Crystal and Molecular Structure of Allylnitrosylbis(triphenylphosphine)ruthenium, Ru(NO)(η^3-C$_3$H$_5$)(P(C$_6$H$_5$)$_3$)$_2$

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The reaction of RuCl(NO)(PPh$_3$)$_2$ with tetraallyltin produces the mixed allyl–nitrosyl complex Ru(NO)(η^3-C$_3$H$_5$)(PPh$_3$)$_2$, whose structure has been determined from three-dimensional X-ray data collected by counter techniques. The material crystallizes in the space group $P2_1$ of the monoclinic system with two molecules in the unit cell. Crystal data are a = 9.04 (1) Å, b = 17.47 (3) Å, c = 11.51 (2) Å, β = 115.39 (8)°, ρ_{measd} = 1.409 (5) g/cm^3, and ρ_{calcd} = 1.410 g/cm^3. The structure has been refined by a full-matrix least-squares procedure to conventional discrepancy factors R_1 and R_2 of 0.0299 and 0.0383 for 2190 observations having $F_o{}^2 > 3\sigma(F_o{}^2)$. The coordination geometry about the ruthenium atom is best described as distorted tetrahedral, similar to other four-coordinate 18-electron complexes. Both the allyl and nitrosyl ligands act as three-electron donors. Important distances and angles are Ru–C1 = 2.214 (7) Å, Ru–C2 = 2.130 (7) Å, Ru–C3 = 2.258 (8) Å, Ru–N = 1.751 (6) Å, C1–C2–C3 = 117.7 (7)°, and Ru–N–O = 173.8 (6)°. A comparison of this structure with those of the isoelectronic complexes Ru(NO)$_2$(PPh$_3$)$_2$ and Ru(η^3-C$_3$H$_5$)$_2$(PPh$_3$)$_2$ is made, and the η^3 mode of allyl coordination is discussed.

Introduction

The ability of nitrosyl and allyl ligands to serve as either one- or three-electron donors in transition-metal complexes is well established.[1,2] Recent attention has focused on the potential role of such species in homogeneous catalytic reactions as a means of generating coordinative unsaturation at the metal center.[3–6]

The conversion of linear nitrosyl to bent nitrosyl appears to occur in several systems including RuCl(NO)$_2$L$_2{}^+$ (L = PPh$_3$),[7] a complex containing both linear and bent NO's on the same metal. As suggested in the ^{15}N labeling study by Collman et al.,[8] the nitrosyls in RuCl(NO)$_2$L$_2{}^+$ interconvert, probably through a TBP intermediate in which the nitrosyls are equivalent.[1c] The bending of the MNO unit in nitrosyls has been discussed extensively in terms of intramolecular redox equilibria[6] and stereochemical control of valence.[1a,9] Bending of the nitrosyl ligand in an intramolecular process leading to coordinative unsaturation is believed to function in certain catalytic systems.[4]

The allyl ligand is closely related to NO in that both η^3 (three-electron donor) and η^1 (one-electron donor) complexes are known. Unlike nitrosyls, however, a direct spectroscopic means of observing coordination geometry is available via ^{1}H NMR. Exchange of syn and anti protons in η^3-allyls is a readily observed phenomenon, proceeding in most cases through an intermediate η^1 species.[2b] The utilization of this $\eta^3 \rightleftharpoons \eta^1$ conversion ($\pi \rightleftharpoons \sigma$) is proposed as a key step in a cobalt–allyl complex which catalytically hydrogenates arenes.[3]

The structural duality of both the nitrosyl and allyl ligands places these ligands and their respective complexes in a position of special attention because of the catalytic implications of their dynamic behavior. To date, however, only two allyl–nitrosyl systems are known; they are [(C$_5$H$_5$)Mo(CO)(NO)(η^3-C$_3$H$_5$)]$^+$ [10] and the more extensively studied Fe(NO)(η^3-C$_3$H$_5$)L$_2$, where L is CO or tertiary phosphine.[11,12] In an earlier communication[13] we reported the first platinum-group metal complex of this type, Ru(NO)(η^3-C$_3$H$_5$)L$_2$, L = PPh$_3$, **1**, and its reaction with CO to form a five-coordinate species containing an η^3-allyl and a necessarily bent nitrosyl. In addition, a preliminary description of the crystal structure of **1** was given. We herein provide the full details of that structure and as well provide comparisons with relevant complexes, including Ru(NO)$_2$L$_2$[14] and Ru(η^3-C$_3$H$_5$)$_2$L$_2$.[15]

Experimental Section

Materials. Ruthenium trichloride trihydrate (Matthey Bishop), tetraallyltin (Ventron), triphenylphosphine (Ventron), and Diazald (N-methyl-N-nitroso-p-toluenesulfonamide, Aldrich) were used as

purchased. All solvents were of reagent grade and were dried and degassed before use.

The method of Robinson et al.[16] was used to prepare RuCl$_3$(NO)(PPh$_3$)$_2$. All operations were performed under an atmosphere of prepurified nitrogen using modified Schlenk techniques.

Preparation of (η^3-Allyl)nitrosylbis(triphenylphosphine)ruthenium, Ru(NO)(η^3-C$_3$H$_5$)(PPh$_3$)$_2$. Solid Zn/Cu couple[17] (2.6 g) was added to a suspension of RuCl$_3$(NO)(PPh$_3$)$_2$ (2.0 g, 2.6 mmol) in THF (80 mL) and refluxed 1 h. The resulting green solution of RuCl(NO)(PPh$_3$)$_2$ was then cooled to room temperature and filtered. Tetraallyltin (0.75 mL, 3 mmol) was then added, and the solution was shaken and allowed to sit at room temperature for 1 h, during which time the color turned red. The volume of the solution was reduced to 15 mL under vacuum, and an equal volume of Et$_2$O was added. The solution was again filtered and then placed in a refrigerator at 10 °C. Within 24–72 h red crystals of the product formed (1.1 g, 1.6 mmol). The yield was 61% (based on Ru). Anal. Calcd for C$_{39}$H$_{35}$NOP$_2$Ru: C, 67.2; H, 5.06; N, 2.01; P, 8.89. Found: C, 67.14; H, 5.14; N, 1.98; P, 8.80.[16] The complex shows a characteristic nitrosyl stretch at 1620 cm^{-1} (KBr). The ^{1}H NMR shows the presence of a nonfluxional, essentially symmetric η^3-allyl with the coupling of two equivalent phosphorus nuclei to the anti protons (central proton, δ 4.70; anti protons, δ 1.00; syn protons, δ 2.40 and 2.42 ($^3J_{\text{syn}}$ = 4.0 Hz, $^3J_{\text{anti}}$ = 10.0 Hz, $J_{\text{PH}_{\text{anti}}}$ = 6.0 Hz)). The ^{31}P{^{1}H} NMR shows a singlet at 51.3 ppm downfield from trimethyl phosphate internal reference.[13] The complex is moderately soluble in benzene, THF, and CH$_2$Cl$_2$ and decomposes rapidly in CHCl$_3$ or CCl$_4$ to RuCl$_3$(NO)(PPh$_3$)$_2$. The crystals are air-stable for several months; however, solutions decompose immediately upon contact with air.

Data Collection and Reduction. Red crystals of Ru(NO)(C$_3$H$_5$)(PPh$_3$)$_2$ were obtained as above. On the basis of Weissenberg and precession photographs it was determined that the crystals belong to the monoclinic system. The observed systematic absence of k = $2n$ + 1 for $0k0$ is consistent with the space groups $P2_1$ ($C_2{}^2$) and $P2_1/m$ ($C_{2h}{}^2$).[19] The lattice constants at 22 °C were determined from a least-squares refinement of the setting angles of 12 high-angle reflections ((sin θ)/$\lambda \geq$ 0.4734).[20] The reflections were carefully centered, using Mo Kα radiation (λ 0.709 261 Å), on a Picker FACS-1 diffractometer equipped with a graphite monochromator. The lattice constants are a = 9.04 (1) Å, b = 17.47 (3) Å, c = 11.51 (2) Å, and β = 115.39 (8)°. An experimental density of 1.409 (5) g/cm^3 determined by the flotation method agrees with a value of 1.410 g/cm^3 for Z = 2.

The mosaicity of the crystal used for intensity measurements was examined by means of a narrow-source, open-counter ω-scan technique.[21] The full widths at half-maximum for typical strong reflections were 0.1°.

The crystal dimensions were approximately 0.25 × 0.15 × 0.10 mm^3 and the crystal was mounted with the a^* axis coincident with the φ axis of the diffractometer.

Intensities were measured by the θ–2θ scan technique. The takeoff angle for the X-ray tube was 1.9°. The scan was from 0.6° below the Kα_1 peak to 0.6° above the Kα_2 peak. The scan speed was 1°/min,

Table I

Final Positional and Thermal Parameters for Ru(NO)(η^3-C$_3$H$_5$)(PPh$_3$)$_2$–Nongroup Atoms

	x	y	z	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ru	0.77980 (5)[b]	−0.600000 (0)	0.08806 (4)	73.6 (7)	18.70 (17)	45.8 (5)	−2.1 (4)	20.9 (4)	−0.7 (3)
P1	0.60593 (19)	−0.57601 (9)	−0.13361 (16)	75.5 (25)	16.2 (6)	53.1 (15)	−0.1 (9)	27.8 (17)	−0.2 (7)
P2	0.61786 (20)	−0.67094 (10)	0.16254 (16)	85.4 (27)	18.1 (6)	47.8 (16)	0.6 (11)	24.8 (17)	0.0 (8)
N	0.8408 (7)	−0.5296 (3)	0.2079 (5)	138 (11)	21.2 (22)	68 (6)	−10 (4)	27 (7)	−8 (3)
O	0.8811 (10)	−0.4871 (4)	0.2967 (6)	381 (18)	40.5 (28)	104 (8)	−12 (6)	38 (10)	−30 (4)
C1	0.9873 (8)	−0.5992 (7)	0.0343 (7)	73 (10)	43 (3)	94 (8)	−7 (8)	44 (7)	−7 (7)
C2	0.9869 (9)	−0.6645 (5)	0.1024 (8)	100 (13)	40 (3)	74 (8)	13 (6)	39 (9)	1 (5)
C3	0.8557 (9)	−0.7157 (5)	0.0451 (8)	124 (13)	26 (3)	70 (8)	14 (5)	36 (8)	−4 (4)
C1H1	1.058 (10)	−0.561 (5)	0.073 (8)	5.0000 (0)[c]					
C1H2	0.942 (8)	−0.599 (6)	−0.060 (7)	5.0000 (0)					
C2H	1.054 (10)	−0.661 (5)	0.186 (9)	5.0000 (0)					
C3H1	0.810 (10)	−0.730 (5)	−0.048 (9)	5.0000 (0)					
C3H2	0.858 (10)	−0.762 (5)	0.104 (8)	5.0000 (0)					

Final Group Parameters for Ru(NO)(η^3-C$_3$H$_5$)(PPh$_3$)$_2$[d]

	X_c	Y_c	Z_c	ϕ	θ	ρ	B, Å^2
P1C1	0.7129 (4)	−0.423 60 (18)	−0.239 2 (3)	−1.079 (5)	−2.2363 (27)	−2.234 (5)	0.0 (0)
P1C2	0.6135 (4)	−0.714 95 (18)	−0.314 87 (29)	−1.011 (3)	2.5867 (26)	−0.777 (4)	0.0 (0)
P1C3	0.2264 (4)	−0.528 65 (19)	−0.223 4 (3)	−0.536 (4)	−2.189 (3)	2.859 (5)	0.0 (0)
P2C1	0.4216 (3)	−0.582 03 (17)	0.300 93 (27)	−0.159 (3)	2.6311 (26)	2.203 (3)	0.0 (0)
P2C2	0.8460 (4)	−0.788 62 (18)	0.384 28 (29)	−0.8139 (25)	3.1139 (29)	0.528 (3)	0.0 (0)
P2C3	0.3270 (4)	−0.767 96 (17)	−0.054 93 (28)	−2.4301 (24)	2.9078 (28)	−0.492 (3)	0.0 (0)

[a] The form of the anisotropic thermal ellipsoid is $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. Entries are ×10^4. [b] Numbers in parentheses here and in succeeding tables are estimated standard deviations in the least significant figures. [c] Isotropic thermal parameters which were held fixed. [d] X_c, Y_c, and Z_c are group center-of-mass coordinates; ϕ, θ, and ρ are angular parameters described previously; B is the group thermal parameter which was not refined.

and backgrounds were counted for 10 s at each end of the scan range. Attenuator foils were automatically inserted when the intensity of the diffracted beam reached 10 000 counts/s. The pulse-height analyzer was set for a 90% window centered on Mo Kα radiation.

Data were collected in the range $3° \le 2\theta \le 45°$ from the quadrant with $k \ge 0$ and $l \ge 0$. The three standard reflections were monitored every 77 observations. The intensities of the standards varied by less than ±3%. A total of 2458 reflections were observed. The values I and $\sigma^2(I)$ were obtained using the expressions previously described.[22] The value of p used in the expression of the variance was chosen as 0.04.[23] Values of I and $\sigma^2(I)$ were converted to F^2 and $\sigma^2(F^2)$ by application of Lorentz and polarization corrections. The linear absorption coefficient for Mo Kα radiation is 6.02 cm^{-1} and no correction for absorption was made. The final data set consisted of 2372 independent reflections of which 2190 had $F_o^2 \ge 3\sigma(F_o^2)$.

Solution and Refinement of the Structure. In the space group $P2_1$, the general twofold positions are x, y, z and $-x, \frac{1}{2} + y, -z$. The position of the ruthenium atom was determined from a three-dimensional Patterson map.[24] Application of the direct methods program package MULTAN III, using the 300 largest normalized structure factors, and the tangent formula resulted with the highest figure of merit, confirmed the ruthenium position, and provided the positions of two phosphorus atoms. The position of the ruthenium along the polar axis b was arbitrarily fixed at $y = 0.600$. Refinement of the scale factor, atomic positional, and isotropic thermal parameters for ruthenium and two phosphorus atoms resulted in residuals of $R_1 = 0.33$ and $R_2 = 0.39$.[25] In this and all subsequent refinements the quantity minimized was $\sum w(|F_o| - |F_c|)^2$ where the weights w were taken as $4F^2/\sigma^2(F^2)$. Only those reflections with $F^2 \ge 3\sigma(F^2)$ were included in the refinements. Scattering factors for neutral Ru, P, O, N, and C were those of Cromer and Mann.[26] The scattering factors for hydrogen were those of Stewart et al.[27] The effects of anomalous dispersion were included in the calculation of $|F_c|$; the values for $\Delta f'$ and $\Delta f''$ were those of Cromer and Liberman.[28]

A difference Fourier synthesis phased by the ruthenium and phosphorus atoms revealed the positions of the allyl carbons and four phenyl rings. Two cycles of refinement followed by difference Fourier syntheses revealed the remaining nonhydrogen atoms of the structure. The phenyl rings were treated as rigid groups with d(C–C) = 1.392 Å.[29] Refinement of a model in which all nongroup atoms were treated anisotropically resulted in $R_1 = 0.041$ and $R_2 = 0.054$. The hydrogen atoms of the phenyl rings were included in the rigid groups with d(C–H) = 0.95 Å and isotropic temperature factors $B_H = B_C + 1.0$ Å^2, where B_C is the temperature factor of the corresponding carbon atom. This model was refined to $R_1 = 0.033$ and $R_2 = 0.042$. In

the final cycles of refinement, contributions from all phenyl hydrogen atoms were included in F_c. A difference Fourier map revealed the positions of the five allyl hydrogens, which were refined by least squares with temperature factors fixed at 5.0 Å^2. The total of 159 variables was refined to convergence with residuals of $R_1 = 0.0304$ and $R_2 = 0.0389$. The absolute configuration of the molecule was tested by changing the sign of the y coordinate for all atoms included in the final model. This enantiomeric model was refined to convergence with residuals of $R_1 = 0.0299$ and $R_2 = 0.0383$ and hence is the correct absolute configuration. The final estimated standard deviation for an observation of unit weight[7] was 1.43. The largest peak of a final difference Fourier map was 0.49 e/Å^3 or 13% of the height of a typical carbon peak in this study.

The final positional, thermal, and group parameters are given in Table I. The derived phenyl carbon positions are presented in Table II. A listing of the observed and calculated structure factors is available.[30]

Results

The reaction of RuCl(NO)L$_2$ (L = PPh$_3$) with tetraallyltin at room temperature gives the complex Ru(NO)(η^3-C$_3$H$_5$)L$_2$ in high yield. The success of the synthesis requires (a) the absence of a halide source and (b) a coordinatively unsaturated nitrosyl chloro complex. Attempts to form the title compound by reaction of RuCl(NO)L$_2$ with C$_3$H$_5$MgCl failed, with RuCl$_3$(NO)L$_2$ isolated as the major product. For allylation of Ru to occur using the tin reagent, a coordinatively unsaturated species is required to allow initial π coordination of the olefinic portion of the allyl to the Ru center.[31] Thus, RuCl(NO)(CO)L$_2$, an 18-electron nonlabile complex, does not react with tetraallyltin after several days in refluxing benzene or THF. The ability of allyltin reagents to form an η^3-allyl directly, that is, without prior formation of an η^1-allyl,[31] may also be significant.

From spectroscopic data (see Experimental Section) the allyl is coordinated to the metal in a η^3 symmetric fashion and is static on the NMR time scale up to its decomposition temperature in solution (ca. 50 °C). The two phosphine ligands are equivalent as shown by the phosphorus coupling to the anti allyl protons and by the presence of a singlet in the ^{31}P{^{1}H} NMR spectrum. The IR nitrosyl stretching frequency of 1620 cm^{-1} does not provide any information regarding the MNO geometry; however, analysis of the structural data establishes
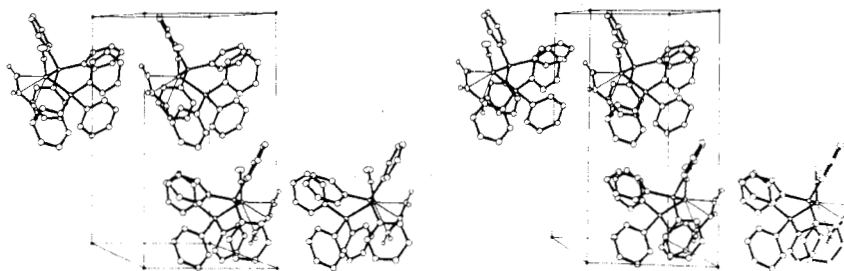
Figure 1. Stereoscopic view of the unit cell of $Ru(NO)(\eta^3\text{-}C_3H_5)(PPh_3)_2$. The vertical direction is the b axis.

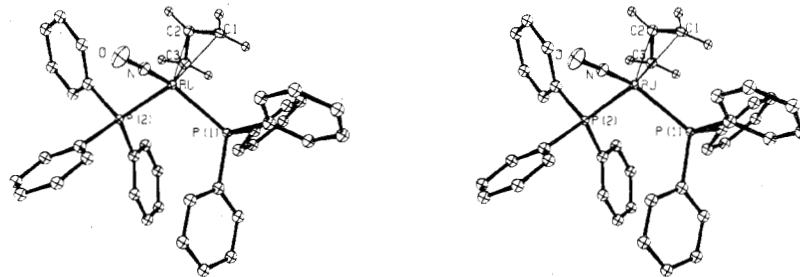**Figure 2.** Stereoscopic view of the molecule $Ru(NO)(\eta^3\text{-}C_3H_5)(PPh_3)_2$.

the coordination geometry of the MNO unit as linear (Ru–N–O = 173.8 (6)°).

Solid-State Structure of $Ru(NO)(\eta^3\text{-}C_3H_5)(PPh_3)_2$. The crystal structure consists of discrete molecules of $Ru(NO)$-$(\eta^3\text{-}C_3H_5)L_2$ occupying the general positions of the space group. The shortest Ru–Ru distance is a unit translation, 9.04 Å. The molecular packing is dominated by the two bulky triphenylphosphines and the allyl groups, with the latter posed between two of the phenyl rings on P(2). There are no specific intermolecular interactions which are significantly shorter than the sum of van der Waals radii. The shortest intermolecular contacts between phenyl hydrogen atoms are 2.47, 2.55, 2.55, and 2.55 Å which correspond to P1C1H1···P1C2H4, P2C2H4···P2C3H4, P1C1H3···P1C2H3, and P2C1H6···P2C3H5, respectively. The closest contact involving a phenyl hydrogen and another atom is 2.61 Å for O···P2C2H4. The packing arrangement is depicted in Figure 1 for one unit cell and two neighboring molecules along a, the shortest crystal direction.

A stereoscopic view of an individual molecule is presented in Figure 2. Interatomic distances and angles as well as selected dihedral angles between planes, together with their estimated standard deviations, are given in Table III. The two Ru–P bond lengths of 2.343 (3) and 2.391 (4) Å are in the general range found for most ruthenium–phosphine complexes (2.30 Å in $RuH(C_{10}H_7)(CH_3)_2PCH_2CH_2P(C-H_3)_2$,[32] 2.34 Å in $RuCl_2((CH_3)(C_6H_5)PCH_2CH_2P(C-H_3)(C_6H_5))_2$,[33] 2.339 (4) Å in $RuH(NO)(P(C_6H_5)_3)_3$,[34] 2.315 (4) Å in $[Ru(NO)(\mu\text{-}P(C_6H_5)_2)(P(CH_3)(C_6H_5))]_2$,[35] 2.345 Å in $Ru(NO)_2(P(C_6H_5)_3)_2$,[14] 2.343 Å in $Ru(\eta^3\text{-}C_3H_5)_2(P-(C_6H_5)_3)_2$,[15] 2.393 (6) Å in $RuCl_2(P(C_6H_5)_3)_3$,[36] 2.359 (6) Å in $RuH(CH_3CO_2)(P(C_6H_5)_3)_3$,[37] and 2.426 (6) Å in $[Ru-(NO)_2Cl(P(C_6H_5)_3)_2]^+$[38]). Because of differences in the coordination geometries, ruthenium oxidation states, ligand arrays, and types of phosphine, the variation in these Ru–P bond lengths cannot be simply rationalized. We note these different values merely to give a range in which the present Ru–P bond lengths may be considered.

The nitrosyl is coordinated in a linear manner with a Ru–N–O bond angle of 173.8 (6)° and a Ru–N bond length of 1.751 (6) Å. These values compare favorably with the values of other linearly coordinated nitrosyls[1] and are consistent with formally NO^+ coordinated to ruthenium.

The allyl is coordinated in a η^3 fashion to ruthenium. The Ru–C bond lengths (Ru–C1 = 2.215 (7) Å, Ru–C2 = 2.130

Table II. Derived Positional and Isotropic Thermal Parameters for Group Carbon Atoms in $Ru(NO)(\eta^3\text{-}C_3H_5)(PPh_3)_2$

	x	y	z	$B, \text{Å}^2$
P1C11[a]	0.6692 (5)	−0.49015 (21)	−0.1951 (4)	2.41 (12)
P1C12	0.6107 (5)	−0.47698 (24)	−0.3266 (4)	3.29 (14)
P1C13	0.6544 (7)	−0.41043 (28)	−0.3707 (3)	4.09 (18)
P1C14	0.7566 (7)	−0.35705 (24)	−0.2834 (5)	4.63 (17)
P1C15	0.8151 (6)	−0.37021 (24)	−0.1519 (4)	3.90 (16)
P1C16	0.7714 (6)	−0.43677 (26)	−0.1077 (3)	3.11 (14)
P1C21	0.6023 (5)	−0.65116 (21)	−0.2466 (4)	2.20 (12)
P1C22	0.5016 (5)	−0.71420 (25)	−0.2614 (4)	2.90 (13)
P1C23	0.5128 (6)	−0.77799 (22)	−0.3296 (5)	3.87 (16)
P1C24	0.6247 (6)	−0.77874 (23)	−0.3831 (5)	4.21 (18)
P1C25	0.7254 (5)	−0.71570 (27)	−0.3684 (5)	3.77 (15)
P1C26	0.7142 (5)	−0.65191 (21)	−0.3001 (4)	2.65 (13)
P1C31	0.3869 (4)	−0.55215 (27)	−0.1888 (4)	2.32 (12)
P1C32	0.2630 (5)	−0.57479 (26)	−0.3061 (4)	3.57 (15)
P1C33	0.1025 (5)	−0.5513 (3)	−0.3407 (4)	4.54 (17)
P1C34	0.0659 (4)	−0.5052 (3)	−0.2579 (5)	4.65 (18)
P1C35	0.1898 (6)	−0.48251 (29)	−0.1406 (4)	4.48 (17)
P1C36	0.3502 (5)	−0.50601 (29)	−0.1061 (3)	3.42 (14)
P2C11	0.5104 (5)	−0.62050 (22)	0.2457 (4)	2.80 (13)
P2C12	0.4457 (6)	−0.66073 (17)	0.3176 (5)	3.38 (14)
P2C13	0.3569 (6)	−0.62226 (24)	0.3729 (4)	3.33 (15)
P2C14	0.3329 (6)	−0.54357 (25)	0.3562 (4)	4.25 (17)
P2C15	0.3976 (6)	−0.50334 (18)	0.2842 (5)	4.68 (18)
P2C16	0.4864 (6)	−0.54180 (22)	0.2290 (4)	3.50 (15)
P2C21	0.7432 (5)	−0.73934 (22)	0.2888 (4)	2.51 (12)
P2C22	0.6873 (4)	−0.81135 (24)	0.3033 (4)	3.15 (14)
P2C23	0.7901 (6)	−0.86063 (20)	0.3988 (5)	3.92 (15)
P2C24	0.9487 (5)	−0.83790 (25)	0.4798 (4)	4.19 (17)
P2C25	1.0046 (4)	−0.76589 (27)	0.4653 (4)	3.99 (16)
P2C26	0.9018 (5)	−0.71661 (20)	0.3697 (4)	3.20 (15)
P2C31	0.4529 (4)	−0.72870 (22)	0.0430 (4)	2.16 (11)
P2C32	0.2962 (5)	−0.69748 (20)	−0.0132 (4)	2.77 (13)
P2C33	0.1703 (4)	−0.73674 (26)	−0.1112 (4)	3.84 (16)
P2C34	0.2011 (5)	−0.80721 (26)	−0.1529 (4)	3.89 (16)
P2C35	0.3577 (5)	−0.83844 (21)	−0.0966 (4)	3.62 (15)
P2C36	0.4837 (4)	−0.79918 (23)	0.0014 (4)	2.94 (13)

[a] In the numbering scheme for phenyl carbons, the number following P denotes the phosphorus containing the ring, the first number following C denotes the phenyl ring, and the last number signifies the position of the carbon atom on the ring, with 1 being bonded to phosphorus.

(8) Å, Ru–C3 = 2.258 (8) Å), the C1–C2–C3 bond angle of 117.7 (7)°, and the C1–C2 and C2–C3 bond lengths of 1.38 (1) and 1.41 (1) Å are in good agreement with the values

Table III. Selected Bond Angles (deg) and Distances (Å) for Ru(NO)(η^3-C$_3$H$_5$)(PPh$_3$)$_2$

Intramolecular Distances[a,b]

Ru–N	1.751 (6)	C3–C3H1	1.01 (8)
Ru–C2	2.130 (7)	C3–C3H2	1.05 (8)
Ru–C1	2.214 (7)	P1···C1	3.174 (8)
Ru–C3	2.258 (8)	P2···N	3.087 (7)
Ru–P2	2.344 (3)	P2···C3	3.091 (8)
Ru–P1	2.391 (4)	N–O	1.188 (8)
Ru···C2H	2.51 (8)	N···C1	3.08 (1)
Ru···C1H1	2.67 (8)	N···C2	3.18 (1)
Ru···C1H2	2.69 (7)	C1–C1H1	0.93 (8)
Ru···C3H1	2.84 (8)	C1–C1H2	0.97 (7)
Ru···C3H2	2.90 (8)	C1–C2	1.38 (1)
Ru···O	2.935 (7)	C2–C2H	0.92 (8)
		C2–C3	1.41 (1)
		Ru–CM	1.94 (1)

Bond Angles

N–Ru–C2	109.9 (3)	C3–Ru–P1	92.6 (2)
N–Ru–C1	101.4 (3)	P2–Ru–P1	104.8 (1)
N–Ru–C3	141.2 (3)	O–N–Ru	173.8 (6)
N–Ru–P2	96.8 (2)	C1H1–C1–C2H2	116 (8)
N–Ru–P1	123.9 (2)	C1H1–C1–C2	118 (5)
C2–Ru–C1	37.0 (4)	C1H2–C1–C2	122 (6)
C2–Ru–C3	37.3 (3)	C2H–C2–C1	114 (5)
C2–Ru–P2	111.0 (3)	C2H–C2–C3	126 (5)
C2–Ru–P1	109.3 (2)	C1–C2–C3	117.7 (7)
C1–Ru–C3	64.6 (4)	C3H1–C3–C3H2	114 (6)
C1–Ru–P2	147.4 (3)	Ru–CM–C2	106 (2)
C1–Ru–P1	87.0 (2)	P1–Ru–CM	96.8 (3)
C3H1–C3–C2	122 (4)	P2–Ru–CM	114.4 (3)
C3H2–C3–C2	114 (4)	N–Ru–CM	120.1 (3)
C3–Ru–P2	84.4 (2)		

Dihedral Angles between Planes

planes	angle, deg	planes	angle, deg
[N, Ru, CM[b]], [P2, Ru, P1]	105.0 (2)	[P1, Ru, N], [P2, Ru, CM]	81.3 (2)
[P2, Ru, N], [CM, Ru, P1]	84.0 (2)	[N, C3, P1], [Ru, C1, P2]	97.0 (2)

[a] Nonbonded contacts including hydrogen atoms are omitted. Maximum nonbonded contact tabulated is less than 3.2 Å. [b] CM refers to the center of mass of the allyl carbons.

found in other transition-metal η^3-allyl complexes.[39]

The coordination geometry about the ruthenium atom is irregular, with the six angles between coordinated phosphorus and nitrogen atoms and the center of mass of the three allyl carbons ranging from 96.8 (2) to 123.9 (2)°. The best limiting coordination polyhedron describing the coordination geometry is a distorted tetrahedron (see below).

The closest intramolecular H···H contact, excluding allyl H···H distances, 2.2 Å, is between phenyl hydrogens bonded to P1C3H6 and P2C1H6. All other phenyl hydrogen contacts are greater than the sum of van der Waals radii (2.4 Å). A partial tabulation of intramolecular nonhydrogen atom contacts may be found in Table III.

Discussion

The complex Ru(NO)(η^3-C$_3$H$_5$)L$_2$ is the first example of a mixed allyl–nitrosyl platinum-group metal complex. In this system the MNO unit is linear and is formally treated as NO$^+$, a three-electron donor. The allyl is a η^3 three-electron donor as well, giving a saturated 18-electron system.

In discussing the bonding geometry of the allyl to the metal, two alternate approaches may be utilized. The more common method involves treating the allyl as "bidentate", as shown by the two resonance forms of structure I. In each of these

I
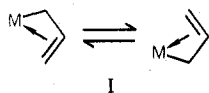
limiting structures, a terminal carbon atom of the allyl is σ

bonded to the metal while the remaining two carbons coordinate through a metal–olefin-type linkage. Following the oxidation-state formalism, the allyl is thus a four-electron donor in this approach; i.e., the metal–allyl interaction is viewed as M$^+$–allyl$^-$. For the sake of stereochemical arguments following this model, and in particular the evaluation of distortions within the coordination polyhedron, one can assume the terminal carbon atoms of the allyl to occupy two adjacent coordination sites. This assignment appears widely throughout the literature in complexes with low total coordination number.[40] As applied to the present structure, one would thus propose a distorted TBP d^8 system with allyl$^-$ in an axial-equatorial bridging position, a linear nitrosyl in the equatorial plane, one phosphine in the equatorial plane, and the remaining phosphine in the other axial site. Considerable distortions from idealized TBP geometry are apparent, however, particularly the P1–Ru–C3 angle of 93° (vs. 120° idealized) and the P2–Ru–C1 angle of 147° (vs. 180° idealized). These distortions are partly due to the small bite of the bidentate allyl. Nevertheless, they raise serious questions concerning the validity of such an assignment in the present structure.

Another view is to consider the allyl as "monodentate", the allyl group as a whole occupying one coordination site. Following the oxidation-state formalism in this treatment, one obtains the view of allyl coordination as via allyl$^+$—i.e., the allyl donates an electron pair from its filled, totally symmetric π^b orbital, while accepting electron density from the metal into its antisymmetric, nonbonding π orbital. Allyl coordination in this formalism is thus analogous to bonding by NO$^+$. Such an assignment has been made for high coordination number complexes[41] as well as Ru(η^3-C$_3$H$_5$)$_2$L$_2$.[15] Using this model for our structure yields a four-coordinate pseudotetrahedral d^{10} system with the allyl group formally treated as C$_3$H$_5$$^+$. If the vector from the center of mass (CM) of the allyl to the metal is treated as the allyl–metal "bond", the relevent angles are P1–Ru–P2 = 104.8 (1), P1–Ru–N = 123.9 (2), P2–Ru–N = 96.8 (2), P1–Ru–CM = 96.8 (3), P2–Ru–CM = 114.4 (3), and N–Ru–CM = 120.1 (3)°. Again, distortions from the idealized geometry are to be expected.

Kaduk, Poulos, and Ibers have recently developed a method for defining allyl coordination based on the orientation of the allyl plane relative to the vector from the metal to the allyl center of mass (CM).[39] For this structure D', the Ru–CM distance, is 1.94 (1) Å, τ, the Ru–CM–C2 angle, is 106 (2)°, α, the C1–C2–C3 angle, is 117.7 (7)°, and β, the bow angle, is 91.1 (4)°. These values are within the ranges reported by Ibers,[39] but at present there is too little structural information concerning allyl coordination to allow any definitive conclusions or predictions to be made regarding which formal mode of allyl coordination exists in the present structure.

While the simplistic models given above for allyl coordination are inadequate to describe the true bonding scheme, we prefer to view the allyl in this structure as "monodentate", and hence allyl$^+$. Such an assignment is consistent both with theoretical calculations[42] which indicate that allyl to metal electron donation is more important to the bonding interaction than is metal–allyl back-donation and with experimental evidence for the electrophilic nature of coordinated η^3-C$_3$H$_5$.[10a,43] That is, coordinated π-allyls behave as C$_3$H$_5$$^+$.

If the monodentate view of allyl binding is assumed in Ru(NO)(η^3-C$_3$H$_5$)L$_2$, then one has a four-coordinate pseudotetrahedral d^{10} system, and comparisons of this structure with other four-coordinate d^{10} complexes can be made in terms of the relative structural influences of the nitrosyl and allyl ligands. Comparisons of this type focusing on ligand π acidities in M(NO)$_2$L$_2$ and M(NO)(CO)L$_2$ systems[44] indicate that, while the P–M–P angle is fairly insensitive to changes in the strong π-acid ligands present, the angle between these ligands

Table IV. Comparison of Selected Bond Distances and Angles for Ru(NO)$_2$(PPh$_3$)$_2$,[14] Ru(NO)(η^3-C$_3$H$_5$)(PPh$_3$)$_2$, and Ru(η^3-C$_3$H$_5$)$_2$(PPh$_3$)$_2$[15]

	Ru(NO)$_2$L$_2$	Ru(NO)-(C$_3$H$_5$)L$_2$	Ru(C$_3$H$_5$)$_2$L$_2$
	Distances, Å		
Ru–N	1.762 (6), 1.776 (6)	1.751 (6)	
Ru–Cl,C3		2.214 (7),	2.25 (2), 2.25 (1),
		2.258 (8)	2.23 (1), 2.24 (2)
Ru–C2		2.130 (8)	2.125 (16),
			2.13 (1)
N–O	1.190 (7), 1.194 (7)	1.188 (8)	
	Angles, deg		
N1–Ru–N2	139.2 (3)		
CM–Ru–N[a]		120.1 (3)	
CM1–Ru–CM2			121 (1)
P1–Ru–P2	103.85 (6)	104.8 (1)	109.9 (1)
P1–Ru–CM		96.8 (3)	116 (1), 97 (1)
P2–Ru–CM		114.4 (3)	117 (1), 96 (1)
P1–Ru–N	107.8 (2), 94.1 (2)	123.9 (2)	
P2–Ru–N	103.0 (2), 104.7 (2)	96.8 (2)	
Ru–N–O	177.7 (6), 170.6 (5)	173.8 (6)	
C1–C2–C3		117.7 (7)	118 (1), 120 (1)

[a] CM refers to allyl center of mass.

of interest correlates well with our notions of relative π acidities. Specifically, as π acidity increases, the relative degree of electron density about such ligands results in increasing interligand repulsions. With the allyl ligand, there is the additional factor of the steric influence of the ligand, which may in fact outweigh the importance of allyl π acidity in the matter of interligand repulsions.

Table IV compares relevant bond angles and distances of the current structure with those of the analogous structures of the dinitrosyl and diallyl complexes, Ru(NO)$_2$L$_2$[14] and Ru(η^3-C$_3$H$_5$)$_2$L$_2$.[15] All three of these molecules are isoelectronic with distorted tetrahedral geometries, and all formally possess d^{10} configurations. The three complexes are structurally very similar. The Ru–N, Ru–C, and N–O distances agree within experimental error. The Ru–N–O angle in Ru(NO)(η^3-C$_3$H$_5$)L$_2$ corresponds to the average value in Ru(NO)$_2$L$_2$, and the C1–C2–C3 angles for this structure and Ru(η^3-C$_3$H$_5$)$_2$L$_2$ are identical within 3σ. Most of the remaining angles about ruthenium agree closely.

An interesting observation is apparent in the values of the angles between nitrosyls and allyls. While the N–Ru–N angle in the dinitrosyl is largest with a value of 139.2 (3)°, the allyl–Ru–N and allyl–Ru–allyl angles for the nitrosylallyl and diallyl structures are identical within experimental error and equal to 120°. The wide N–Ru–N angle in Ru(NO)$_2$L$_2$ has been rationalized in terms of the π acidity of NO$^+$, one of the strongest π-acid ligands known, and large interligand repulsions occur as a result of a large degree of electron density back-donated to these ligands. The fact that there is no difference between the nitrosyl–metal–allyl angle and the allyl–metal–allyl angle suggests that, for these systems, the allyl and nitrosyl ligands influence structural distortions to a similar degree, the nitrosyl as a result of its π acidity and the allyl as a result of the combined factors of steric influence and π acidity. The P1–Ru–P2 angles range from 103.85 to 109.9° and, as in other studies of this type, are rather insensitive to the presence of other ligands.[44]

We have previously described the reaction of Ru(NO)-(η^3-C$_3$H$_5$)L$_2$ with CO to form the 18-electron complex Ru-(NO)(CO)(η^3-C$_3$H$_5$)L$_2$,[13] in which bending of the nitrosyl is more facile than $\eta^3 \rightarrow \eta^1$ (π–σ) allyl conversion. In contrast, studies of ligand addition to [(C$_5$H$_5$)Mo(CO)(NO)(η^3-C$_3$H$_5$)]$^+$[10] and Fe(NO)(η^3C$_3$H$_5$)(CO)$_2$[11,12] show that changes in allyl bonding geometry occur quite easily, with no evidence for nitrosyl bending. Further studies probing the one-electron,

three-electron duality of nitrosyl and allyl in mixed-ligand complexes will prove to be useful in delineating the factors governing bonding and reactivity of these two ligands.

Registry No. Ru(NO)(η^3-C$_3$H$_5$)(PPh$_3$)$_2$, 65230-38-8; RuCl$_3$-(NO)(PPh$_3$)$_2$, 15349-78-7; tetraallyltin, 7393-43-3.

Supplementary Material Available: A listing of observed and calculated structure factors (7 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) J. H. Enemark and R. D. Feltham, *Coord. Chem. Rev.*, **13**, 339 (1974); (b) B. A. Frenz and J. A. Ibers, *MTP Int. Rev. Sci.: Phys. Chem., Ser. One, 1972*, **11**, 33 (1972); (c) R. Eisenberg and C. D. Meyer, *Acc. Chem. Res.*, **8**, 26 (1975).
(2) (a) M. L. H. Green and P. L. I. Nagy, *Adv. Organomet. Chem.*, **2**, 325 (1964); (b) K. Vrieze, "Dynamic Nuclear Magnetic Resonance Spectroscopy", L. M. Jackman and F. A. Cotton, Ed., Academic Press, New York, N.Y., 1975, Chapter 11, p 441; (c) N Rösch and R. Hoffmann, *Inorg. Chem.*, **13**, 2656 (1974); (d) J. Powell, *MTP Int. Rev. Sci.: Inorg. Chem., Ser. One, 1972*, **6**, 273 (1972); (e) J. Powell, *MTP Int. Rev. Sci.: Inorg. Chem., Ser. Two, 1975*, **6**, 189 (1975).
(3) E. L. Muetterties and F. J. Hirsekorn, *J. Am. Chem. Soc.*, **96**, 4063 (1974); F. J. Hirsekorn, M. C. Rakowski, and E. L. Muetterties, *ibid.*, **97**, 237 (1975); L. S. Stuhl, M. Rakowski DuBois, F. J. Hirsekorn, J. R. Bleeke, A. E. Stevens, and E. L. Muetterties, *ibid.*, **100**, 2405 (1978).
(4) J. P. Collman, N. W. Hoffman, and D. E. Morris, *J. Am. Chem. Soc.*, **91**, 5659 (1969).
(5) S. T. Wilson and J. A. Osborn, *J. Am. Chem. Soc.*, **93**, 3068 (1971).
(6) J. P. Collman, P. Farnham, and G. Dolcetti, *J. Am. Chem. Soc.*, **93**, 1788 (1971).
(7) C. G. Pierpont and R. Eisenberg, *Inorg. Chem.*, **11**, 1088 (1972).
(8) J. P. Collman, P. Farnham, and G. Dolcetti, *J. Am. Chem. Soc.*, **93**, 1788 (1971).
(9) J. H. Enemark and R. D. Feltham, *Proc. Natl. Acad. Sci. U.S.A.*, **69**, 3534 (1972).
(10) (a) N. A. Bailey, W. G. Kita, J. A. McCleverty, A. J. Murray, B. E. Mann, and N. W. J. Walker, *J. Chem. Soc., Chem. Commun.*, 592 (1974); (b) J. W. Faller and A. M. Rosan, *J. Am. Chem. Soc.*, **98**, 3388 (1976).
(11) (a) H. D. Murdoch, *Z. Naturforsch., B*, **20**, 179 (1965); (b) R. Bruce, F. M. Chaudari, G. R. Knox, and P. L. Pauson, *ibid.*, **20**, 73 (1965); (c) F. M. Chaudari, G. R. Knox, and P. L. Pauson, *J. Chem. Soc. C*, 2255 (1967).
(12) G. Cardaci and A. Foffani, *J. Chem. Soc., Dalton Trans.*, 1808 (1974); G. Cardaci, *ibid.*, 2452 (1974).
(13) M. Schoonover and R. Eisenberg, *J. Am. Chem. Soc.*, **99**, 8371 (1977).
(14) A. P. Gaughan, Jr., B. J. Corden, R. Eisenberg, and J. A. Ibers, *Inorg. Chem.*, **13**, 786 (1974).
(15) A. E. Smith, *Inorg. Chem.*, **11**, 2306 (1972).
(16) N. Ahmad, J. J. Levison, S. D. Robinson, and M. F. Uttley, *Inorg. Synth.*, **15**, 51 (1974).
(17) J. Reed, C. G. Pierpont, and R. Eisenberg, *Inorg. Synth.*, **16**, 21 (1976).
(18) Elemental Analysis performed by Galbraith Laboratories, Inc., Knoxville, Tenn.
(19) "International Tables for X-ray Crystallography", Vol. I., Kynoch Press, Birmingham, England, 1960, p 79.
(20) The programs for refinement of lattice constants and automated operation of the diffractometer are those of Busing and Levy as modified by Picker Corp.
(21) T. C. Furnas, "Single Crystal Orienter Instruction Manual", General Electric Co., Milwaukee, Wis., 1957, Chapter 10.
(22) S. Z. Goldberg, C. Kubiak, C. D. Meyer, and R. Eisenberg, *Inorg. Chem.*, **14**, 1650 (1975).
(23) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).
(24) All computations were performed on an IBM 360/65 computer. The data processing program was an extensively modified version of Raymond's URFACS. In addition, local versions of the following were used: Ibers' NUCLS, a group least-squares program; Zalkins' FORDAP Fourier program; ORFFE, a function and error program by Busing, Martin, and Levy; Johnson's ORTEP thermal ellipsoid plotting program.
(25) $R_1 = \sum ||F_o| - |F_c||/\sum |F_o|$; $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. The estimated standard deviation of an observation of unit weight is given by $[\sum w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$, where N_o and N_v are the number of observations and variables, respectively.
(26) D. T. Cromer and B. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968).
(27) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
(28) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).
(29) R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **4**, 773 (1965); S. J. LaPlaca and J. A. Ibers, *J. Am. Chem. Soc.*, **87**, 2851 (1965); *Acta Crystallogr.*, **18**, 511 (1965).
(30) Supplementary material.

(31) E. W. Abel and S. Moorhouse, *J. Chem. Soc., Dalton Trans.*, 1706 (1973).
(32) U. A. Gregory, S. D. Ibekwe, B. T. Kilbourn, and D. R. Russell, *J. Chem. Soc. A*, 1118 (1971).
(33) I. Kawada, *Tetrahedron Lett.*, **10**, 793 (1969).
(34) C. G. Pierpont, A. Pucci, and R. Eisenberg, *J. Am. Chem. Soc.*, **93**, 3050 (1971); C. G. Pierpont and R. Eisenberg, *Inorg. Chem.*, **11**, 1096 (1972).
(35) R. Eisenberg, A. P. Gaughan, Jr., C. G. Pierpont, J. Reed, and A. J. Schultz, *J. Am. Chem. Soc.*, **94**, 6240 (1972).
(36) S. J. LaPlaca and J. A. Ibers, *Inorg. Chem.*, **4**, 778 (1965).
(37) A. C. Shapski and F. A. Stephens, *Chem. Commun.*, 1008 (1969).
(38) C. G. Pierpont, D. V. VanDerveer, W. Durland, and R. Eisenberg, *J. Am. Chem. Soc.*, **92**, 4760 (1970); C. G. Pierpont and R. Eisenberg, *Inorg. Chem.*, **11**, 1088 (1972).
(39) J. A. Kaduk, A. T. Poulos, and J. A. Ibers, *J. Organomet. Chem.*, **127**, 245 (1977).
(40) See, for example: M. R. Churchill and R. Mason, *Nature (London)*,

204, 777 (1964); A. E. Smith, *Acta Crystallogr.*, **18**, 331 (1965); M. McPartlin and R. Mason, *Chem. Commun.*, 16 (1967); R. Mason and P. O. Whimp, *J. Chem. Soc. A*, 2709 (1969); A. Sirigu, *Inorg. Chem.*, **9**, 2245 (1970); Y. Kitano, K. Kajimoto, M. Kashiwagi, and Y. Kinoshita, *J. Organomet. Chem.*, **33**, 123 (1971); R. Claverini, P. Ganis, and C. Pedone, *ibid.*, **50**, 327 (1973); Y. Kitano, M. Kashiwagi, and Y. Kinoshita, *Bull. Chem. Soc. Jpn.*, **46**, 723 (1973).
(41) A. J. Graham and R. H. Fenn, *J. Organomet. Chem.*, **17**, 405 (1969); R. H. Fenn and A. J. Graham, *ibid.*, **37**, 137 (1972); F. A. Cotton, B. A. Frenz, and A. G. Stanislowski, *Inorg. Chim. Acta*, **7**, 503 (1973).
(42) S. F. A. Kettle and R. Mason, *J. Organomet. Chem.*, **5**, 573 (1966); P. W. N. M. van Leeuwen and A. P. Praat, *ibid.*, **21**, 501 (1970); M.-M. Rohmer, J. Demuynck, and A. Veillard, *Theor. Chim. Acta*, **36**, 93 (1974).
(43) T. H. Whitesides, R. W. Arhart, and R. W. Slaven, *J. Am. Chem. Soc.*, **95**, 5792 (1973).
(44) C. P. Brock and J. A. Ibers, *Inorg. Chem.*, **11**, 2812 (1972).

Group 6 Transition Metal Peroxo Complexes Stabilized by Polydentate Pyridinecarboxylate Ligands

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The solution and crystalline properties of hydrogen oxodiperoxo(pyridine-2-carboxylato)molybdate(VI) bis(pyridine-2-carboxylic acid) monohydrate, $H^+[Mo(O)(O_2)_2(C_5H_4NCO_2)]^-\cdot2C_5H_4NCO_2H\cdot H_2O$ (4), and oxoperoxo(pyridine-2,6-dicarboxylato)aquomolybdenum(VI), $Mo(O)(O_2)[C_5H_3N(CO_2)_2](H_2O)$ (5), have been studied. The structures of the two complexes in the solid state have been determined by single-crystal X-ray diffraction methods. In 4, the two peroxo bridges and the oxygen atom of the pyridine-2-carboxylato ligand lie approximately in the pentagonal plane. The nitrogen of the pyridine-2-carboxylato ligand and the oxo oxygen are located in the apical positions. The outer-sphere cationic moiety consists of a proton hydrogen bonded to several solvate molecules. Several similar complexes were synthesized and characterized with different solvates apparently hydrogen bonded to the proton. In complex 5, the peroxo bridge and the two oxygen atoms as well as the nitrogen of the pyridine-2,6-dicarboxylato ligand occupy the pentagonal plane. The water molecule and the oxo group are located in the apical positions. Based on ^{13}C NMR, conductivity measurements, and alkalimetric titrations, it was concluded that the structures of complexes 4 and 5 in nonaqueous solvents correspond to that of the crystalline state. The tungsten complexes analogous to 4 and its derivatives exist in nonaqueous solution principally as nonionic species and exhibit greater ligand lability.

Very few Mo(VI) and W(VI) peroxo complexes have been isolated and well characterized. Single-crystal structures have been reported[1,2] only for $(C_5H_5NH)_2^+(Mo_2O_{11})^{-2}$ (1) and $Mo(O)(O_2)_2(HMPA)(L)^3$ (2, L = H_2O; 3, L = C_5H_5N). Complex 1 contains no bound organic ligand and belongs to a class of binuclear peroxo anions where the pyridinium ion can be substituted by various cations. Complexes 2 and 3 are the first well-characterized covalent molybdenum peroxo complexes. They are stoichiometric reagents for epoxidation of olefins[4] and catalysts for epoxidation of allylic alcohols to the corresponding epoxy alcohols and derivatives.[5] These results suggest a relationship between the chemistry of group 6 metal peroxo complexes and organic peracids. We have been interested in the extension of this analogy for oxidation of substrates such as alcohols and ketones. Preliminary experiments using the known group 6 peroxo complexes as catalysts showed that complexes of increased stability are needed for the transformation. Molybdenum and tungsten peroxo complexes containing polydentate ligands based on pyridinecarboxylic acids have been chosen as candidates. Some of these complexes have been prepared previously.[6] However, their structures, which are essential for the understanding of the catalytic activity, have not been established. We have, therefore, undertaken an investigation of these complexes in the crystalline state and in solution. The results of this work are summarized in this paper. The catalytic properties of these complexes are the subjects of forthcoming publications.[7]

Results and Discussion

Preparation of Complexes. The general preparation of these complexes involved reaction of molybdenum trioxide or

Table I. Group 6 Transition Metal Complexes

1. $(C_5H_5NH)_2^+(Mo_2O_{11})^{2-}$
2. $Mo(O)(O_2)_2(HMPA)(H_2O)$
3. $Mo(O)(O_2)_2(HMPA)(C_5H_5N)$
4. $H^+[Mo(O)(O_2)_2(C_5H_4NCO_2)]^-\cdot2C_5H_4NCO_2H\cdot H_2O$
5. $Mo(O)(O_2)[C_5H_3N(CO_2)_2](H_2O)$
6. $H^+[W(O)(O_2)_2(C_5H_4NCO_2)]^-\cdot2C_5H_4NCO_2H$
7. $H^+[Mo(O)(O_2)_2(C_5H_4NCO_2)]^-\cdot H_2O$
8. $H^+[W(O)(O_2)_2(C_5H_4NCO_2)]^-\cdot H_2O$
9. $W(O)(O_2)[C_5H_3N(CO_2)_2](H_2O)\cdot H_2O$
10. $H^+[Mo(O)(O_2)_2(C_5H_4NCO_2)]^-\cdot C_5H_4NCO_2H\cdot H_2O$
11. $H^+[Mo(O)(O_2)_2(C_5H_4NCO_2)]^-\cdot C_5H_4NCO_2CH_3$
12. $Mo(O)(O_2)[C_5H_3N(CO_2)_2](HMPA)$
13. $W(O)(O_2)[C_5H_3N(CO_2)_2](HMPA)\cdot H_2O$

tungstic acid, 30% aqueous hydrogen peroxide, and the appropriate ligand. This method avoided the necessity of sulfuric acid as in previous attempts[6] and substantially increased the yields obtained for the molybdenum and tungsten derivatives.

Crystal and Molecular Structures of $H^+[Mo(O)(O_2)_2$-$(C_5H_4NCO_2)]^-\cdot2C_5H_4NCO_2H\cdot H_2O$ (4) and $Mo(O)(O_2)$-$[C_5H_3N(CO_2)_2](H_2O)$ (5).[8] The complexes hydrogen oxodiperoxo(pyridine-2-carboxylato)molybdate(VI) bis(pyridine-2-carboxylic acid) monohydrate, $H^+[Mo(O)(O_2)_2$-$(C_5H_4NCO_2)]^-\cdot2C_5H_4NCO_2H\cdot H_2O$ (4), and oxoperoxo-(pyridine-2,6-dicarboxylato)aquomolybdenum(VI), $Mo(O)(O_2)(C_5H_4N(CO_2)_2](H_2O)$ (5), crystallize as stable yellow and yellow-orange prisms, respectively. The crystals of 4 are monoclinic, space group $P2_1/c$.[9] They contain four molecules of $MoC_{18}H_{16}N_3O_{12}$ per unit cell. The crystals of 5 are also monoclinic, space group Cc. They contain four molecules of $MoC_7H_5NO_8$ per unit cell. Hydrogen atoms in