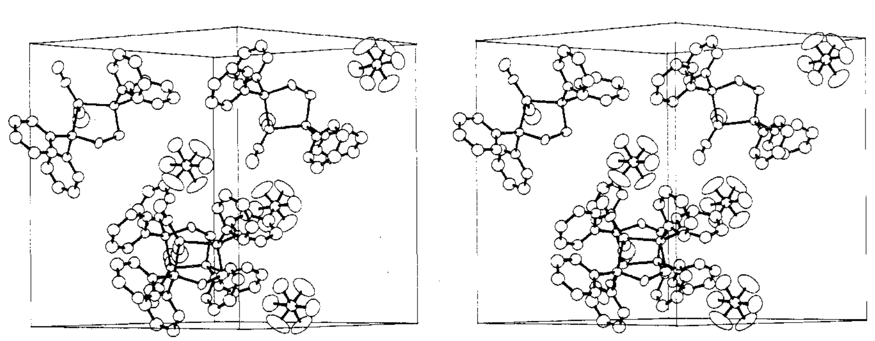

Figure 3. A stereodrawing illustrating the packing in $[Co(NO)_2diphos][PF_6]$. The view is approximately along [101], with the y axis vertical and the x axis horizontal and to the right. The shapes of the atoms in this drawing represent 40% probability contours of thermal motion.

Table I. Positional and Thermal Parameters for the Nongroup Atoms of $[Co(NO)_2((C_6H_5)_2PC_2H_4P(C_6H_5)_2)][PF_6]$

ATOM	X[A]	Y	Z	B11[B]	B22	B33	B12	B13	B23
CO	0	0.203782(68)	1/4	63.75(93)	27.99(42)	70.3(10)	-10.98(53)	32.87(81)	-6.66(59)
P(1)	0.04623(20)	0.32177(13)	0.33078(21)	53.6(15)	25.19(73)	44.3(15)	-1.37(84)	18.4(13)	-0.90(84)
P(2)	0.14214(20)	0.21464(12)	0.20664(20)	56.1(16)	24.94(73)	47.5(16)	-3.39(84)	20.9(13)	-1.52(85)
P(3)	0.34919(26)	0.42996(17)	0.04295(30)	67.5(19)	39.1(11)	98.3(25)	8.7(11)	41.6(19)	6.3(14)
F(1)	0.22276(64)	0.42166(61)	0.0102(12)	63.2(61)	90.2(55)	287.(17)	2.2(43)	66.5(83)	19.9(77)
F(2)	0.32937(81)	0.49770(66)	-0.0364(11)	140.0(90)	91.7(51)	290.(17)	7.4(60)	57.(10)	122.0(82)
F(3)	0.33710(97)	0.36631(72)	-0.04259(87)	214.(13)	104.7(65)	140.(11)	56.4(76)	28.4(95)	-29.9(66)
F(4)	0.47357(61)	0.43553(57)	0.07618(84)	64.0(60)	93.0(51)	175.(10)	11.6(40)	39.6(63)	32.6(56)
F(5)	0.37325(68)	0.36043(52)	0.13011(74)	128.4(75)	72.3(42)	121.4(82)	9.9(45)	48.5(64)	36.3(48)
F(6)	0.36137(96)	0.49077(79)	0.1315(11)	209.(12)	104.1(67)	201.(13)	55.6(74)	32.(10)	-62.7(80)
N(1)	0.02377(88)	0.13212(50)	0.3398(10)	126.(10)	30.8(32)	152.(11)	2.6(43)	99.7(91)	15.8(49)
N(2)	-0.10951(77)	0.22520(63)	0.13397(91)	44.5(66)	61.7(46)	84.6(87)	-13.8(43)	15.2(65)	-19.3(51)
O(1)	0.0452(13)	0.08311(67)	0.4016(13)	344.(22)	66.1(53)	291.(20)	58.7(85)	268.(19)	71.7(88)
O(2)	-0.17766(83)	0.24682(72)	0.05376(87)	86.1(76)	102.6(66)	108.7(87)	-19.6(58)	-10.4(70)	-14.9(64)
C(1)	0.17331(71)	0.35248(52)	0.32276(78)	57.4(65)	34.6(33)	57.5(67)	-6.3(36)	32.9(55)	2.8(38)
C(2)	0.17004(83)	0.32166(50)	0.21215(81)	86.2(78)	27.8(30)	54.2(70)	-9.7(37)	28.8(64)	-6.5(36)

[A] ESTIMATED STANDARD DEVIATIONS IN THE LEAST SIGNIFICANT FIGURE(S) ARE GIVEN IN PARENTHESES IN THIS AND ALL SUBSEQUENT TABLES. [B] THE FORM OF THE ANISOTROPIC THERMAL ELLIPSOID IS: $EXP[-(B11H^2+B22K^2+B33L^2+2B12HK+2B13HL+2B23KL)]$. THE QUANTITIES GIVEN IN THE TABLE ARE THE THERMAL COEFFICIENTS X 10^4.

Table II. Derived Parameters for the Rigid Group Atoms of $[Co(NO)_2((C_6H_5)_2PC_2H_4P(C_6H_5)_2)][PF_6]$

ATOM	X	Y	Z	B, A^2	ATOM	X	Y	Z	B, A^2
C(111)	-0.05788(48)	0.39379(33)	0.25420(57)	3.44(16)	C(211)	0.12290(51)	0.18252(37)	0.07307(45)	3.16(15)
C(112)	-0.03298(44)	0.46461(37)	0.21915(62)	4.72(21)	C(212)	0.19740(48)	0.20387(39)	0.03191(58)	5.12(23)
C(113)	-0.11671(60)	0.51589(34)	0.15693(69)	5.77(27)	C(213)	0.18344(60)	0.17717(45)	-0.07045(62)	5.78(25)
C(114)	-0.22536(52)	0.49635(43)	0.12977(70)	6.38(28)	C(214)	0.09498(66)	0.12912(46)	-0.13166(49)	5.79(27)
C(115)	-0.25026(42)	0.42553(47)	0.16482(73)	6.30(29)	C(215)	0.02048(52)	0.10777(40)	-0.09050(53)	5.34(23)
C(116)	-0.16652(55)	0.37424(35)	0.22704(67)	4.91(22)	C(216)	0.03443(47)	0.13447(38)	0.01186(54)	4.22(18)
C(121)	0.07441(51)	0.33069(36)	0.47311(41)	3.37(15)	C(221)	0.26863(44)	0.16769(34)	0.29844(54)	3.49(16)
C(122)	0.02898(52)	0.27730(33)	0.51970(53)	4.52(19)	C(222)	0.26122(44)	0.09365(36)	0.33778(62)	4.38(19)
C(123)	0.05249(62)	0.28287(40)	0.63020(55)	5.87(28)	C(223)	0.35608(58)	0.05314(33)	0.40398(66)	5.63(24)
C(124)	0.12144(65)	0.34184(44)	0.69410(42)	5.59(25)	C(224)	0.45834(47)	0.08667(43)	0.43084(66)	6.12(27)
C(125)	0.16687(56)	0.39524(35)	0.64751(49)	4.94(22)	C(225)	0.46575(42)	0.16072(44)	0.39150(70)	5.81(27)
C(126)	0.14336(51)	0.38966(32)	0.53702(51)	4.15(18)	C(226)	0.37089(54)	0.20123(32)	0.32530(63)	4.63(21)

RIGID GROUP PARAMETERS

GROUP	X_C[A]	Y_C	Z_C	DELTA[B]	EPSILON	ETA
R(11)	-0.14162(41)	0.44507(28)	0.19198(44)	-2.2793(40)	-2.8828(47)	-2.7538(52)
R(12)	0.09793(37)	0.33627(26)	0.58361(40)	-0.6289(44)	2.9627(34)	-1.6976(45)
R(21)	0.10894(40)	0.15582(26)	-0.02929(42)	-0.358(12)	-1.9279(39)	-0.927(12)
R(22)	0.36348(39)	0.12718(28)	0.36464(42)	1.0321(38)	2.8907(46)	2.7897(51)

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

packing diagram is presented in Figure 3. A selection of distances and angles is given in Table VI.

The ions are separated generally by van der Waals contacts; no nonbonded distances are particularly short. The hexafluorophosphate ion is exceptionally well-behaved for an ion which is often found to be disordered. The P–F distances range from 1.521 (8) to 1.605 (8) Å, F–P–F cis angles range from 87.3 (6) to 94.4 (8)°, and F–P–F trans angles range from 177.6 (9) to 178.3 (6)°.

We favor the description of the cation as a distorted tetrahedral d^{10} Co(–I) complex. The complex possesses approximate twofold symmetry; if the chelate ring is neglected, the approximate symmetry is C_{2v}. All the bond distances and angles are within expected ranges. The $Co(NO)_2$ group is planar; the least-squares plane through these five atoms is given by the equation $8.84x - 9.47y - 10.08z + 4.45 = 0$. The maximum deviation from this plane is 0.01 Å for both atoms O(1) and O(2). The N–Co–N angle of 131.7 (5)° and the O–Co–O angle of 135.9 (4)° demonstrate that the nitrosyl groups are bent slightly away from each other in this plane. This is consistent with the intuitive idea that the decrease of the M–N–O angle reflects increasing NO^- character of the nitrosyl groups and that the partial negative charges on these groups repel each other, increasing the N–M–N angle. The slight difference in the Co–N–O angles can be attributed to differences in the environments of the nitrosyl groups. The plane determined by the Co and P atoms is given by the equation $3.35x - 7.54y + 9.10z - 0.74 = 0$. The angle between the $Co(NO)_2$ and CoP_2 planes is 92°, illustrating that the deviations from tetrahedral geometry are not large. The chelate ring is decidedly nonplanar; the distances of atoms C(1) and C(2) from the CoP_2 plane are 0.12 and –0.66 Å, respectively.

Useful comparisons can be made between the results reported here and the structures of $[Co(NO)_2(PPh_3)_2][PF_6]$[4] and $Co(NO)_2(SacSac)$.[12] The difference of 26° in the P–Co–P angles (87.87 (9)° for $Co(NO)_2diphos^+$ vs. 113.5 (2)° for $Co(NO)_2(PPh_3)_2{}^+$) is large and expected; the S–Co–S angle of 100.0 (1)° is similarly unexceptional. The difference in the N–Co–N angles in the phosphine complexes (131.7 (5) and

Table VI. Distances and Angles in $[Co(NO)_2((C_6H_5)_2PC_2H_4P(C_6H_5)_2)][PF_6]$

Cation Intramolecular Distances, Å

Co–P(1)	2.249 (3)	P(1)–C(1)	1.842 (8)
Co–P(2)	2.244 (3)	P(2)–C(2)	1.861 (9)
Co–N(1)	1.656 (10)	P(1)–C(111)[a]	1.820 (6)
Co–N(2)	1.671 (11)	P(1)–C(121)	1.802 (6)
N(1)–O(1)	1.130 (14)	P(2)–C(211)	1.797 (7)
N(2)–O(2)	1.142 (13)	P(2)–C(221)	1.811 (6)
C(1)–C(2)	1.569 (13)		

Cation Angles, Deg

P(1)–Co–P(2)	87.87 (9)	Co–P(2)–C(2)	104.6 (4)
N(1)–Co–N(2)	131.7 (5)	Co–P(2)–C(211)	117.8 (2)
O(1)–Co–O(2)	135.9 (4)	Co–P(2)–C(221)	116.4 (3)
Co–N(1)–O(1)	176.6 (14)	P(1)–C(1)–C(2)	108.4 (6)
Co–N(2)–O(2)	172.3 (11)	P(2)–C(2)–C(1)	106.8 (6)
N(1)–Co–P(1)	112.3 (4)	C(1)–P(1)–C(111)	106.6 (4)
N(1)–Co–P(2)	109.6 (3)	C(1)–P(1)–C(121)	105.3 (4)
N(2)–Co–P(1)	102.1 (4)	C(111)–P(1)–C(121)	108.0 (4)
N(2)–Co–P(2)	104.4 (3)	C(2)–P(2)–C(211)	106.2 (4)
Co–P(1)–C(1)	107.3 (3)	C(2)–P(2)–C(221)	107.0 (3)
Co–P(1)–C(111)	110.1 (2)	C(211)–P(2)–C(221)	103.9 (3)
Co–P(1)–C(121)	118.8 (2)		

Intramolecular Nonbonded Contacts, Å[b]

Co–O(1)	2.784 (11)	Co–H(116)	3.21
Co–O(2)	2.807 (10)	Co–H(222)	3.22
Co–H(216)	3.05	N(1)–H(222)	2.54
Co–H(122)	3.17	O(1)–H(222)	2.57

Intermolecular Contacts, Å[b]

O(2)–H1C(1)	2.37	C(114)–C(222)	3.34
F(4)–H(115)	2.39	C(216)–H(114)	2.72
F(3)–H(122)	2.46	C(211)–H(114)	2.74
F(1)–H(224)	2.47	C(212)–H(225)	2.74
F(5)–H(123)	2.50	C(113)–H(223)	2.85

[a] The labels C(1) and C(2) denote the methylene carbon atoms of the diphos ligand. In the labels C(*xyz*) of the phenyl carbon atoms, *x* denotes the phosphorus atom to which the ring is attached, *y* specifies the number of the phenyl ring, and *z* indicates the position of the particular carbon atom in the ring. [b] In the calculation of these distances, the hydrogen atoms were placed in the calculated idealized positions listed in Table V.

136.7 (4)°) is surprisingly small, considering the large difference in the P–Co–P angles, and is of questionable chemical significance; the N–Co–N angle of 115.5 (3)° in $Co(NO)_2$(SacSac) is considerably smaller. The difference in the average Co–P distances (2.247 (4) and 2.266 (3) Å) can be rationalized by the usual notion that a diphos ligand is more basic and less sterically demanding than two triphenylphosphine ligands. The average Co–N distances (1.664 (11), 1.645 (6), and 1.650 (6) Å in the diphos, triphenylphosphine, and SacSac complexes, respectively) are equal within experimental error. The average N–O distances (1.136 (12), 1.174 (6), and 1.120 (5) Å) are probably not different, especially when the thermal motions of the nitrosyl groups are considered. The average Co–N–O angles (174.4 (14), 171.0 (5), and 168.9 (5)° differ slightly. The nitrosyl groups in the phosphine complexes are bent away from each other (i.e., O–Co–O > N–Co–N), while in the SacSac complex they are bent toward each other (O–Co–O < N–Co–N). Clearly, any useful bonding scheme must rationalize all these differences in geometry, especially the differences in the N–Co–N angles. Unfortunately, no such scheme appears to be extant.

Martin and Taylor[12] have found a very good linear correlation between the N–M–N and O–M–O angles in $M(NO)_2L_2$ complexes and have noted that the trend is in agreement with the molecular orbital scheme for $\{MNO\}^{10}$ complexes of C_{2v} symmetry proposed by Enemark and Feltham.[8] Complexes which exhibit the greatest N–M–N angles also show the most pronounced bending of the nitrosyl groups away from each other, and conversely. An encouraging feature of this scheme is the fact that it rationalizes the bending of the nitrosyl groups toward each other in complexes for which the N–M–N angle is small, an observation that is otherwise difficult to explain. Enemark and Feltham discuss these two modes of distortion from the ideal geometry of linear nitrosyl groups in terms of the nature of the filled $1b_1$ and empty $2b_1$ orbitals. The discussion is based on the relative energies of the π^*b_1 (NO) and d_{xz} orbitals, from which the b_1 orbitals are formed. The ML_2 geometry is not considered explicitly, apart from the fact that the complex is assumed to possess C_{2v} symmetry.

In the pair of complex ions $Co(NO)_2diphos^+$ and $Co(NO)_2(PPh_3)_2{}^+$, the Co atom in the diphos complex is expected to be more electron rich, and thus the splitting between the $1b_1$ and $2b_1$ orbitals should be larger than that for the bis(triphenylphosphine) complex. The observed visible spectra for this pair of complexes in CH_2Cl_2 solution (λ_{max}(diphos) 450 (sh) nm and $\lambda_{max}(PPh_3)$ 590 (sh) nm) are in agreement with this prediction. The Co–N–O angles, however, are not: Co–N–O(diphos) = 174.4 (14)° and Co–N–O(PPh_3) = 171.0 (5)°. The complex ion $Co(NO)_2(diphos)^+$ seems to be an exception to the general trend observed by Martin and Taylor, and, indeed, lies farthest from the line correlating the N–M–N and O–M–O angles. Although differences in the electronic properties of a diphos ligand and two triphenylphosphine ligands should affect the separation between the $1b_1$ and $2b_1$ orbitals, this separation should also be sensitive to purely geometrical differences in the P–Co–P angles, but qualitative molecular orbital schemes provide no guidance as to the magnitude or direction of this effect.

While the scheme of Enemark and Feltham may be employed to rationalize certain features of these complexes (with perhaps a surprising degree of success), the difficulties lie not in this nor in any other scheme but in the inability to know how certain geometrical changes affect the relative ordering of the energy levels. Thus the effects on the energy levels critical for a discussion of the N–M–N and O–M–O angles of changing the L–M–L angle and the bonding properties of L in $M(NO)_2L_2$ systems have not been considered and are probably beyond present computational techniques. Therefore, the empirical approach of making chemical modifications and observing their geometrical effects[19] has much merit at the present time and will ultimately provide a wealth of useful tests for more sophisticated bonding schemes.

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Registry No. $[Co(NO)_2diphos][PF_6]$, 37662-50-3.

Supplementary Material Available: Table III, the list of structure amplitudes, Table IV, the root-mean-square amplitudes of vibration and Table V, the idealized positions of the hydrogen atoms (21 pages). Ordering information is given on any current masthead page.

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(18) Supplementary material.

(19) For the complexes $M(NO)_2(PPh_3)_2^+$ (M = Co, Rh, Ir) we have noted a correlation between the average corrected nitrosyl stretching frequency ν_{av}' (ref 10) and the M–N–O angle, ω. This correlation is given by the unit-weighted least-squares line ω (deg) = $0.231\nu_{av}' - 230$ (cm^{-1}). From the ν_{av}' for $[Co(NO)_2diphos][PF_6]$ of 1749 cm^{-1} we predict that the average value of the Co–N–O angle is 174°, in excellent agreement with the observed value of 174.4 (14)°.

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A Linear RN_2–Transition Metal Linkage. The Structure of $RuH_2(N_2B_{10}H_8S(CH_3)_2)(P(C_6H_5)_3)_3{\cdot}3C_6H_6$

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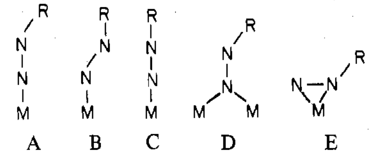
The structure of $RuH_2(N_2B_{10}H_8S(CH_3)_2)(P(C_6H_5)_3)_3{\cdot}3C_6H_6$ has been determined crystallographically and consists of discrete molecules of the diazo complex and solvent. The complex crystallizes from benzene–methanol in the triclinic space group C_i^1-$P\bar{1}$ with two formula units in a unit cell of dimensions a = 23.80 (1) Å, b = 12.683 (6) Å, c = 12.793 (6) Å, α = 105.63 (2)°, β = 99.16 (2)°, γ = 101.00 (3)°, ρ_{exptl} = 1.25 (3) g/cm^3, and ρ_{calcd} = 1.242 g/cm^3. The structure was solved by Patterson methods. Least-squares refinement has led to a final value of the conventional R index for $F_o > 3\sigma(F_o)$ of 0.072 based on 5590 reflections. This complex of Ru(II) possesses pseudooctahedral geometry with cis hydrido ligands and meridinal phosphine ligands. The diazo group $N_2B_{10}H_8S(CH_3)_2$ is trans to H(1): H(1)–Ru–N(1) = 173 (2)°. The RuNNB segment is essentially linear: Ru–N(1)–N(2) = 175.9 (6)° and N(1)–N(2)–B(1) = 172.7 (8)°. This is the first reported example of a transition metal–diazo complex containing the totally linear MNNR linkage. The boron cage possesses regular bicapped Archimedean antiprism geometry; the B–B distances within the square plane are 1.83–1.87 Å with B–B–B bond angles of approximately 90°. The B–B′ distances of bridging boron atoms range from 1.76 to 1.81 Å with B–B′–B angles of approximately 60°. Some important distances are Ru–N(1) = 1.889 (8), N(1)–N(2) = 1.115 (8), and N(2)–B(1) = 1.50 (1) Å.

Introduction

Current interest in aryldiazo ligands arises 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 synthesis of aryldiazene and arylhydrazine ligands.[1-9] The varied coordination geometries attainable by nitrosyl and aryldiazo ligands are indicative of their chemical versatility:



Structural studies have shown that the aryldiazo ligand can adopt a doubly bent geometry (B)[10,11] and a singly bent geometry (A)[12-16] and can bridge two metal atoms (D).[17] In these bonding modes the aryldiazo ligand (RN_2^+) is similar to the isoelectronic nitrosyl ligand; indeed, nitrosyl and aryldiazo ligands have been compared structurally in almost identical coordination environments.[14,18,19]

In the search for as yet unobserved bonding modes (e.g., C) and for intermediate geometries,[20] the use of infrared ν(NN) stretching frequencies and especially of empirically corrected frequencies ν'(NN)[11,14] has proved invaluable. The complex $RuH_2(N_2B_{10}H_8SMe_2)(PPh_3)_3$ (Ph = phenyl; Me = methyl), prepared by Knoth[21] by the reaction of $RuH_2(N_2)(PPh_3)_3$ with $N_2B_{10}H_8SMe_2$, shows a value of ν(NN) of 2060 cm^{-1} and an empirically corrected value ν'(NN) of 1910 cm^{-1}. This complex is thus a prime candidate to be the first example of the totally linear coordination mode (C). Moreover, on the basis of our recent work on the Ni(diazofluorene)(t-BuNC)$_2$ complex,[20,22] in which bonding mode E was observed for the first time, it appears as though the reaction chemistry and the bonding modes of neutral RN_2 species with transition metals will differ considerably from those of the more heavily studied RN_2^+ species. We have thus begun a systematic investigation of the bonding and chemistry of transition metal–RN_2 species. Here we report the structure of $RuH_2(N_2B_{10}H_8SMe_2)(PPh_3)_3$ which indeed does provide the first example of the totally linear bonding mode (C).

Experimental Section

A sample of $RuH_2(N_2B_{10}H_8SMe_2)(PPh_3)_3$ was kindly supplied by Dr. W. H. Knoth. Recrystallization of the yellow powder from benzene–methanol yielded yellow, slightly air-sensitive crystals. Because the crystals slowly lose benzene of crystallization, freshly prepared crystals were mounted in capillaries in an atmosphere of the solvent in order to prevent desolvation during data collection.

Preliminary film data showed the crystals to belong to the triclinic system with no systematic absences. The centrosymmetric space group $P\bar{1}$ was shown to be the correct choice on the basis of successful refinement of the structure with acceptable positional parameters, thermal parameters, and agreement indices. Accurate unit cell dimensions were determined by a least-squares analysis of the angular positions of 14 hand-centered reflections in diverse regions of reciprocal space (in the range $37 \geq 2\theta \geq 30°$). See Table I for pertinent details on the crystal and data collection.

Data collection was carried out on a Picker four-circle diffractometer. Background counts were measured at both ends of the scan range with both the counter and the crystal stationary. The intensities of six standard reflections were measured every 100 reflections. The deviations of these standards were all within counting statistics. The intensities of 6759 reflections (all $-h$, $\pm k$, and $\pm l$ reflections) were measured out to 2θ = 95.00° using Cu Kα radiation. A value of p