Structural Studies of Two Ruthenium(0)–Nitrosyl Complexes

Sir:

Structural studies have shown that nitric oxide can coordinate to transition metal ions in either a linear mode of attachment as *formally* NO^+,[1] or in a bent configuration as NO^- with a metal–N–O bond angle approaching 120°.[2] Recently, Osborn and Wilson have synthesized the complex $Ru(NO)H(P(C_6H_5)_3)_3$ (**1**), which they find to be a catalytically active system.[3] A closely related complex, $Ru(NO)(diphos)_2^+$ (**2**, diphos = 1,2-bis(diphenylphosphino)ethane), has also been synthesized recently by Townsend.[4] Both of these complexes have nitrosyl stretching frequencies (1640 cm^{-1} in **1** and 1673 cm^{-1} in **2**) closely comparable with ν(NO) values found in related systems possessing bent nitrosyl groups,[2] but other physical data, at least in the case of **1**,[3] appeared to rule against a nitrosyl coordination of this type. We have therefore determined the structures of these two complexes in order to unequivocally establish the molecular geometry and mode of nitrosyl coordination in each, and possibly shed further light on the structure–function relationship of the nitrosyl group in certain catalytically active systems.

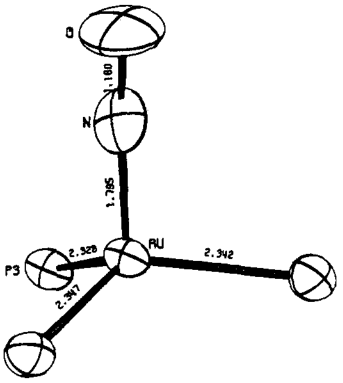

Figure 1. A perspective drawing of the inner coordination geometry of $Ru(NO)(H)(P(C_6H_5)_3)_3$. The estimated standard deviations for the bond lengths shown are: Ru–N, 0.012; Ru–P, 0.004; N–O, 0.012 Å. The coordinated hydride is not shown. Important bond angles (deg) are: Ru–N–O, 176; N–Ru–P(1), 99.5; N–Ru–P(2), 99.9; N–Ru–P(3), 112.0; P(1)–Ru–P(2), 119.0; P(1)–Ru–P(3), 111.5; P(2)–Ru–P(3), 113.3; with estimated standard deviations of 1.0° for Ru–N–O, 0.3° for N–Ru–P, and 0.1° for P–Ru–P.

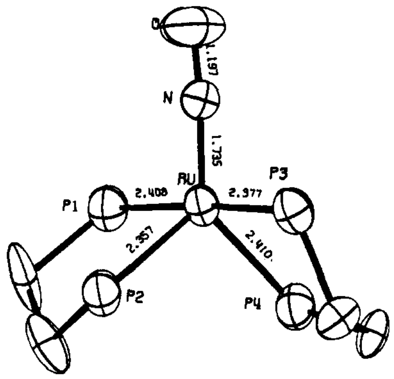

Figure 2. A perspective drawing of the inner coordination geometry of $[Ru(NO)((C_6H_5)_2PCH_2CH_2P(C_6H_5)_2)_2]^+$. The estimated standard deviations for the bond lengths shown are: Ru–N, 0.013; Ru–P, 0.005; N–O, 0.013 Å. Important bond angles (deg) are: Ru–N–O, 174; N–Ru–P(1), 90.0; N–Ru–P(3), 93.1; N–Ru–P(2), 126.2; N–Ru–P(4), 134.5; P(1)–Ru–P(3), 175.5; P(2)–Ru–P(4), 99.3; with estimated standard deviations of 1.0° for Ru–N–O, 0.4° for N–Ru–P, and 0.2° for P–Ru–P.

Crystals of **1** suitable for X-ray study were grown from a methanol–dichloromethane solution, while crystals of **2** as its $B(C_6H_5)_4^-$ salt were grown from acetone–ethanol solutions.

Unit Cell and Space Group Data. **1** has a unit cell with dimensions $a = 10.12$ (1), $b = 33.49$ (2), $c = 13.38$ (1) Å, $\beta = 90.28$ (1)°, $V = 4532$ Å^3; space group, $P2_1/n$; ρ_{exptl}, 1.34 (1) g/cm^3; ρ_{calcd}, 1.334 g/cm^3; $Z = 4$. **2** has a unit cell with dimensions $a = 19.06$ (2), $b = 23.09$ (2), $c = 15.40$ (1) Å, $\beta = 93.66$ (1)°, $V = 6766$ Å^3; space group, $P2_1/n$; ρ_{exptl}, 1.29 (1) g/cm^3; ρ_{calcd} 1.286 g/cm^3; $Z = 4$, with a molecule of acetone crystallizing per molecule of complex.

Intensity data for both complexes were collected by the θ–2θ scan technique using Zr-filtered Mo Kα radiation and pulse-height analysis on a Picker automated diffractometer. Intensities within the angular range $5° \leqslant 2\theta_{Mo} \leqslant 40°$ for **1** and within the angular range $5° \leqslant 2\theta_{Mo} \leqslant 45°$ for **2** were measured, thereby yielding 2779 and 3195 reflections for **1** and **2**, respectively, above 2σ. The intensity data were reduced in the usual way and both structures were then solved by standard Patterson and Fourier methods. The two structures were refined by a least-squares procedure in which the phenyl rings were treated as rigid groups and all nongroup atoms were assigned anisotropic thermal parameters. Efforts to locate the hydride ligand in **1** have not as yet been successful. The refinements of the two structures have converged to respective conventional and weighted R factors of 0.063 and 0.068 for **1** and 0.074 and 0.083 for **2**.

The structure of complex **1** is that of a slightly distorted trigonal bipyramid with the three triphenylphosphine groups comprising the equatorial plane, and the hydride and nitrosyl ligands occupying the axial positions as shown in Figure 1. Important bond distances and angles are summarized in the figure. The nitrosyl group is coordinated to the ruthenium atom in a linear manner with an Ru–N distance of 1.80 (1) Å. This value is short relative to a Ru–N single bond distance estimated in the range 1.95–2.00 Å.[5] As expected, the Ru atom lies significantly out of the plane of the three phosphines, being displaced 0.55 Å toward the axial nitrosyl ligand. In addition, the coordination geometry of the complex is distorted significantly from C_{3v} sym-

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[1] (a) P. T. Manoharan and W. C. Hamilton, *Inorg. Chem.*, 2, 1043 (1963); (b) S. H. Simonsen and M. H. Mueller, *J. Inorg. Nucl. Chem.*, 27, 307 (1965); (c) A. Domenicano, A. Vaciago, L. Zambonelli, P. L. Loader, and L. M. Venanzi, *Chem. Commun.*, 476 (1966); (d) B. A. Frenz, J. H. Enemark, and J. A. Ibers, *Inorg. Chem.*, **8**, 1288 (1969).

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[5] A value of 1.95–2.00 Å may be estimated for the Ru–N distance from the sum of covalent radii, where the Ru(0) radius is either taken as 1.25 Å from the element (L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, Chapter 11) or is estimated from the Ru–P distances in the present structures.

metry to effective C_s symmetry by virtue of unequal P–Ru—P and N–Ru–P bond angles. These results are thus in close agreement with those found very recently for the isoelectronic $Ir(NO)H(P(C_6H_5)_3)_3^+$ complex.[6]

The coordination geometry of complex **2** is also best described as a distorted trigonal bipyramid with a linear nitrosyl group as shown in Figure 2, but in this structure, the nitrosyl occupies an *equatorial* position in the coordination polyhedron. The bond angles about the Ru atom (see Figure 2 caption) give the complex effective C_{2v} symmetry in its inner coordination geometry. One further point of structural interest is that the conformations of the two diphos rings differ, as has been found in other diphos-containing complexes such as $Rh(diphos)_2^+$ [7] and $M(O_2)(diphos)_2^+$ (M = Rh, Ir).[8]

The structural results for complexes **1** and **2** show that in each case the nitrosyl group coordinates to the ruthenium in a linear manner with considerable metal → ligand π bonding. This linear bonding mode is conventionally described in terms of NO^+ and, hence, these systems are coordinatively saturated complexes of Ru(0). These results contrast with those found for the related complex $Ru(NO)_2Cl(P(C_6H_5)_3)_2^+$ [2d] in which the coordination geometry is a tetragonal pyramid with a bent apical nitrosyl coordinating as NO^- and a linear equatorial nitrosyl bonding as NO^+. This dinitrosyl complex is therefore a d^6 coordinatively unsaturated Ru(II) system. The differences in the coordination geometries and the degree of coordinative saturation in these relatively similar complexes thus strongly support the notion that the nitrosyl group in certain catalytically active systems functions as an "electron pair reservoir" capable of donating and withdrawing an electron pair from the metal center.[9,10] In this regard, Collman and coworkers[11] have recently shown that the two nitrosyl groups in $Ru(NO)_2Cl(P(C_6H_5)_3)_2^+$ interconvert, presumably through a trigonal-bipyramidal structure analogous to **1** or **2**. Finally, the nitrosyl stretching frequencies for the three Ru-nitrosyl complexes (ν(NO) values for $Ru(NO)_2Cl(P(C_2H_5)_3)_2^+$ are 1687 and 1845 cm^{-1}) clearly illustrate the danger associated with correlating ν(NO) with the M–N–O bond angle and underscore the notion that ν(NO) is sensitive to the *composition* of filled bonding molecular orbitals regardless of the formal assignment of metal and ligand charges.[12]

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Restricted Rotation in a Bisphosphinohydrazine[1]

Sir:

Large torsional barriers about P–N bonds[2–7] and rotational and/or inversional barriers in hydrazines[8–12] have been reported. We have recently isolated $F_2PN(CH_3)N(CH_3)PF_2$[13] and have observed similar stereochemical processes occurring in this molecule. Figure 1 shows representative ^{19}F nmr spectra taken between −145 and +160° on a Varian HA-100 spectrometer operating at 94.1 MHz. Spectra were run between about −110 and +60° in $FCCl_3$, between −145 and +20° in isopentane, between +20 and +160° in *n*-undecane and 1,1,2,2-tetrachloroethane, and between −145 and +20° in F_2CCl_2. Within experimental uncertainty, the temper-

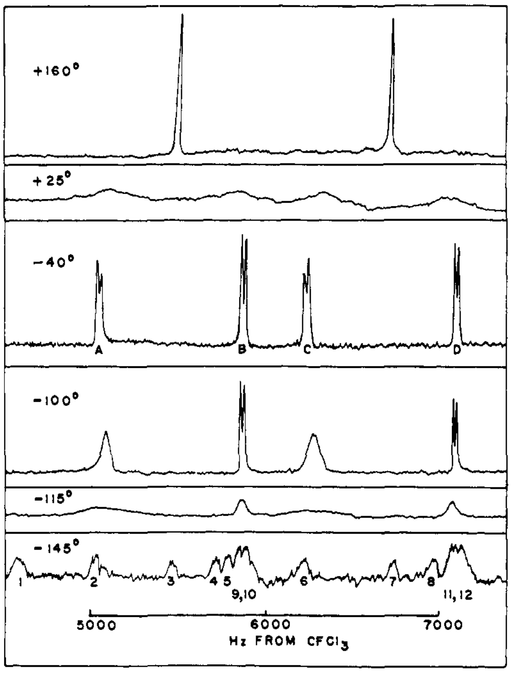

Figure 1. ^{19}F nmr spectrum of $F_2PN(CH_3)N(CH_3)PF_2$ between +160 and −145°.

(1) Acknowledgment is gratefully made to the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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(13) Synthesized by fluorination of $Cl_2PN(CH_3)N(CH_3)PCl_2$, a product of the reaction between PCl_3 and either $HN(CH_3)N(CH_3)H$ or $P[N(CH_3)N(CH_3)]_3P$. $F_2PN(CH_3)N(CH_3)PF_2$ is a volatile, fairly unstable liquid. Its characterization is lengthy and is based upon ^1H and ^{19}F nmr, including ^{31}P and ^1H double resonance and crude indor experiments, mass and ir spectra, as well as chemical behavior and physical properties. The details of these reactions and experiments will appear in a full paper now being prepared.