could occur via dissociation of one of the coordinated bonds, followed by rotation of the now unconstrained methyl group, and subsequent recoordination of a new C–H(D) bond.

The rate difference between the site exchange reaction and the reductive elimination reaction appears to be almost entirely enthalpic in origin, amounting to ca. 6 kcal mol^{-1}. The transition states for these two reactions presumably differ in that the former contains bound methane, while in the latter the methane is essentially dissociated. Thus the enthalpy difference may approximate the binding energy of methane.[19] For comparison, calculated binding energies for methane in $Pd(CH_4)$ and $Pt(CH_4)$ are 2 and 5 kcal mol^{-1}, respectively.[17]

We are continuing to investigate the coordination chemistry of other alkanes to the rhenocene cation and derivatives in order to assess the steric and electronic factors which influence alkane binding.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. Support for this investigation was also provided by the National Science Foundation (Grant CHE-8814191). The receipt of a Cottrel Grant from the Research Corporation is gratefully acknowledged. We thank Professors Jack Norton and John Bercaw for providing information prior to publication.

Supplementary Material Available: Kinetic data and Eyring plots for reductive elimination and site exchange reactions and proton NMR spectrum of methane-d_3 formed by reductive elimination from **2**-d_3 (6 pages). Ordering information is given on any current masthead page.

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[17] There is some theoretical support for this description of the intermediate provided by GVB calculations on the interaction of methane with Pd and Pt atoms. Low, J.; Goddard, W. A. *Organometallics* **1986**, *5*, 609–622. Experimental evidence for species having two C–H bonds coordinated to a transition-metal center is provided by the studies of Fehlner and co-workers on $Fe_3(CO)_9(CH_4)$.[18]

[18] Fehlner, T. P.; Jacobsen, G. B.; Vites, J. C.; Dutta, T. K. *Organometallics* **1987**, *6*, 842–847.

[19] This enthalpy difference would actually represent the *minimum* binding energy for methane since it actually corresponds to the enthalpy differences between the two transition states (reductive elimination versus site exchange processes). The actual binding energy will be greater by an amount equal to the stabilization of the intermediate, which is not known.

Isolation, Structure, and Magnetic Properties of a Novel Mononuclear Rhodium(II) Complex

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The chemistry of divalent rhodium is confined almost exclusively to binuclear metal–metal bonded complexes,[1] with only sporadic reports of isolated Rh(II) monomers having appeared in the literature to date.[2,3] In many cases, the assignment of the +2 oxidation state is ambiguous; in fact, to our knowledge, only one paramagnetic mononuclear rhodium compound, the square-planar molecule $Rh(MNT)_2^{2-}$, has been structurally characterized.[2a] The paucity of mononuclear d^7 rhodium species as opposed to the abundance of cobalt(II) monomers may be understood in terms of the greater stability of the Rh–Rh single bond. A great deal of synthetic and theoretical work has been devoted to the understanding of the bonding in Rh_2^{4+} complexes.[1]

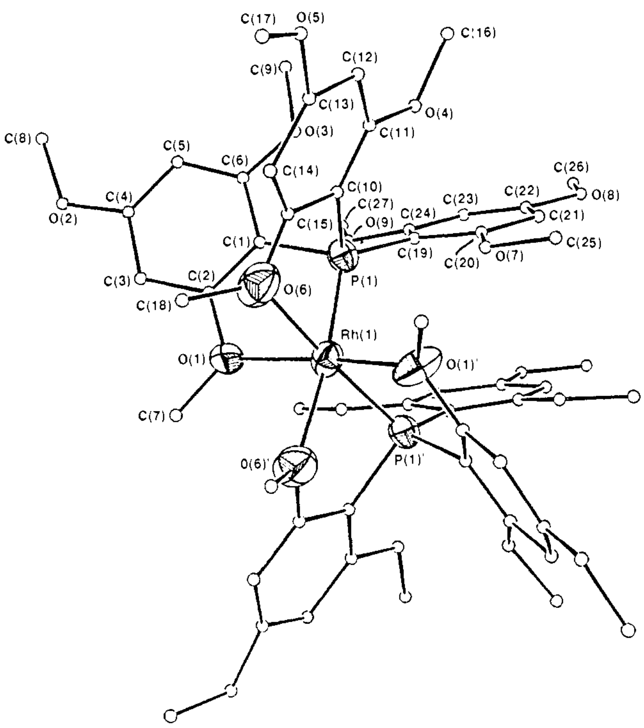

Figure 1. ORTEP representation of the $[Rh(TMPP)_2]^{2+}$ molecular cation. Some important distances (Å) and angles (deg) are as follows: Rh(1)–P(1), 2.216 (2); Rh(1)–O(1), 2.398 (5); Rh(1)–O(6), 2.201 (6); O(1)–C(2), 1.393 (9); P(1)–Rh(1)–P(1), 105.2 (1); P(1)–Rh(1)–O(1), 80.5 (1); P(1)–Rh(1)–O(6), 171.5 (2); O(1)–Rh(1)–O(1), 167.8 (3).

One of our current research interests is the coordination chemistry of solvated polynuclear metal cations, especially our recently reported rhodium(II,II) complex, $[Rh_2(CH_3CN)_{10}](BF_4)_4$.[4] Few entirely solvated binuclear transition-metal cations are known, the only other examples being $M_2(aq)^{4+}$ (M = Mo,[5] Rh[6]) and $[Mo_2(CH_3CN)_8]^{4+}$;[7] the chemistry of these remains virtually unexplored. In order to circumvent the problems associated with preparing and handling aqua species, we have developed a convenient synthesis for the CH_3CN derivative of Rh_2^{4+} (vide supra), a compound that allows easy access to unusual monomeric and polynuclear compounds of Rh(II). We now wish to report the synthesis of a pseudo-octahedral rhodium(II) monomer stabilized only by two bulky phosphine ligands. The ligand is TMPP (TMPP = tris(2,4,6-trimethoxyphenyl)phosphine) which has been recently synthesized and fully characterized.[8] We are engaged in a broad study of the coordination and organometallic

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[1] (a) Felthouse, T. R. *Prog. Inorg. Chem.* **1982**, *29*, 73 and references therein. (b) Boyar, E. B.; Robinson, S. D. *Coord. Chem. Rev.* **1983**, *50*, 109 and references therein.

[2] For mononuclear Rh(II) coordination complexes, see: (a) Billig, E.; Shupack, S. I.; Waters, J. H.; Williams, R.; Gray, H. B. *J. Am. Chem. Soc.* **1964**, *86*, 926. (b) Mezharaush, G. P. *Izv. Akad. Nauk. Latv. SSR, Ser. Khim.* **1965**, 263. (c) Pneumatikakis, G.; Psaroulis, P. *Inorg. Chim. Acta.* **1980**, *46*, 97. (d) Bennett, M. A.; Bramley, R.; Longstaff, P. A. *J. Chem. Soc., Chem. Commun.* **1966**, 806. (e) Bennett, M. A.; Longstaff, P. A. *J. Am. Chem. Soc.* **1969**, *91*, 6266. (f) Masters, C.; Shaw, B. L. *J. Chem. Soc. A* **1971**, 3679. (g) Moers, F. G.; de Long, J. A. M.; Beaumont, P. M. H. *J. Inorg. Nucl. Chem.* **1973**, *35*, 1915.

[3] For mononuclear organometallic Rh(II) complexes, see: (a) Fischer, E. O.; Lindner, H. H. *J. Organomet. Chem.* **1964**, *1*, 307. (b) Fischer, E. O.; Wawersik, H. *J. Organomet. Chem.* **1966**, *5*, 559. (c) Keller, H. J.; Wawersik, H. *J. Organomet. Chem.* **1967**, *8*, 185. (d) Dessy, R. E.; King, R. B.; Waldrop, M. *J. Am. Chem. Soc.* **1966**, *88*, 5112. (e) Dessy, R. E.; Kornmann, R.; Smith, C.; Hayter, R. *J. Am. Chem. Soc.* **1968**, *90*, 2001.

[4] (a) Dunbar, K. R. *J. Am. Chem. Soc.* **1988**, *110*, 8247. (b) Dunbar, K. R.; Pence, L. E., unpublished results.

[5] (a) Bowen, A. R.; Taube, H. *J. Am. Chem. Soc.* **1971**, *93*, 3287. (b) Bowen, A. R.; Taube, H. *Inorg. Chem.* **1974**, *13*, 2245.

[6] (a) Maspero, F.; Taube, H. *J. Am. Chem. Soc.* **1968**, *90*, 7361. (b) Wilson, C. R.; Taube, H. *Inorg. Chem.* **1975**, *14*, 2276. (c) Wilson, C. R.; Taube, H. *Inorg. Chem.* **1975**, *14*, 405. (d) Ziolkowski, J. J.; Taube, H. *Bull. Acad. Pol. Sci. Ser. Chim.* **1973**, *21*, 113.

[7] Mayer, J. M.; Abbott, E. H. *Inorg. Chem.* **1983**, *22*, 2274.

[8] (a) Wada, M.; Higashizaki, S. *J. Chem. Soc., Chem. Commun.* **1984**, 482. (b) Dunbar, K. R.; Haefner, S. C., manuscript in preparation.

0002-7863/89/1511-5504$01.50/0

chemistry of this PPh_3 derivative with both early and late transition elements.[9]

Addition of 4 equiv of TMPP to $[Rh_2(CH_3CN)_{10}](BF_4)_4$ in methanol leads to the immediate formation of an orange-brown solution and rapid precipitation of a purple microcrystalline product in approximately 50% yield. Alternatively, the reaction may be carried out in acetonitrile to yield a deep purple solution from which the product can be obtained in 70% yield by addition of diethyl ether. $[Rh(TMPP)_2](BF_4)_2$, **2**, was recrystallized by slow diffusion of toluene into a concentrated solution of the product in dichloromethane.[10] Small dark parallelpipeds that were suitable for X-ray study were obtained by this method.

The formulation of **2** as $[Rh(TMPP)_2](BF_4)_2$ was confirmed by single-crystal X-ray diffraction.[11,12] The complete molecule, shown in Figure 1, consists of a single rhodium center with two TMPP ligands in a cis disposition interacting through the P lone pairs. Each TMPP is further coordinated to the Rh atom via two ortho methoxy substituents on separate rings to give a total of four "cyclometalated" groups. The ORTEP emphasizes this coordination geometry and reveals that there are two different types of oxygen interactions in the molecule. The overall structure can best be described as a distorted octahedron with four weak Rh–O bonds and two strong Rh–P bonds; the molecular symmetry is C_2. This compound represents the first unequivocal example of a discrete monomer for a d^7 rhodium ion.[13] The bond distance of 2.216 (2) Å is typical for a Rh–P interaction,[14] but the Rh–O distances of 2.201 (6) and 2.398 (5) Å are very long, which is not surprising in view of the fact that they are metal–ether interactions. The remarkable air stability of the complex in the solid state and in solution is evidently a consequence of the protection afforded by the pendant methoxy groups. The molecule is quite reactive with a variety of substrates, however, including CO, which binds reversibly, NO^+, which affords the oxidized Rh(III) monomer $[Rh(TMPP)_2]^{3+}$, and excess phosphine ligand. Details of these and other small molecule reactions of $[Rh(TMPP)_2]^{2+}$ will be published in due course.

The unusual compound was further characterized by a variety of spectroscopic and magnetic techniques. A ^1H NMR of the product in CD_2Cl_2 gave a broad and featureless signal, indicating a paramagnetic complex. The magnetic properties of the compound were further probed by measuring the susceptibility over the temperature range 5–286 K at several field strengths. The sample displayed Curie–Weiss behavior with an average magnetic moment of $1.80 \pm 0.03\ \mu_B$ after correcting for diamagnetism and temperature independent paramagnetism.[15] Solution paramagnetism, investigated by the Evans method,[16] is also consistent with the presence of an $S = 1/2$ ground state ($\mu_{eff} = 2.10\ \mu_B$). The presence of an unpaired electron was substantiated by EPR spectroscopy at several temperatures; these spectra are presented in Figure 2. The spectrum at 8 K exhibits near axial symmetry with $g_x \cong g_y = 2.250 > g_z = 2.004$, signifying a d_{z^2} ground state. Indeed the solid-state structure is consistent with these observations in that the molecule exhibits a Jahn–Teller tetragonal elongation that is characteristic for a d^7 ion in an octahedral ligand environment. The very long Rh–O(1) bonds (2.398 (5) Å) are evidently a consequence of this distortion. The g_z region of the EPR spectrum consists of a doublet due to the expected coupling of the electron with the rhodium center ($I = 1/2$) and an extra spike which can be eradicated by increasing the power at low temperature. The behavior of this signal suggests the presence of an organic radical as a minor impurity in the sample, possibly a metal oxygen adduct or superoxide species. Detailed EPR studies under rigorous anaerobic conditions are in progress. ENDOR experiments designed to elucidate the phosphorus hyperfine coupling are also underway.[17]

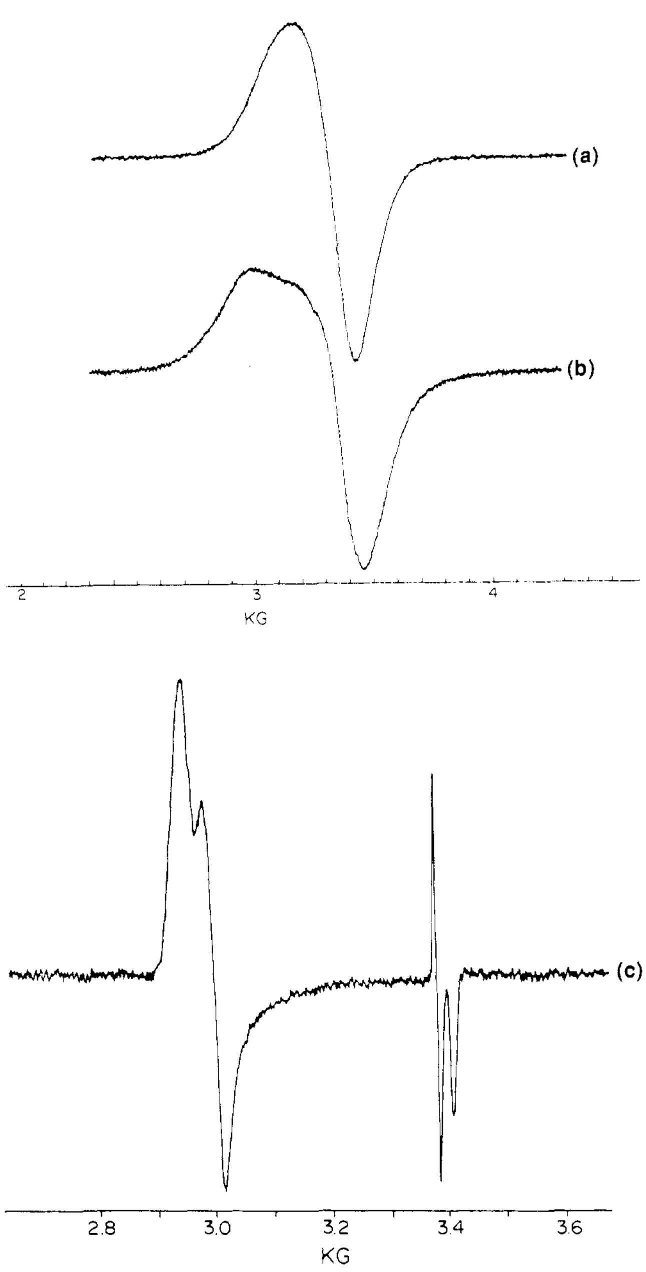

Figure 2. X-band EPR spectra of $[Rh_2(TMPP)_2](BF_4)_2$ recorded on CH_2Cl_2/toluene solutions (2/1 v:v) at 298 K (a), 100 K (b), and 8 K (c).

The electronic spectrum of **2** in CH_2Cl_2 displays five major bands at λ_{max}, nm (ϵ) = 540 (2050 $M^{-1}\ cm^{-1}$), 329 (13 405), 298 (15 280), 285 (17 518), 233 (62 440) as well as a shoulder at 420 nm. A cyclic voltammogram of $[Rh(TMPP)_2](BF_4)_2$ in 0.2 M TBAH/CH_2Cl_2 reveals the presence of two couples, a reversible

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(9) Chen, S. J.; Dunbar, K. R.; Haefner, S. C., unpublished results.

(10) Anal. Calcd for $C_{54}H_{66}F_8P_2O_{18}B_2Rh$: C, 48.34; H, 4.96. Found: C, 48.55; H, 4.86.

(11) (a) Bino, A.; Cotton, F. A.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 3558. (b) Cotton, F. A.; Frenz, B. A.; Deganello, G.; Shaver, A. *J. Organomet. Chem.* **1973**, *50*, 227.

(12) The compound crystallizes in the orthorhombic space group *Pbcn* with $a = 15.938$ (5) Å, $b = 17.916$ (7) Å, $c = 21.015$ (8) Å, $V = 6001$ (6) $Å^3$, $Z = 4$, $d_{calcd} = 1.427$ g/cm^3, and $\mu(MoK_\alpha) = 4.20\ cm^{-1}$. A Nicolet P3/F diffractometer was used to collect 3952 unique data in the range $4 \leq 2\theta \leq 45°$ at 22 ± 2 °C; 2462 data with $F_o^2 > 3\sigma(F_o^2)$ were used in the refinement. Residuals of $R = 0.080$ and $R_w = 0.098$ were obtained after 369 parameters had refined to convergence. The quality-of-fit index is 2.89, and the largest shift/esd = 0.58.

(13) (a) Townsend, M. G. *J. Chem. Phys.* **1964**, *41*, 3149. (b) Townsend, M. G.; Orton, J. W. *J. Chem. Phys.* **1966**, *45*, 4135.

(14) Tortorelli, L. J.; Tucker, C. A.; Woods, C.; Bordner, J. *Inorg. Chem.* **1986**, *25*, 3534.

(15) A diamagnetic correction of -724×10^{-6} cgsu was applied based on -20×10^{-6} for Rh^{2+}, -39×10^{-6} for BF_4^- and -313×10^{-6} for TMPP. The T.I.P. contribution was estimated to be 424×10^{-6} cgsu from a plot of χ_m vs $1/T$.

(16) (a) Evans, D. F. *J. Chem. Soc.* **1959**, 2003. (b) Deutsch, J. L.; Poling, S. M. *J. Chem. Educ.* **1969**, *46*, 167.

(17) Bender, C.; Dunbar, K., unpublished results.

oxidation at $E_{1/2}$ = +0.46 V, and a quasi-reversible reduction at $E_{1/2}$ = −0.65 V vs Ag/AgCl. This redox behavior suggests that the parent Rh(II) complex easily converts to stable Rh(I) and Rh(III) species and with minimal structural change or decomposition. We are investigating appropriate chemical routes in an effort to isolate these products.

The present study illustrates the ability of an alkoxide-substituted triphenylphosphine ligand to stabilize a rarely encountered oxidation state for mononuclear rhodium. The methoxy groups are capable of coordinating to the metal center through weak interactions, which helps to lightly stabilize low coordination numbers but does not render the molecule inert as is often the case with very bulky ligands and with cyclometalated groups possessing strong M–C bonds. Furthermore, the phosphine has a very flexible coordination mode in that it may behave as a mono-, bi-, or tridentate ligand depending on the electronic and geometric preferences of the metal center. Further work is underway to elucidate the coordination geometry of TMPP with metals possessing d^n electronic configurations of n = 2–10.

Acknowledgment. We thank Judith Eglin for help with the SQUID measurements and Chris Bender for his assistance in obtaining EPR data. We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to Michigan State University for an All-University Research Initiation Grant. X-ray equipment was supported by a grant from the National Science Foundation (CHE-8403823).

Supplementary Material Available: Tables of crystallographic parameters and equivalent isotropic displacement parameters, bond distances and angles, and anisotropic thermal parameters (9 pages); table of observed and calculated structure factors (24 pages). Ordering information is given on any current masthead page.

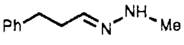
Additions and Corrections

Reduction of Azoalkanes by Benzhydryl Radicals [*J. Am. Chem. Soc.* **1989**, *111*, 1830]. Paul S. Engel* and Wen-Xue Wu

Page 1831: In Table I, the structure (designated #It) accompanying product 25 is missing. It is located incorrectly immediately below the structure for the azoalkane **37**. The correct sequence for the azoalkane/product combinations **24**/**25** and **37**/**38** follows.

24

25



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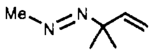

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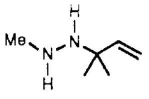

Book Reviews

Vitamins. By Wilhelm Friedrich (Institut für Physiologische Chemie). Walter de Gruyter: Berlin and New York. 1988. 1060 pp. DM380. ISBN 3-11-010244-7.

Professor Wilhelm Friedrich was one of the pioneering and successful researchers with Professor K. Bernhauer in Stockstadt/Main/Germany on vitamin B_{12} and particularly on the corrinoids. The expertise of Professor Friedrich on vitamin B_{12} is also exemplified by his co-editorship with B. Zagalak on *Vitamin B_{12}*, 1979, which is the Proceedings of the Third European Symposium on Vitamin B_{12}, and the *Intrinsic Factor* in Zurich, March 1979.

His *Vitamins* of 1988 is encyclopedic although in one volume, and it is a monumental and extraordinarily useful book. This remarkable book includes the important historical aspects but emphasizes the basic information on vitamins. The book is divided into special chapters for the 13 vitamins: vitamin A and its provitamins; vitamin D; vitamin E; vitamin K; thiamin, vitamin B_1, aneurin; vitamin B_2: riboflavin and its bioactive variants; niacin: nicotinic acid, nicotinamide, NAD (P); vitamin B_6, folic acid and unconjugated pteridines; biotin; pantothenic acid; vitamin B_{12}; and vitamin C.

This book has an appendix that provides the more important publications, particularly those that are relevant to medicine, that appeared after the chapters had been written. This appendix extends to May 1986.

The scope of information in this book is truly extensive and embraces history, discovery, organic chemistry, physical characteristics, biochemistry, biological activities such as antitumor effects, distribution in tissues, absorption, transport, enzymes, proteins, deficiencies, and many other relevant aspects.

This comprehensive book should be in the personal library of all scientists, whether academic or otherwise, and all investigators and all physicians who have a responsibility depending upon knowledge of the vitamins.

Not many scientists have the painstaking and persevering skill and knowledge to create such a book. For his stupendous accomplishment, Professor Friedrich deserves congratulations by all concerned with vitamins.

The chapters are very extensive. For example, the chapter on vitamin D consists of 76 pages with 73 sections and 8 pages of references. The chapter on vitamin B_6 consists of 75 pages with 70 sections and 8 pages of references. The chapter on vitamin B_{12} consists of 89 pages with 97 sections and 14 pages of references.

It is understandable that Professor Friedrich selected only the very well established vitamins for inclusion. Certain other nutritional entities were largely omitted on the basis of their "questionable vitamin character" but are cited in Table 1–34, which requires only half a page. Included in this table are lipoic acid, myo-inositol, and particularly ubiquinone or coenzyme Q. If Professor Friedrich publishes a future new edition of this book, surely he will include a chapter on coenzyme Q comparable in coverage to that for the majority of the 13 vitamins that are included.