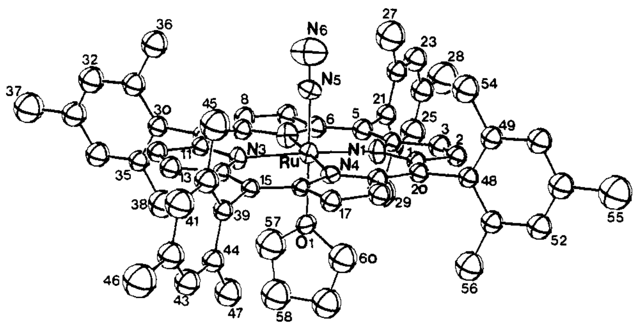

Figure 1. Drawing of the Ru(TMP)(THF)(N_2) molecule showing 50% probability ellipsoids and a partial labeling scheme. Hydrogen atoms have been omitted for the sake of clarity.

Fe(porp)(py)(N_2) where porp = the dianion of a protoporphyrin IX diester.[19] It is clear from the limited literature available[6,18-20] and our own more recent observations, that the N_2 ligand in the mono(dinitrogen) complexes is highly thermolabile and radiation labile (laboratory lighting and X-rays). The growing of a crystal of **1**, and its subsequent analysis by X-ray diffraction, were not trivial problems.

The structure of **1** is shown in Figure 1. The complex shows the typically linear $Ru \leftarrow N \equiv N$ arrangement with the metal being essentially in the plane (0.014 Å above the weighted least-squares plane of the 25-atom porphyrin skeleton). The Ru-N(5) distance of 1.822 (13) Å is slightly shorter than that found in the $Ru(N_2)(N_3)(en)_2^{2+}$ ion[21] (1.894 (9) Å). Other features of the Ru-N-N geometry are comparable in the two compounds and in the less accurately determined structures of two ruthenium dinitrogen hydrido phosphine complexes.[22,23] Other averaged bond lengths and angles for the metalloporphyrin moiety within **1** show no unusual features when compared with those of other monomeric, 6-coordinate Ru porphyrin complexes.[24-30]

The chemistry and redox properties of the Ru(II) porphyrin dinitrogen complexes, particularly the reactivity of the bound N_2, remain to be elucidated.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada (B.R.J.) and the U.S. National Institutes of Health (Grants AM 17989 to D.D. and HL 13157 to J.A.I.) for financial support and Johnson Matthey Ltd. for the loan of Ru.

Registry No. **1**, 106210-10-0; **2**, 106210-09-7; **3**, 106210-11-1; **4**, 115227-06-0; **5**, 115227-07-1; Ru(TMP)(CO), 92669-43-7; Ru(TMP)(THF)$_2$, 97877-73-1; Ru(TMP)(MeCN)$_2$, 97877-74-2; Ru(TMP), 79235-76-0.

Supplementary Material Available: Table S1 (bond distances), Table S2 (bond angles), Table S3 (displacements from the porphyrin plane), Table S4 (dihedral angles), Table S5 (hydrogen atom parameters), and Table S6 (anisotropic thermal parameters) (8 pages); Table S7 (structure amplitudes) (23 pages). Ordering information is given on any current masthead page.

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(19) McCoy, S.; Caughey, W. S. *Biochemistry* **1970**, *9*, 2387.
(20) Hoffman, B. M.; Gibson, Q. H. *Proc. Natl. Acad. Sci. U.S.A.* **1978**, *75*, 21.
(21) Davis, B. R.; Ibers, J. A. *Inorg. Chem.* **1970**, *9*, 2768.
(22) Chaudret, B.; Devillers, J.; Poilblanc, R. *J. Chem. Soc., Chem. Commun.* **1983**, 641.
(23) Chaudret, B.; Devillers, J.; Poilblanc, R. *Organometallics* **1985**, *4*, 1727.
(24) James, B. R.; Pacheco, A.; Rettig, S. J.; Ibers, J. A. *Inorg. Chem.* **1988**, *27*, 2414.
(25) James, B. R.; Dolphin, D.; Leung, T. W.; Einstein, F. W. B.; Willis, A. C. *Can. J. Chem.* **1984**, *62*, 1238.
(26) Collman, J. P.; Barnes, C. E.; Brothers, P. J.; Collins, T. J.; Ozawa, T.; Gallucci, J. C.; Ibers, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 5151.
(27) Ariel, S.; Dolphin, D.; Domazetis, G.; James, B. R.; Leung, T. W.; Rettig, S. J.; Trotter, J.; Williams, G. M. *Can. J. Chem.* **1984**, *62*, 755.
(28) Ball, R. G.; Domazetis, G.; Dolphin, D.; James, B. R.; Trotter, J. *Inorg. Chem.* **1981**, *20*, 1556.
(29) Little, R. G.; Ibers, J. A *J. Am. Chem. Soc.* **1973**, *95*, 8583.
(30) Bonnet, J. J.; Eaton, S. S.; Eaton, G. R.; Holm, R. H.; Ibers, J. A. *J. Am. Chem. Soc.* **1973**, *95*, 2141.

Contribution from the Department of Chemistry
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A Phosphido-Capped Tritungsten Alkoxide Cluster: $W_3(\mu_3\text{-}P)(\mu\text{-}OCH_2\text{-}t\text{-}Bu)_3(OCH_2\text{-}t\text{-}Bu)_6$ and Speculation upon the Existence of a Reactive $(t\text{-}BuCH_2O)_3W{\equiv}P$ Intermediate

Malcolm H. Chisholm,* Kirsten Folting,
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Lappert and co-workers[1] ended "The Quest for Terminal Phosphinidene Complexes"[2] with their reported synthesis and structural characterizations of $(\eta^5\text{-}C_5H_5)_2M({=}PAr)$ where M = Mo (X-ray) and W and Ar = $C_6H_2(t\text{-}Bu)_3$-2,4,6. We wish to report here our synthesis and characterization of a novel[3] phosphido-capped tritungsten cluster supported by alkoxide ligands and further to speculate that its formation may involve the reactive intermediate of formula $(t\text{-}BuCH_2O)_3WP$ having a W-P triple bond.

The reaction between $W_2(OCH_2\text{-}t\text{-}Bu)_6(HNMe_2)_2$[4] and white phosphorus, P_4, proceeds in hydrocarbon solvents according to the stoichiometry (as determined by ^1H NMR spectroscopy) shown in eq 1.[5]

$$2W_2(OCH_2\text{-}t\text{-}Bu)_6(HNMe_2)_2 + P_4 \xrightarrow[\text{toluene}]{75°,\ 4\ h} (HNMe_2)(t\text{-}BuCH_2O)_3W(\eta^3\text{-}P_3) + W_3(P)(OCH_2\text{-}t\text{-}Bu)_9 + 3HNMe_2 \quad (1)$$

The compound $(HNMe_2)(t\text{-}BuCH_2O)_3W(\eta^3\text{-}P_3)$ was previously characterized[6] from reaction 1, but the nature of the major tungsten-containing compound $W_3(P)(OCH_2\text{-}t\text{-}Bu)_9$ was not readily established. The elemental analysis indicated an approximate empirical formula $W(OCH_2\text{-}t\text{-}Bu)_3$, and though the presence of phosphorus was indicated, none could initially be detected by ^{31}P NMR studies.[7] The compound $W_3(P)(OCH_2\text{-}t\text{-}Bu)_9$ is only sparingly soluble in hydrocarbon solvents though this allowed the observation by NMR spectroscopy of two types of $OCH_2\text{-}t\text{-}Bu$ groups in the integral ratio 2:1, with the former having diastereotopic methylene protons.[7] Repeated attempts to obtain single crystals suitable for a single-crystal X-ray study failed until crystals appeared in an NMR tube in which the course of reaction 1 was being followed.[8]

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(1) Hitchcock, P. B.; Lappert, M. F.; Leung, W.-P. *J. Chem. Soc., Chem. Commun.* **1987**, 1282.
(2) Cowley, A. H.; Barron, A. R. *Acc. Chem. Res.* **1988**, *21*, 81.
(3) Phosphorus-, arsenic-, and even bismuth-capped triangular carbonyl clusters are known for the later transition elements, e.g. $Co_3(\mu_3\text{-}Bi)(CO)_9$: Whitmire, K. H.; Leigh, J. S.; Gross, M. E. *J. Chem. Soc., Chem. Commun.* **1987**, 926. Martinengo, S.; Ciani, G. *J. Chem. Soc., Chem. Commun.* **1987**, 1589. To our knowledge, however, no triangular phosphido-capped clusters are known for the early transition elements (groups 4–6) in oxidation states M^{x+} where $x = 3$ or 4. See: Herrmann, W. A. *Angew. Chem., Intl. Ed. Engl.* **1986**, *25*, 56 and references therein.
(4) Chisholm, M. H.; Huffman, J. C.; Leonelli, J.; Ratermann, A. L. In *Inorganic Chemistry: Toward the 21st Century*; Chisholm, M. H., Ed.; ACS Symposium Series 211; American Chemical Society: Washington, DC, 1983; poster abstract, p 527.
(5) Note the use of dry and oxygen-free atmospheres (N_2) and solvents throughout. Anal. Calcd (found) for $W_3(P)(OCH_2\text{-}t\text{-}Bu)_9$: C, 39.54 (38.30); H, 7.30 (6.95); P, 2.27 (2.27).
(6) Chisholm, M. H.; Huffman, J. C.; Pasterczyk, J. W. *Inorg. Chim. Acta* **1987**, *133*, 17.
(7) Ultimately, the ^{31}P signal was found: $\delta = 274.8$ vs 85% H_3PO_4, flanked by satellites due to coupling to ^{183}W, $I = {}^1/_2$, 14.5% natural abundance, $^1J_{^{183}W-^{31}P} = 45$ Hz. ^1H NMR data are temperature invariant (+60 to −60 °C) in toluene: δ 1.03 (18 H), 1.08 (9 H), 4.14 (2 H), 4.23 (2 H), 4.39 (2 H) ($J_{AB} = 10.8$ Hz).
(8) Crystal data for $W_3(\mu_3\text{-}P)(\mu\text{-}OCH_2\text{-}t\text{-}Bu)_3(OCH_2\text{-}t\text{-}Bu)_6$ at −156 °C: $a = b = 23.55$ (8) Å, $c = 17.97$ (6) Å, $\gamma = 120°$, space group *R*3. Of the 5360 reflections collected (Mo Kα, $5° < 2\theta < 45°$), 2488 were unique and the 2325 having $F > 3\sigma(F)$ were used in the full-matrix least-squares refinement. All non-hydrogen atoms were refined using anisotropic thermal parameters. H atoms were located but placed in idealized fixed positions during the final refinements. The final residuals are $R(F) = 0.029$ and $R_w(F) = 0.029$.

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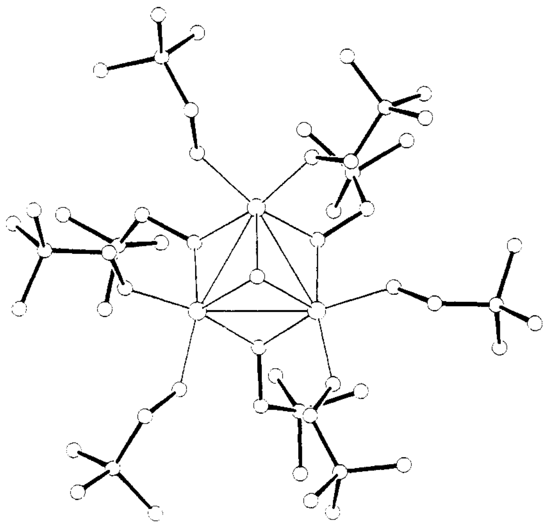

Figure 1. A ball-and-stick drawing of the $W_3(\mu_3\text{-}P)(\mu\text{-}OCH_2\text{-}t\text{-}Bu)_3(OCH_2\text{-}t\text{-}Bu)_6$ molecule. Pertinent bond distances and angles are given in the text. The molecule has a crystallographically imposed C_3 axis of symmetry.

In the space group R_3, there are two independent $W_3(\mu_3\text{-}P)(\mu\text{-}OCH_2\text{-}t\text{-}Bu)_3(OCH_2\text{-}t\text{-}Bu)_6$ molecules in the unit cell. Each molecule has crystallographically imposed C_3 symmetry, and the two molecules are virtually superimposable, differing so little that all parameters are virtually equivalent within the criteria of 3σ. A view of one of the molecules is given in Figure 1.

Each tungsten atom is in a square-based-pyramidal coordination geometry with the W-P bond occupying the axial site; W-P = 2.365(4) Å. The W-W distance is 2.757 (1) Å, and the angles within the distorted W_3P tetrahedron are W-W-W = 60°, W-P-W = 71.3 (1)°, and P-W-W = 54.3 (1)°. the W-O(terminal) and W-O(bridging) distances are 1.92 (1) and 2.05 (2) Å (average), respectively. Structurally and electronically the clusters $W_3(\mu_3\text{-}X)(\mu\text{-}OR)_3(OR)_6$ where X = CMe[9] and P are closely related. Of course, RC and P are isolobal,[10] and we have previously reported the characterization of $W_2(\mu\text{-}X_2)(OR)_6(py)_n$ compounds where n = 1 or 2 and X = CH[11] and P.[12] Also, the $(\eta^3\text{-}C_3R_3)$ moiety seen in the molecular structure of $(Me_2NCH_2CH_2NMe_2)Cl_3W(\eta^3\text{-}C_3Me_2(t\text{-}Bu))$[13] is isolobal with the $(\eta^3\text{-}P_3)$ moiety in $(HNMe_2)(t\text{-}BuCH_2O)_3W(\eta^3\text{-}P_3)$. Given the extensive chemistry of $(RO)_3W{\equiv}CR'$ compounds[14] and to a lesser extent $(RO)_3W{\equiv}N$ compounds,[15] we suggest a similar chemistry for $(RO)_3W{\equiv}P$.[16] In particular, the formation of $W_3(\mu_3\text{-}P)(OCH_2\text{-}t\text{-}Bu)_9$ in eq 1 could well follow the reaction scheme outlined in eq 2.

$$W_2(OR)_6 + P_4 \xrightarrow{\text{slow}} W_2(OR)_6(P_4) \qquad (2a)$$

$$W_2(OR)_6(P_4) \xrightarrow{\text{fast}} (RO)_3W(\eta^3\text{-}P_3) + (RO)_3W{\equiv}P \qquad (2b)$$

$$W_2(OR)_6 + (RO)_3W{\equiv}P \xrightarrow{\text{fast}} W_3(\mu_3\text{-}P)(\mu\text{-}OR)_3(OR)_6 \qquad (2c)$$

It should be noted that (1) P_4 metal-containing compounds are known,[17] (2) asymmetric cleavage of $(RO)_3M{\equiv}M(OR)_3$ compounds,[18] as well as $Cp(CO)_2M{\equiv}M(CO)_2Cp$ compounds[19] (M = Mo, W), is well documented, and (3) the comproportionation reaction, reaction 2c, has ample precedent in the preparation of $W_3(\mu_3\text{-}CR')(OR)_9$,[20] $W_3(\mu_3\text{-}O)(OR)_{10}$,[21] and $W_3(\mu_3\text{-}NH)(OR)_{10}$ compounds.[22] Also, given the existence of phosphaalkyne compounds,[23] $RC{\equiv}P$, and the propensity, perhaps above all other metals, for tunsten to form $W{\equiv}CR$ bonds, we believe the quest for compounds containing $W{\equiv}P$ bonds will shortly be fulfilled.[24]

Registry No. $W_2(OCH_2\text{-}t\text{-}Bu)_6(HNMe_2)_2$, 83437-02-9; P_4, 12185-10-3; $W_3(P)(OCH_2\text{-}t\text{-}Bu)_9$, 115436-98-1.

Supplementary Material Available: A complete listing of atomic coordinates for $W_3(\mu_3\text{-}P)(\mu\text{-}OCH_2\text{-}t\text{-}Bu)_3(OCH_2\text{-}t\text{-}Bu)_6$ (3 pages). Ordering information is given on any current masthead page.

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(9) Chisholm, M. H.; Hoffman, D. M.; Huffman, J. C. *Inorg. Chem.* **1984**, *23*, 3683. Chisholm, M. H.; Folting, K.; Heppert, J. A.; Hoffman, D. M.; Huffman, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 1234.

(10) Hoffman, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 711.

(11) Chisholm, M. H.; Folting, K.; Hoffman, D. M.; Huffman, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 6794.

(12) Chisholm, M. H.; Folting, K.; Huffman, J. C.; Koh, J. J. *Polyhedron* **1985**, *4*, 893.

(13) Schrock, R. R.; Pedersen, S. F.; Churchill, M. R.; Ziller, J. W. *Organometallics* **1984**, *3*, 1574.

(14) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. In *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; Chapter 9 and references therein.

(15) Chisholm, M. H.; Hoffman, D. M.; Huffman, J. C. *Inorg. Chem.* **1983**, *22*, 2903. Chan, D.-T.; Chisholm, M. H.; Huffman, J. C.; Marchant, N. S. *Inorg. Chem.* **1986**, *25*, 4170.

(16) Fenske-Hall calculations on the mononuclear fragments $(HO)_3W{\equiv}X$ where X = N (W-N = 1.74 Å) and X = P (W-P = 2.0975 Å) indicate that although P-to-W π bonding is less effective than N-to-W π bonding, the σ-bonding character is in the reverse order: Chisholm, M. H.; Pasterczyk, J. W.; results to be submitted for publication.

(17) Di Vaira, M.; Stoppioni, P.; Peruzzini, M. *Polyhedron* **1987**, *6*, 351.

(18) Chisholm, M. H.; Folting, K.; Huffman, J. C.; Kirkpatrick, C. C. *Inorg. Chem.* **1984**, *23*, 1021.

(19) Curtis, M. D. *Polyhedron* **1987**, *6*, 759.

(20) Chisholm, M. H.; Conroy, B. K.; Eichhorn, B. W.; Folting, K.; Hoffman, D. M.; Huffman, J. C.; Marchant, N. S. *Polyhedron* **1987**, *6*, 783. Chisholm, M. H.; Conroy, B. K.; Huffman, J. C. *Organometallics* **1986**, *5*, 2384.

(21) Chisholm, M. H.; Folting, K.; Huffman, J. C.; Kober, E. M. *Inorg. Chem.* **1985**, *24*, 241. For related synthesis of $W_3(\mu_3\text{-}O)(CH_2Ph)(O\text{-}i\text{-}Pr)_9$ and $W_3(\mu_3\text{-}O)(CH_2Ph)_2(O\text{-}i\text{-}Pr)_8$ compounds, see: Chisholm, M. H.; Folting, K.; Eichhorn, B. W.; Huffman, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 3146.

(22) Chisholm, M. H.; Hoffman, D. M.; Huffman, J. C. *Inorg. Chem.* **1985**, *24*, 796.

(23) Appel, R.; Knoll, F.; Ruppert, I. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 731.

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Experimental Determination of the ^{27}Al NMR Quadrupole Coupling Constant of the Hexaaquoaluminum Ion in Aqueous Perchloric Acid and Mixed Acetone–Aqueous Perchloric Acid Solution

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The ^{27}Al nucleus is quadrupolar, having a nuclear spin, I, of $^5/_2$ and a quadrupole moment, Q, of 0.149×10^{-24} cm^2. Interaction of the quadrupole moment with local electric field gradients couple the nucleus to molecular motions, thereby giving rise to an efficient magnetic relaxation mechanism.[1] Electric field gradients are generated or imposed about the ^{27}Al nucleus by the ligand field asymmetry of ligands or solvent molecules bound to the aluminum(III) metal ion. In the limit of fast motion, nuclear spin quadrupolar relaxation is governed by eq 1, where T_Q, T_1, and T_2 are the quadrupolar, spin–lattice, and spin–spin relaxation

$$\frac{1}{T_Q} = \frac{1}{T_1} = \frac{1}{T_2} = \frac{3}{40}\left[\frac{2I+3}{I^2(2I-1)}\right]\left(\frac{\eta^2}{3}+1\right)\left(\frac{e^2qQ}{\hbar}\right)^2\tau_c \qquad (1)$$

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