Acknowledgment. We thank the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research, the National Science Foundation for major instrument grants used in purchasing spectroscopic equipment, and Mr. David Hillenbrand for running the deuterium-decoupled nmr spectra.[13]

(13) NOTE ADDED IN PROOF. We thank Professor Meinwald for communicating his results in this area prior to publication.

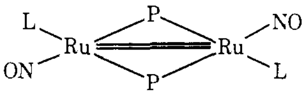
S. F. Nelsen,* J. P. Gillespie
Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706

Received March 24, 1972

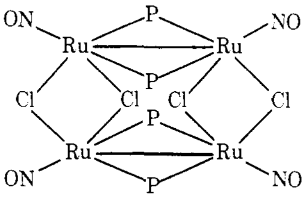
Nitrosyls and Metal–Metal Bonding in μ-Diphenylphosphido Ruthenium Clusters

Sir:

Metal nitrosyl cluster compounds are intriguing systems because of the current interest in metal–nitrosyl bonding[1–3] and the potential applicability of these systems as homogeneous multicenter catalysts.[4,5] Nitrosyl, unlike carbonyl, can coordinate to a metal ion in one of several ways,[1–3] and it has been suggested[6] that in doing so the NO ligand can activate the metal ion by alternately withdrawing and donating an electron pair. In nitrosyl clusters, this feature is coupled with the presence of more than one metal center and consequent metal–metal bonding which has attracted attention during recent years.[7–10] We report herein the synthesis and structure determination of two novel ruthenium nitrosyl cluster compounds, **1** and **2**, in which the mode of nitrosyl coordination changes from linear to slightly bent and the degree of metal–metal bonding differs significantly.



1, L = $P(CH_3)(C_6H_5)_2$;
P = $P(C_6H_5)_2$



2, P = $P(C_6H_5)_2$

Complex **1** was initially obtained in small amounts from a recrystallization of $RuH(NO)(P(CH_3)(C_6H_5)_2)_3$[11] using excess phosphine apparently contaminated with $HP(C_6H_5)_2$. The structure determination of **1**, outlined below, led us to devise a more rational synthesis of the complex which also yielded several other products including **2**. The synthesis consists of the addition of a benzene solution of $RuCl_3(NO)(P(CH_3)(C_6H_5)_2)_2$ and $HP(C_6H_5)_2$ (1 : 1) to a stirred Zn|Cu couple followed by filtration, evaporation, and separation of products. To date, difficulties in the last step have produced **1** and **2** in low yield only. Crystals of **2** for X-ray work were grown from a benzene–methanol solution.

Unit Cell and Space Group Data. **1** has a unit cell with dimensions a = 13.12 (1), b = 12.95 (1), c = 15.94 (2) Å; β = 120.2 (1)°; V = 2341 Å^3; space group $P2_1/c$; ρ_{exptl} = 1.46 (2) g/cm^3; ρ_{calcd} = 1.47 g/cm^3; Z = 2. **2** has a unit cell of dimensions a = 15.92 (1), b = 12.49 (1), c = 26.16 (1) Å; V = 5200 Å^3; space group, $Fmmm$; ρ_{exptl} = 1.79 (2) g/cm^3; ρ_{calcd} = 1.80 g/cm^3; Z = 4.

Intensity data for both complexes were collected by the θ–2θ scan technique using Zr-filtered Mo Kα radiation and pulse height analysis. Intensities within the angular ranges $5° \leqslant 2\theta_{\mathrm{Mo}} \leqslant 50°$ for **1** and $5° \leqslant 2\theta_{\mathrm{Mo}} \leqslant 55°$ for **2** were measured thereby yielding 1659 reflections above 3σ for **1** and 1415 above 2σ for **2**. Both structures were solved by standard Patterson and Fourier methods and were refined by a least-squares procedure in which individual atoms were assigned anisotropic thermal parameters. In **1**, the phenyl rings were treated as rigid groups.[12,13] The refinements of the two structures have converged to conventional and weighted R factors of 0.054 and 0.065 for **1** and 0.049 and 0.073 for **2**.

The structures of the two complexes are illustrated in Figures 1 and 2, respectively, with the important bond distances and angles summarized in the figure captions. **1** is a centrosymmetric binuclear complex with the ruthenium atoms bridged by diphenylphosphido groups and the coordination geometry distorted tetrahedral. The nitrosyl ligand is coordinated in an essentially linear manner although the Ru–N–O bond angle of 174.1 (9)° deviates significantly from 180°. The Ru–N distance of 1.697 (12) Å is slightly shorter than other observed Ru–linear nitrosyl bond lengths[1] and is indicative of a strong π-backbonding interaction as would be expected for linearly bonded nitrosyl. The dihedral angle of 85.6 (2)° between the planes defined by Ru,P_1,P_1' and Ru,P_2,N (see Figure 1) is in accord with that expected for a slightly distorted tetrahedron. One of the most striking features of the structure is the occurrence of a strong metal–metal bond (*vide infra*) as evidenced by the short Ru–Ru distance of 2.629 (2) Å and the Ru–P–Ru bond angle of 69.7 (1)°.

Complex **2** is a tetranuclear system which is crystallographically required to have mmm (D_{2h}) symmetry. The four Ru atoms of the cluster form a rectangular array in which opposite pairs of the metal atoms are bonded covalently with a Ru–Ru distance of 2.787 (2) Å and the pairs are separated by a nonbonding Ru–Ru distance of 3.672 (1) Å (see Figure 2). The metal–metal bonded ruthenium atoms are bridged by diphenylphosphido groups as in **1** while the nonbonding ruthenium atoms are bridged by chlorines. The coordination

---

(1) C. G. Pierpont and R. Eisenberg, *J. Amer. Chem. Soc.*, **93**, 4905 (1971); *Inorg. Chem.*, 11, 1088, 1094 (1972), and references cited therein.

(2) D. M. P. Mingos and J. A. Ibers, *ibid.*, 10, 1479 (1971), and references cited therein.

(3) Abstracts of the American Crystallographic Association Meeting, Albuquerque, N. Mex., April 3–7, 1972, further underscore the structural interest in these systems. See C. S. Pratt, *et al.*, Abstract H3; J. H. Enemark and R. D. Feltham, Abstract H4; and R. M. Kirchner and J. A. Ibers, Abstract H6.

(4) J. Norton, D. Valentine, Jr., and J. P. Collman, *J. Amer. Chem. Soc.*, **91**, 7537 (1969).

(5) J. R. Norton, J. P. Collman, G. Dolcetti, and W. T. Robinson, *Inorg. Chem.*, 11, 382 (1972).

(6) J. P. Collman, N. W. Hoffman, and D. E. Morris, *J. Amer. Chem. Soc.*, **91**, 5659 (1969).

(7) B. R. Penfold, *Perspect. Struct. Chem.*, 2, 71 (1968).

(8) M. C. Baird, *Progr. Inorg. Chem.*, **9**, 1 (1968).

(9) F. A. Cotton, *Accounts Chem. Res.*, 2, 240 (1969).

(10) D. L. Stevenson, C. H. Wei, and L. F. Dahl, *J. Amer. Chem. Soc.*, **93**, 6027 (1971), and references cited therein.

(11) S. T. Wilson and J. A. Osborn, *ibid.*, **93**, 3068 (1971).

(12) S. J. LaPlaca and J. A. Ibers, *Acta Crystallogr.*, 18, 511 (1965); R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, 4, 773 (1965).

(13) R. J. Doedens in "Crystallographic Computing," F. R. Ahmed, Ed., Munksgaard, Copenhagen, 1970, p 198.

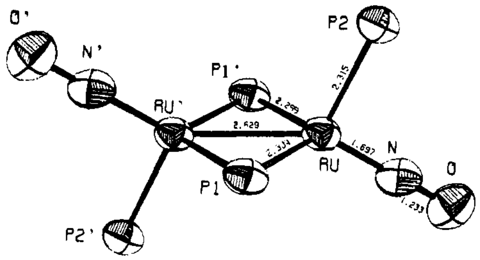


Figure 1. A perspective drawing of the inner coordination geometry of $[Ru(NO)(\mu\text{-}P(C_6H_5)_2)(P(CH_3)(C_6H_5)_2)]_2$ with the phosphorus substituents omitted for clarity. The estimated standard deviations for the bond lengths (Å) are: Ru–Ru; 0.002; Ru–P, 0.004; Ru–N, 0.012; N–O, 0.012. Important bond angles (deg) are: Ru–P(1)–Ru′, 69.7 (1); P(1)–Ru–P(1)′, 110.3 (1); P(1)–Ru–P(2), 102.0 (1); P(1)′–Ru–P(2), 106.1 (1); N–Ru–P(1), 123.5 (4); N–Ru–P(1)′, 113.4 (4); N–Ru–P(2), 98.4 (4); Ru–N–O, 174.1 (9).

geometry about each ruthenium atom (neglecting metal–metal bonding) is square pyramidal with two chlorines and two phosphido groups in the basal plane and the nitrosyl ligand at the apex. The Ru atom is displaced 0.62 Å out of the basal plane toward the apical nitrosyl. One intriguing and noteworthy aspect of this structure is the slightly bent mode of nitrosyl coordination which has a Ru–N–O bond angle of 160.3 (8)° and a Ru–N distance of 1.779 (7) Å. While this distance is longer than that found in **1**, it does not differ significantly from corresponding values in $RuH(NO)(P(C_6H_5)_3)_3$, $[Ru(NO)(diphos)_2]^+$, and other Ru complexes containing linearly coordinated nitrosyl.[1] The ruthenium–nitrosyl bond in **2** thus exhibits considerable metal–ligand π interaction despite the 160.3° Ru–N–O bond angle. This type of slightly bent coordination, which is intermediate between the linear and 120° bent modes of NO bonding, has been suggested by us[1] for discrete tetragonal-pyramidal complexes with a 21-electron count. (This count is based on 10 electrons from the ligand σ^b functions, 4 electrons in the π^b NO set, and 7 electrons from the metal ion which, in this case, is formally Ru(I).) The occurrence of metal–metal bonding in **2** apparently does not affect this conclusion regarding NO bonding although it does alter slightly the bonding scheme presented previously.[1]

Assessing the degree of metal–metal bonding in systems such as **1** and **2** is fraught with difficulties, but it is clear from the structural parameters that a significant difference in the metal–metal bonding does exist between these systems. If the noble gas rule is followed in assigning metal–metal bond orders, then the 2.787-Å Ru–Ru bond in **2** has a bond order of 1 and the much shorter 2.629-Å Ru–Ru bond in **1** has formal bond order of 2. These distances may be compared with Ru–Ru bond lengths ranging from 2.650 Å in elemental ruthenium[14] to 2.848 Å in $Ru_3(CO)_{12}$[15] and the range 2.70–2.95 Å observed in a number of ruthenium carbonyl cluster compounds.[16] This comparison of distances underscores the problem in assigning metal–metal bond orders.[17] An alternative formulation of **1** which eliminates the necessity of the Ru–Ru double bond is $[RuH(NO)(\mu\text{-}P(C_6H_5)_2)L]_2$ but infrared, nmr, and chemical evidence do not support the presence of a hydride. Further studies of these systems designed to examine the relationship of metal–metal bonding with mode of nitrosyl coordination and the reactivity of these systems toward small molecules are in progress.[18]

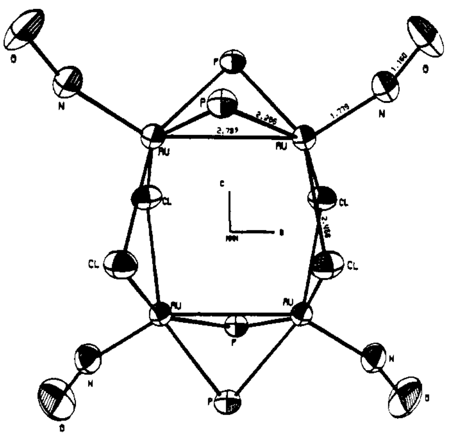


Figure 2. A perspective drawing of the inner coordination geometry of $[RuCl(NO)(\mu\text{-}P(C_6H_5)_2)]_4$. The phenyl rings are omitted for clarity. The estimated standard deviations for the bond lengths (Å) are: Ru–Ru, 0.002; Ru–Cl, 0.002; Ru–P, 0.002; Ru–N, 0.007; N–O, 0.010. Important bond angles (deg) are: Ru–P–Ru, 75.14 (7); Ru–Cl–Ru, 96.11 (8); P–Ru–P, 79.71 (10); Cl–Ru–Cl, 80.61 (8); Ru–N–O, 160.3 (8); P–Ru–N, 104.1 (2); Cl–Ru–N, 106.1 (2).

Acknowledgments. We wish to thank Mr. Donald G. VanDerveer for measuring the nmr spectra of the compounds and to acknowledge the National Science Foundation (NSF Grant GP-23139) and the Advanced Research Projects Agency for support of this work.

---

[14] A. Hellawell and W. Hume-Rothery, *Phil. Mag.*, **45**, 797 (1954).

[15] R. Mason and A. I. M. Rae, *J. Chem. Soc. A*, 778 (1968).

[16] (a) R. Belford, M. I. Bruce, M. A. Cairns, M. Green, H. P. Taylor, and P. Woodward, *Chem. Commun.*, 1159 (1970); (b) M. R. Churchill, K. Gold, and P. H. Bird, *Inorg. Chem.*, **8**, 1956 (1969); (c) M. R. Churchill and J. Wormald, *J. Amer. Chem. Soc.*, **93**, 5670 (1971); (d) R. Mason and W. R. Robinson, *Chem. Commun.*, 468 (1968); (e) P. J. Roberts and J. Trotter, *J. Chem. Soc. A*, 3246 (1970); (f) D. B. W. Yawney and R. J. Doedens, *Inorg. Chem.*, **11**, 838 (1972).

[17] A referee has also suggested that the Ru–Ru bond in **2** is constrained to its larger value by virtue of nonbonded repulsions between Cl atoms across the tetranuclear cluster (the Cl···Cl vector which parallels the Ru–Ru bond). However, we believe a shorter Ru–Ru bond in **2** could be accommodated by a decrease in the Ru–Cl–Ru bond angle from the observed value of 96.11° with no increase in Cl···Cl contacts. This suggestion, though, does point out one more possible factor in determining the most stable geometry of a system and, hence, the observed metal–metal bond length.

[18] Listings of coordinates and anisotropic temperature factors will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-72-6240. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

Richard Eisenberg,* Arthur P. Gaughan, Jr.
Cortlandt G. Pierpont, Joseph Reed, Arthur J. Schultz
Department of Chemistry, Brown University
Providence, Rhode Island 02912

Received May 12, 1972

Electron Paramagnetic Resonance of Free Radicals in an Adamantane Matrix. IV. The Structure of the *tert*-Butyl Radical

Sir:

It is well known that the methyl radical is planar[1] and that sequential replacement of hydrogen by fluorine

---

[1] G. Herzberg, "The Spectra and Structures of Simple Free Radicals," Cornell University Press, Ithaca, N. Y., 1971.