II → I → III, although the more direct path II → III cannot be ruled out. The presence of the tungsten center seems significant; pyrolysis of $Os_3(CO)(C_2Ph_2)$ results simply in CO loss to form the unsaturated species $Os_3(CO_9)(C_2Ph_2)$ without cleaving the alkyne.[18] Fehlner and co-workers[19] have suggested that scission of alkyne moieties in carboranes and on metal surfaces is driven by charge transfer from the relatively electropositive boron or metal atoms to the resulting alkylidyne groups. Our results are consistent with this idea in that the alkylidyne ligands in 4–6 end up coordinated to a relatively oxidized tungsten center.

Supplementary Material Available: Tables of positional and anisotropic thermal parameters for compounds 1 and 4 (4 pages). Ordering information is given on any current masthead page.

(18) Tachikawa, M.; Shapley, J. R.; Pierpont, C. G. J. Am. Chem. Soc. 1975, 97, 7172.

(19) (a) Deshmukh, P.; Dutta, T. K.; Hwang, J. L.-S.; Housecroft C. E.; Fehlner, T. P. J. Am. Chem. Soc. 1982, 104, 1740. (b) DeKock, R. L.; Fehlner, T. P.; Housecroft, C. E.; Lubben, T. V.; Wade, K. Inorg. Chem. 1982, 21, 25.

Synthesis and X-ray Crystal Structure of Mo2(μ-t-Bu2P)2(t-Bu2P)2(Mo≣Mo): The First Structurally Characterized Binary Transition-Metal Phosphide

Richard A. Jones,* Jon G. Lasch, Nicholas C. Norman, Bruce R. Whittlesey, and Thomas C. Wright

Department of Chemistry
The University of Texas at Austin
Austin, Texas 78712

There is currently considerable interest in the chemistry of transition-metal phosphido (R_2P^-) complexes.[1] As part of the study of the steric and electronic effects of phosphido ligands, we have investigated the use of sterically demanding (bulky) alkyl groups attached to phosphorus.[2-4]

We report here the synthesis, characterization, and X-ray crystal structure of $Mo_2(\mu\text{-}t\text{-Bu}_2P)_2(t\text{-Bu}_2P)_2$ (1) which, to our knowledge, is the first structurally characterized binary dialkyl or diaryl phosphide of a transition metal.[5,20] Binary transition-metal phosphides were reported some time ago by Issleib and Abel for

(1) See, for example, Kreter, P. E.; Meek, D. W. Inorg. Chem. 1983, 22, 319. Carty, A. J. Adv. Chem. Ser. 1982, No. 196, 163. Keiter, R. L.; Madigan, M. J. Organometallics 1982, 1, 409. Vahrenkamp, H.; Wolters, D. Organometallics 1982, 1, 874. Foley, H. C.; Finch, W. C.; Pierpont, C. G.; Geoffroy, G. L. Ibid. 1982, 1, 1379. Breen, M. J.; Geoffroy, G. L. Ibid. 1982, 1, 1437. Mott, G. N.; Granby, R.; MacLaughlin, S. A.; Taylor, N. J.; Carty, A. J. Ibid. 1983, 2, 189 and references therein.

(2) Jones, R. A.; Stuart, A. L.; Atwood, J. L.; Hunter, W. E.; Rogers, R. D. Organometallics 1982, 1, 1721.

(3) Atwood, J. L.; Hunter, W. E.; Jones, R. A.; Wright, T. C. Inorg. Chem. 1983, 22, 993.

(4) Jones, R. A.; Wright, T. C.; Atwood, J. L.; Hunter, W. E. Organometallics 1983, 2, 470.

(5) Binary (homoleptic) complexes of the transition metals are known for many types of ligands. See: Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley: New York, 1980; Chapters 3 and 4, pp 61-194.
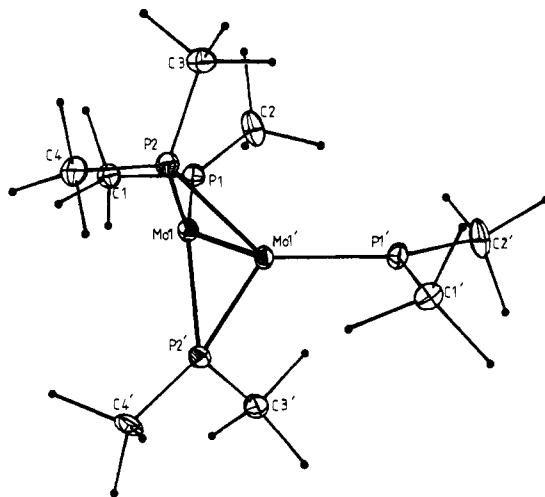

Figure 1. General view of 1. For clarity the methyl groups of the *t*-Bu units are represented as sticks. Key bond lengths and angles are in ref 13 and the text.

Ti,[6] V,[6] Cr,[6] Mn,[7] Fe,[8] Ni,[9,10] and Pd[10] although these compounds are very poorly characterized.

The interaction of 4 equiv of Li-t-Bu$_2$P with dimolydenum tetraacetate in diethyl ether at −78 °C yields a bright red solution from which $Mo_2(\mu\text{-}t\text{-Bu}_2P)_2(t\text{-Bu}_2P)_2$ (1) can be isolated in ca. 45% yield.[11] In the solid state this red crystalline compound can be handled briefly in air. It decomposes rapidly in solution when exposed to the atmosphere and is thermally unstable in solution at ambient temperature. The X-ray structure is shown in Figure 1.[12] Two Mo(II) atoms, linked by a multiple bond (Mo–Mo = 2.209 (1) Å), are bridged by two t-Bu$_2$P groups giving the central Mo_2P_2 core a butterfly type of configuration. Each Mo atom also bears a terminal phosphido unit. There is a crystallographically imposed twofold axis bisecting the Mo–Mo vector and the line connecting P(2) and P(2)′, giving unique terminal and bridging phosphorus atoms, P(1) and P(2), respectively.

There are several noteworthy features.[13] The bridging μ-t-Bu$_2$P groups are symmetrical within experimental error (Mo(1)–P(2) and Mo(1)′–P(2) = 2.437 (1) and 2.434 (1) Å). These distances, similar to those found in other dinuclear μ-t-Bu$_2$P systems,[2-4] are slightly larger than the terminal metal phosphorus distance (Mo–P (1) = 2.382 (1) Å), which is considerably longer than that in $[Mo(P(OMe)_3)_5P(OMe)_2]^+$ (2.29 (4) Å).[14]

(6) Issleib, K.; Wenschuh, E. Chem. Ber. 1964, 97, 715.

(7) Issleib, K.; Wenschuh, E. Z. Naturforsch., B 1962, 17B, 778.

(8) Issleib, K.; Wenschuh, E. Z. Naturforsch, B 1964, 19B, 199.

(9) Issleib, K.; Fröhlich, H. O.; Wenschuh, E. Chem. Ber. 1962, 95, 2742.

(10) Abel, E. W.; McLean, R. A. N.; Sabherwal, I. H. J. Chem. Soc. A 1968, 2371.

(11) Full experimental details will be published separately. Mp 1: darkens at 50 °C and decomposes slowly over the range 50–150 °C. No evidence for a hydride species, possibly not detected in the X-ray structure, could be obtained from high-field ^1H NMR (in PhMe-d_8 at −80 °C, 1000 scans on a Nicolet NT-200) or via solution IR data. ^1H NMR δ 1.04 s, 1.14 s (1:1).

(12) CAD-4, crystal data: $Mo_2P_4C_{32}H_{72}$, orthorhombic, space group Pnna (No. 52), a = 13.715 (3) Å, b = 17.055 (3) Å, b = 17.055 (3) Å, c = 17.937 (2) Å, U = 4196.72 (19) Å^3, D_c = 1.876 g cm^{-3}, Z = 4, λ(Mo Kα) = 0.71069 Å (graphite monochromator), μ(Mo Kα) = 11.5 cm^{-1}. Methods: Patterson, difference Fourier, full matrix least squares. Refinement of 2232 observed, 4121 measured (2° < 2θ < 50°) gave R = 0.0514 and R_w = 0.063. All non-hydrogen atoms anisotropic. Final difference maps showed no unusual features.

(13) A complete listing of bond distances and angles is provided as supplementary material. For convenience the key bond lengths (Å) and angles (deg) are as follows. Lengths: P(1)–C(1) = 1.880 (6), C(1)–C(11) = 1.536 (8), P(2)–C(3) = 1.931 (5), C(3)–C(31) = 1.568 (8). Angles: P(2)–Mo(1)–P(2)′ = 105.12 (5), Mo(1)–Mo(1)′–P(1) = 137.76 (3), Mo(1)′–Mo(1)–P(2) = 63.11 (4), Mo(1)–Mo(1)′–P(2) = 62.96 (4), Mo(1)–P(1)–C(1) = 108.8 (2), Mo(1)–P(1)–C(2) = 138.4 (2), Mo(1)–P(2)–C(3) = 114.0 (2), Mo(1)–P(2)–C(4) = 126.0 (2). Deviations from the least-squares plane through Mo(1)–P(1)–C(2)–C(1) are as follows: Mo 0.014 (1) Å, P(1) −0.046 (3) Å, C(2) 0.019 (17) Å, C(1) 0.013 (13) Å.

(14) Meutterties, E. L.; Kirner, J. F.; Evans, W. J.; Watson, P. A.; Abdel-Meguid, S.; Tavanaiepour, I.; Day, V. W. Proc. Natl. Acad. Sci. U.S.A. 1978, 75, 1056.

The Mo–Mo distance (2.209 (1) Å) is longer by ca. 0.1 Å than that normally observed in Mo_2 quadruply bonded systems that have been extensively studied by Cotton and co-workers.[15] It seems reasonable to assume a bond order of four that has been lengthened due to the nature of the bridging groups. The short Mo–Mo distance results in an abnormally acute angle subtended at the bridging phosphorus atoms (Mo(1)–P(2)–Mo(1)′ = 53.95 (3)°). This now stands as the most acute M–P–M angle so far reported for a phosphido bridged complex.[16] The strain imposed at P(2) may therefore be partly relieved by a slightly longer than normal Mo—⁴Mo distance.

The butterfly arrangement of the μ-t-Bu$_2$P groups is also of interest. We have previously suggested that the steric demands of the μ-t-Bu$_2$P unit were largely responsible for planar geometries observed in the M_2P_2 cores of a number of $M_2(\mu$-t-Bu$_2$P)$_2$ complexes.[2-4] The structure of **1** shows that this is no longer a valid assumption, although the dihedral angle between the Mo(1)–P(2)′–Mo(1)′ and Mo(1)–P(2)′–Mo(1)′ planes of 125.9 (5)° is not as severe as those observed in other bis-Ph$_2$P bridged systems such as Fe$_2$(CO)$_6$(μ-Ph$_2$P)$_2$; dihedral angle = 100.0°.[17] The terminal phosphido units are bent back away from the side of the molecule bearing the two bridging groups (Mo(1)–Mo(1)′–P(1)′ = 137.76 (3)°). The coordination geometry about each molybdenum, consisting of two bridging and one terminal phosphorus nuclei, is accurately planar (P(2)–P(2)′–Mo(1)–P(1)). The geometry about each terminal phosphorus is also virtually planar[13] (Mo-(1)–P(1)–C(2)–C(1)), and these planes are almost orthogonal to their respective P(1)–P(2)–Mo(1)–P(2)′ planes (85.1°). The planar geometry of the terminal phosphido groups suggests that they act as three-electron donors via additional π donation to Mo as suggested for various dialkylamide derivatives of the transition metals.[18]

The ^{31}P{^{1}H} of **1** in toluene-d_8 at −80 °C shows two sharp singlets (1:1) at δ 334.91 and 33.51 (rel 85% H$_3$PO$_4$(aq)) assigned to the bridging and terminal phosphorus nuclei, respectively.[19] These signals remain as singlets in the proton-coupled spectrum. The absence of J_{P-P} coupling is presumably a result of different sets of metal orbitals being used for Mo–P(bridge) and Mo–P-(terminal) bonding. The structure of **1** with low-coordinate Mo(II) atoms and a large gap on the side of the molecule opposite to the two μ-t-Bu$_2$P groups suggests that it might be unusually reactive. This is consistent with the thermal instability; **1** is unstable in hexane, aromatic (benzene or toluene), or diethyl ether solutions at ambient temperature. The solutions darken rapidly and ^{31}P NMR spectra show the presence of t-Bu$_2$PH (δ 19.41, J_{P-H} = 195.3 Hz in the ^{1}H-coupled spectrum). No other phosphorus-containing species apart from **1** are detectable in these solutions (^{31}P NMR), and we have been unable to isolate any molybdenum-containing complexes from solutions that have been warmed to room temperature.

Registry No. 1, 86802-71-3; Mo$_2$(O$_2$CMe)$_4$, 14221-06-8; Mo, 7439-98-7.

Supplementary Material Available: Listings of atomic coordinates, thermal parameters, bond lengths and angles, and structure factors (31 pages). Ordering information is given on any current masthead page.

Electron Correlation and Basis Set Effects on the Relative Stabilities of Classical and Nonclassical Structures of the 2-Norbornyl Cation

M. Yoshimine, A. D. McLean, and B. Liu*

*IBM Research Laboratory
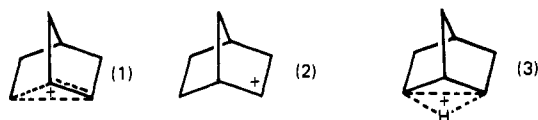San Jose, California 95193*

D. J. DeFrees

*Molecular Research Institute
Palo Alto, California 94304*

J. S. Binkley

*Sandia National Laboratory
Livermore, California 94550*

Our ab initio SCF and CI calculations indicate that the potential surface of the 2-norbornyl cation has a minimum corresponding to a nonclassical structure (**1**) and no minimum corresponding

to a classical structure (**2**). It follows that, in the gas phase, the 2-norbornyl cation has a symmetrical, carbon-bridged structure, and there is no classical ion. The SCF calculations, using extended basis sets, show that the classical and H-bridged, edge-protonated nortricyclene (**3**) structures found by a previous 4-21G SCF calculation[1] are respectively an artifact of the limited basis set and a saddle point on the potential surface.

The single and double CI calculations, with quadruple-excitation contributions estimated by Davidson's formula,[2] performed at the three stationary points on the 4-21G SCF potential surface,[1] show that electron correlation significantly favors the nonclassical structures over the classical structure. This work was motivated by the long-standing nonclassical ion controversy[3] and the recent low-temperature, solid-state, ^{13}C NMR study of the 2-norbornyl cation by Yannoni, Macho, and Myhre.[4] Previous theoretical studies of the 2-norbornyl cation have been inconclusive due to inadequate basis sets and/or limited treatment of electron correlation effects. A review of recent theoretical work on the 2-norbornyl cation can be found in ref 1.

We have performed SCF structure optimization and analytic force constant calculations using the GAUSSIAN82 program[5] and

(15) See: Cotton, F. A.; Walton, R. A. "Multiple Bonds Between Metal Atoms"; Wiley: New York, 1982; p 89.

(16) The most acute M–P–M angle previously reported was 65.23 (5)° in Co$_2$(μ-Ph$_2$P)$_2$(CO)$_2$(PEt$_2$Ph)$_2$; see: Harley, A. D.; Whittle, R. R.; Geoffroy, G. L. *Organometallics* **1983**, *2*, 60.

(17) Ginsburg, R. E.; Rothrock, R. K.; Finke, R. G.; Collman, J. P.; Dahl, L. F. *J. Am. Chem. Soc.* **1979**, *101*, 6550.

(18) See: Lappert, M. F.; Power, P. P.; Sanger, A. R.; Srivastava, R. C. "Metal and Metalloid Amides"; Ellis Harwood Ltd.: New York, **1980**, p 468.

(19) Downfield shifts in the δ 50–200 range in the ^{31}P NMR of Ph$_2$P groups bridging metal-metal bonds have been noted by several groups of workers. See, for example: Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229. Harley, A. D.; Guskey, G. J.; Geoffroy, G. L. *Organometallics* **1983**, *2*, 53 and references therein. See also ref 1 and references therein.

(20) **Note Added in Proof:** Other homoleptic dicyclohexyl phosphides of the early transition metals are now known, see: Baker, R. T.; Krusic, P. J.; Tulip, T. H.; Calabrese, J. C.; Wreford, S. S. *J. Am. Chem. Soc.*, submitted for publication.

(1) Goddard, J.D.; Osamura, Y.; Schaefer III, H. F. *J. Am. Chem. Soc.* **1982**, *104*, 3258.

(2) Langhoff, S. R.; Davidson, E. R. *Int. J. Quant. Chem.* **1974**, *8*, 61.

(3) Brown, H. C. "The Non-classical Ion Problem"; Plenum Press: New York, 1977.

(4) Yannoni, C. S.; Myhre, P. C.; Macho, V. *J. Am. Chem. Soc.* **1982**, *104*, 7380.