

and diazo carbons at 54 and 26 ppm (Me_4Si reference) are masked by the solvent peaks. The sample was removed from the spectrometer (again without melting) and immersed in a quartz Dewar containing liquid nitrogen, shown in Figure 1b. The rotor was suspended so that the quartz lid faced the radiation from a 150-W xenon high-pressure lamp (ILC Model VIX-150) fitted with a Pyrex filter. The sample was then photolyzed for 24 h at 77 K. The rotor was removed and again transferred without melting to the MAS apparatus.^{6,7} The ^{13}C spectrum of the photolyzed material was obtained at 80 K and is shown in Figure 2b. The same four solvent peaks are observed; however, the downfield peak has shifted further downfield by 8 ppm, while two new peaks appear on the upfield edge of the MTHF resonances. These three peaks, at 201, 12, and 4 ppm, are within 1 ppm of the carbonyl, terminal, and methyl carbon peaks reported in the ^{13}C solution spectrum of **2**.⁸ The spectra show that the precursor (**1**) has been quantitatively converted to the ketene (**2**).

Although the techniques described here appear to be promising as a general method for the study of photolytically generated species by NMR spectroscopy, refinements may lead to even wider applicability. For example, if the photoproduct absorbs the light, it may not be possible to build up a concentration of product that is sufficiently high for detection by NMR. Therefore, the use of a much more dilute solution of the precursor is desirable to reduce optical density. In turn, this would also decrease the strength of the ^{13}C signals, so that enrichment of the precursor in ^{13}C may be necessary. The spectra obtained in this study suggest that it should be possible to use 0.1 mol % solutions of enriched precursor, which would decrease such internal filtering effects considerably. Another problem could arise (and is seen in the spectra in Figure 2) if the strong solvent peaks interfere with the spectrum of the precursor or photoproduct.⁵ This challenge could be met by using deuterated solvents, which should reduce solvent peaks and concomitant spectral interference considerably. The reason for this is that the strength of the ^{13}C signals in a CP experiment is roughly proportional to the inverse third power of the distance between carbon and proton(s), so that deuterated solvent molecules would not gain carbon polarization nearly so efficiently as the protonated precursor or photoproduct.

These ideas have been tested using an 0.1 mol % solution of acetic acid enriched (90%) in the methyl-carbon position in perdeuteriodioxane (98.5 atom % in deuterium). At 100 K, it was possible to observe the methyl carbon in only 2 min with a 2:1 signal-to-noise ratio. No ^{13}C signal was observed for the dioxane, even after several hours. This result suggests that it should be possible to detect concentrations of 0.01 mol % without solvent interference, even at the rather low spectrometer frequency (15 MHz) used in these experiments. Clearly, operation at higher field strengths would permit detection of concentrations at least as low as 10^{-3} mol % (10^{-4} M).

The experimental procedures described in this note, which have resulted in the first detection by NMR of a molecule photochemically generated in the solid state, constitute a prototype experiment for matrix-isolation NMR spectroscopy in organic glasses. Both photochemical production and characterization by NMR were carried out at temperatures very close to 77 K. Thus, the methodology developed here should be applicable to the NMR characterization of species that may not be stable at higher temperatures.

Acknowledgment. We acknowledge the skillful technical assistance of R. D. Kendrick. Discussions with R. D. Miller, who

(5) The ^{13}C spectrum of **1** shows peak at 192, 54, and 26 ppm for the carbonyl, diazo, and methyl carbons, respectively. The peaks at 54 and 26 ppm are masked by the 2-MTHF solvent peaks in the spectrum shown in Figure 2a.

(6) The geometry of our CPMAS probe would permit in situ photolysis with the light shining on the walls of the rotor.⁷ Thus an additional requirement for in situ photolysis is that the rotor material be transparent to the light.

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suggested the diazo ketone photolysis, were very helpful. The support of the Deutsche-Forschungsgemeinschaft (Grant Ma 328/13-1) for H.P.R. is also gratefully acknowledged.

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Coordination and Scission of Alkynes on a Tungsten-Triosmium Framework

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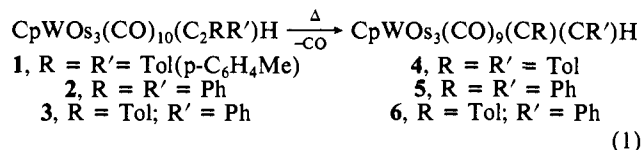
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Reports of $\text{C}\equiv\text{C}$ bond scission in alkynes to provide bi- or trinuclear dialkyldiyne complexes¹ have involved reactions of alkynes with mononuclear complexes, in which cases the nature of the metal unit coordinating the alkyne prior to scission is not clear. We now wish to report the first examples of well-characterized alkyne complexes that undergo clean, unimolecular transformations into dialkyldiyne compounds (eq 1, $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$). In addition, both types of compounds display unique structural features.



The alkyne complexes **1-3** have been prepared by treatment of $\text{CpWOS}_3(\text{CO})_{12}\text{H}^2$ first with Me_3NO and then with the alkyne.³ Spectroscopic data⁴ and an X-ray study of **1** (vide infra) provide characterization. The alkyldiyne clusters **4-6** are obtained in low yields (10-20%) by direct pyrolysis of the corresponding alkyne complexes either in solution (toluene, 110 °C) or in vacuo (hot tube, 250 °C). However, initial decarbonylation with $\text{Me}_3\text{NO}/\text{MeCN}$ followed by pyrolysis in boiling toluene results in **4-6** as major products (ca. 60%).⁵ Note that pyrolysis of the unsymmetrical

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(3) A dry CH_2Cl_2 solution of $\text{CpWOS}_3(\text{CO})_{12}\text{H}$ was treated with a MeCN solution of sublimed Me_3NO (ca. 1.05 equiv) under N_2 and then taken to dryness. The residue was dissolved in dry toluene, excess $\text{C}_2\text{H}_5\text{I}$ added, and the resulting solution refluxed under N_2 for 1 h. Purification (TLC, silica, $n\text{-C}_4\text{H}_9/\text{CH}_2\text{Cl}_2$, 3:2) gave orange **1** in 45% yield. Compounds **2** and **3** were prepared similarly.

(4) Compound **1**: IR (CCl_4) $\nu(\text{CO})$ 2080 (vw), 2064 (s), 2019 (vs), 2005 (w), 1988 (m), 1960 (w) cm^{-1} ; ^1H NMR (CDCl_3 , 25 °C) δ 6.78-6.89 (m, 8 H), 5.50 (s, 5 H), 2.25 (s, 6 H), -21.23 (s, 1 H); MS (field desorption, ^{192}Os , ^{184}W), m/z 1312 (M^+). Anal. Calcd for $\text{C}_{31}\text{H}_{20}\text{O}_{10}\text{WOS}_3$: C, 28.49; H, 1.54. Found: C, 28.46; H, 1.37. Compounds **2** and **3** had analogous spectroscopic properties and satisfactory elemental analyses.

(5) Compound **1** was treated with sublimed Me_3NO in $\text{CH}_2\text{Cl}_2/\text{MeCN}$, and then the residue was heated in refluxing toluene for 1 h. Dark red crystalline **4** was isolated in 63% yield. Compound **4**: IR (C_6H_{12}) $\nu(\text{CO})$ 2072 (s), 2036 (vs), 2031 (vs), 1999 (w), 1991 (m), 1980 (m) cm^{-1} ; ^1H NMR (CD_2Cl_2 , 25 °C) δ 7.03-7.11 (m, 8 H), 5.40 (s, 5 H), 3.75 (m, 1 H), $J_{\text{WH}} = 89$ Hz), 2.36 (s, 6 H); MS (70 eV, ^{192}Os , ^{184}W), m/z 1284 (M^+). Anal. Calcd for $\text{C}_{30}\text{H}_{20}\text{O}_9\text{WOS}_3$: C, 28.18; H, 1.58. Found: C, 28.10; H, 1.56. Compounds **5** and **6** were prepared and characterized analogously.

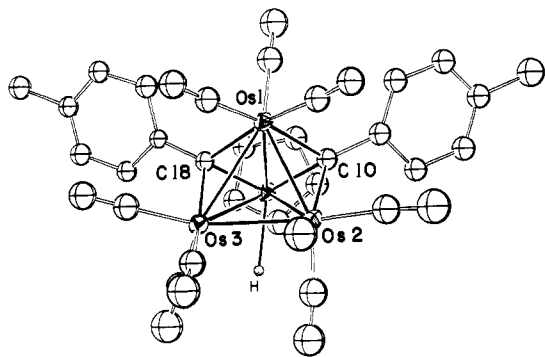


Figure 1. ORTEP diagram of the molecular structure of $\text{CpW}(\text{Os})_3(\text{CO})_9(\text{CTol})_2\text{H}$ (**4-B**). Distances within the molecule: metal-metal, $\text{W}-\text{Os}(1) = 2.831(1)$, $\text{W}-\text{Os}(2) = 2.910(1)$, $\text{W}-\text{Os}(3) = 2.891(1)$, $\text{Os}(1)-\text{Os}(2) = 2.791(1)$, $\text{Os}(1)-\text{Os}(3) = 2.857(1)$, $\text{Os}(2)-\text{Os}(3) = 2.827(1)$ Å; metal-(μ_3 -C), $\text{Os}(1)-\text{C}(10) = 2.254(21)$, $\text{Os}(2)-\text{C}(10) = 2.166(21)$, $\text{W}-\text{C}(10) = 1.977(22)$, $\text{Os}(1)-\text{C}(18) = 2.224(20)$, $\text{Os}(3)-\text{C}(18) = 2.136(19)$, $\text{W}-\text{C}(18) = 1.978(19)$ Å; $\text{W}-\text{H} = 1.92(18)$ Å.

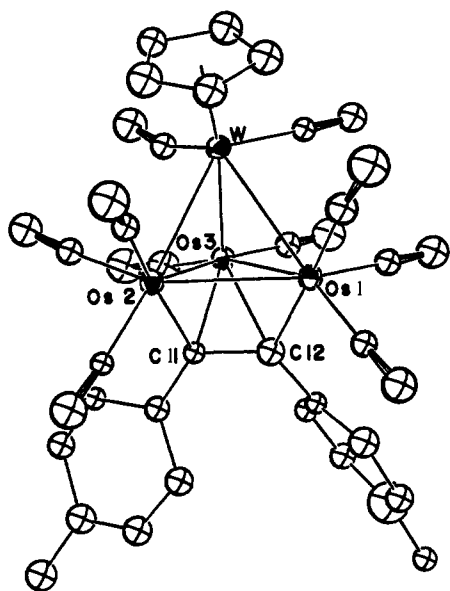


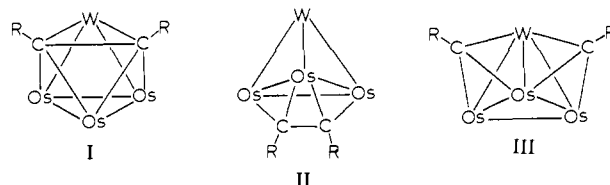
Figure 2. ORTEP diagram of the molecular structure of $\text{CpW}(\text{Os})_3(\text{CO})_{10}(\text{C}_2\text{Tol})_2\text{H}$ (**1-A**). Metal-metal distances: $\text{W}-\text{Os}(1) = 3.066(3)$, $\text{W}-\text{Os}(2) = 3.010(3)$, $\text{W}-\text{Os}(3) = 2.663(3)$, $\text{Os}(1)-\text{Os}(2) = 2.922(3)$, $\text{Os}(1)-\text{Os}(3) = 2.823(3)$, $\text{Os}(2)-\text{Os}(3) = 2.775(3)$ Å. The hydride ligand was not definitively located but is believed to bridge the lengthened $\text{Os}(1)-\text{Os}(2)$ edge.¹⁵ Metal-carbon (μ_3 - η^2 -alkyne) distances: $\text{Os}(2)-\text{C}(11) = 2.17(4)$, $\text{Os}(3)-\text{C}(11) = 2.13(4)$, $\text{Os}(1)-\text{C}(12) = 2.21(5)$, $\text{Os}(3)-\text{C}(12) = 2.18(5)$ Å.

alkyne complex **3** yields only the unsymmetrical dialkyldyne complex **6**; there is no evidence for the formation of the symmetrical compounds **4** and **5**.

Key features of compounds **4-6** are revealed by ^{13}C and ^1H NMR data.^{5,6} The acetylenic carbon resonance for **2** (prepared from $\text{Ph}^{13}\text{C}\equiv\text{CPh}$) occurs at δ 143.8, whereas for **5** the corresponding signal is shifted markedly downfield, characteristic of alkyldyne centers,¹⁶ at δ 268.1 ($J_{\text{WC}} = 106$ Hz). There is no evidence for coupling of this alkyldyne carbon with the hydride, which is assigned to the ^1H NMR signal at δ 3.75.⁷ This unusually low chemical shift (for a cluster hydride) together with the observed $^{183}\text{W}-^1\text{H}$ coupling (89 Hz) is consistent with the hydride ligand being bound only to the tungsten center; several

mononuclear tungsten(VI) hydride compounds display signals in this low-field region.⁸ Support for a terminal hydride is provided by the observation that **4** reacts with CCl_4 in the presence of $t\text{-BuOCl}$ to produce $\text{CpW}(\text{Os})_3(\text{CO})_9(\text{CTol})_2\text{Cl}$.⁹ An X-ray study¹⁰ of **4** (see Figure 1) confirms the presence of two μ_3 -CTol ligands and a terminal hydride ligand. Only in one other case¹³ has a terminal hydride in a cluster compound been established by X-ray diffraction data.

Typically, alkyne coordination to M_4 clusters results in metal-metal bond cleavage to give pseudooctahedral M_4C_2 structures¹⁴ (seven framework bonding pairs, see I). Solution ^{13}C NMR data¹⁵



for $\text{CpW}(\text{Os})_3(\text{CO})_{10}(\text{C}_2\text{Tol})_2\text{H}$, however, are inconsistent with such a configuration. A single-crystal X-ray diffraction study¹⁶ (see Figure 2 shows that compound **1** has an intact pseudotetrahedral metal framework with the μ_3 - η^2 -acetylenic moiety coordinated to the triangular Os_3 face. This structure (see II) may be viewed as a capped square pyramid (with the tungsten atom as the capping center), which is an alternative geometry for six atoms and seven bonding pairs that has been observed previously only for $\text{H}_2\text{Os}_6(\text{CO})_{18}$.^{17a} In contrast isoelectronic $\text{Os}_6(\text{CO})_{18}^{2-}$ is octahedral.^{17b} However, both compounds **4** and $\text{Os}_6(\text{CO})_{18}$,^{17c} each with just six bonding pairs, adopt the unique bicapped tetrahedral geometry (see III). Thus, these metallobicyclopentadiene $\text{W}(\text{Os})_3\text{C}_2$ clusters display structures previously seen only for the homometallic Os_6 clusters.

The exact pathway for converting compounds **1-3** into **4-6** is not established. One reasonable possibility is a sequence such as

(8) For instance, the hydride signal for $\text{W}(\text{CH})\text{H}(\text{PMe}_3)_3\text{Cl}_2$ occurs at δ 4.53 but that for $\text{W}(\text{CCMe}_3)\text{H}(\text{dmpe})_2$ at δ -6.27: Holmes, S. J.; Clark, D. N.; Turner, H. W.; Schrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 6322.

(9) $\text{CpW}(\text{Os})_3(\text{CO})_9(\text{CTol})_2\text{Cl}$: IR (C_6H_{12}) $\nu(\text{CO})$ 2080 (s), 2046 (vs), 2041 (vs), 1999 (m), 1980 (w) cm^{-1} ; ^1H NMR (CD_2Cl_2 , 25 °C) δ 7.15-7.33 (m, 8 H), 5.56 (s, 5 H), 2.47 (s, 6 H); MS (field desorption, ^{182}Os , ^{184}W , ^{35}Cl), m/z 1318 (M^+). Anal. Calcd for $\text{C}_{30}\text{H}_{19}\text{O}_9\text{ClW}(\text{Os})_3$: C, 27.44; H, 1.46. Found: C, 27.54; H, 1.40.

(10) Crystal data for **4**, $\text{C}_{30}\text{H}_{20}\text{O}_9\text{W}(\text{Os})_3$: $M_r = 1278.9$; monoclinic; space group $\text{P}2_1/n$ [C_{2h}^5 , No. 14]; $a = 19.067(3)$, $b = 16.828(3)$, $c = 19.947(3)$ Å; $\beta = 98.62(1)^\circ$; $V = 6327(2)$ Å³; $D_c = 2.68$ g cm^{-3} ; $Z = 8$; $\mu(\text{Mo K}\alpha) = 166.1$ cm^{-1} . Diffraction data were collected¹¹ using a Syntex P2₁ diffractometer. The structure was solved by MULTAN.¹² The final discrepancy indices were $R_F = 5.4\%$, $R_{wF} = 5.1\%$, and GOF = 1.376 for 388 parameters refined against 6169 reflections that had $I > 1.50\sigma(I)$. There are two equivalent molecules (**4-A** and **4-B**), which have similar stereochemistry except for the conformation of the carbonyl ligands on the $\text{Os}(3)$ center. A terminal hydride ligand was located from a difference-Fourier synthesis (**4-B** only).

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(15) At 25 °C the signals observed (90 MHz, toluene- d_6) are δ 214.6 (s, 2 C, $J_{\text{WC}} = 175$ Hz), 184.5 (s, 2 C), 181.4 (s, 2 C), 177.8 (s, 2 C), and 166.5 (d, 2 C, $J_{\text{CH}} = 10.5$ Hz). The last signal is assigned to the two carbonyls located essentially trans to the hydride bridging $\text{Os}(1)-\text{Os}(2)$ (figure 2).

(16) Crystal data for **1**, $\text{C}_{31}\text{H}_{20}\text{O}_{10}\text{W}(\text{Os})_3$: $M_r = 1309.0$; monoclinic; space group $\text{P}2_1/n$ [C_{2h}^5 , No. 14]; $a = 23.600(5)$, $b = 9.343(2)$, $c = 28.774(4)$ Å; $\beta = 97.39(2)^\circ$; $V = 6292(2)$ Å³; $D_c = 2.76$ g cm^{-3} ; $Z = 8$; $\mu(\text{Mo K}\alpha) = 167.1$ cm^{-1} . Diffraction data were collected and treated as described for **4**. Final discrepancy indices were $R_F = 8.6\%$, $R_{wF} = 7.6\%$, and GOF = 1.18 for 409 parameters refined against all 5816 reflections with $2\theta = 4.5-40.0^\circ$. There are two equivalent molecules (**1-A** and **1-B**) in the crystallographic asymmetric unit.

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(6) The ^{13}C NMR spectrum (-95 °C, 90 MHz, CD_2Cl_2) of **4** (from ca. 50% ^{13}C -enriched $\text{Os}_3(\text{CO})_{12}$) shows a 2:2:1:2:2 pattern at δ 185.5, 179.6, 175.7, 172.6, and 172.3. Specific assignments will be presented in a full paper.

(7) This signal is absent in the ^1H NMR spectrum of $\text{CpW}(\text{Os})_3(\text{CO})_9(\text{CTol})_2\text{D}$, generated from $\text{CpW}(\text{Os})_3(\text{CO})_{10}(\text{CTol})_2\text{D}$: Park, J. T.; Shapley, J. R.; Churchill, M. R.; Bueno, C. *Inorg. Chem.* **1983**, *22*, 1579.

II \rightarrow I \rightarrow III, although the more direct path II \rightarrow III cannot be ruled out. The presence of the tungsten center seems significant; pyrolysis of $\text{Os}_3(\text{CO})(\text{C}_2\text{Ph}_2)$ results simply in CO loss to form the unsaturated species $\text{Os}_3(\text{CO}_9)(\text{C}_2\text{Ph}_2)$ without cleaving the alkyne.¹⁸ Fehlner and co-workers¹⁹ 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 alkyldiene groups. Our results are consistent with this idea in that the alkyldiene ligands in 4-6 end up coordinated to a relatively oxidized tungsten center.

Acknowledgment. This research was supported by the National Science Foundation through Grants CHE81-00140 (J.R.S., University of Illinois) and CHE80-23448 (M.R.C., SUNY—Buffalo). Instruments at the University of Illinois supported by the Grants NSF-CHE79-16100 and NIH-GM27029 were utilized for NMR and mass spectra, respectively.

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.

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Synthesis and X-ray Crystal Structure of

$\text{Mo}_2(\mu-t\text{-Bu}_2\text{P})_2(t\text{-Bu}_2\text{P})_2(\text{Mo}^4\text{Mo})$: The First Structurally Characterized Binary Transition-Metal Phosphide

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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 $\text{Mo}_2(\mu-t\text{-Bu}_2\text{P})_2(t\text{-Bu}_2\text{P})_2$ (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

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(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.

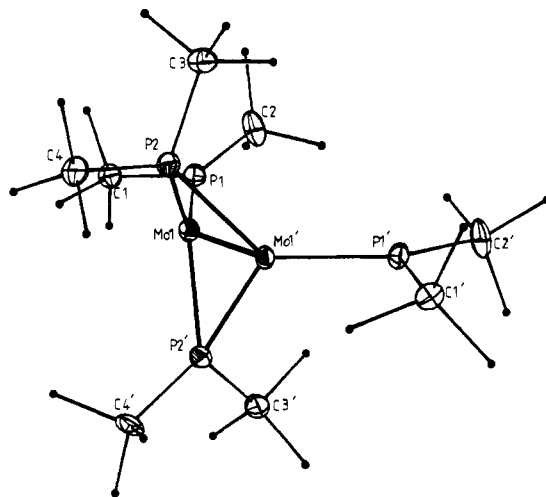


Figure 1. General view of 1. For clarity the methyl groups of the *t*-Bu units are represented as sticks. Key bond lengths and angles are in ref 13 and the text.

Ti,⁶ V,⁶ Cr,⁶ Mn,⁷ Fe,⁸ Ni,^{9,10} and Pd¹⁰ although these compounds are very poorly characterized.

The interaction of 4 equiv of Li-*t*-Bu₂P with dimolydenum tetracetate in diethyl ether at -78 °C yields a bright red solution from which $\text{Mo}_2(\mu-t\text{-Bu}_2\text{P})_2(t\text{-Bu}_2\text{P})_2$ (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*-Bu₂P groups giving the central Mo₂P₂ 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 $\mu-t\text{-Bu}_2\text{P}$ 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 $\mu-t\text{-Bu}_2\text{P}$ 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 $[\text{Mo}(\text{P}(\text{OMe})_3)_5\text{P}(\text{OMe})_2]^+$ (2.29 (4) Å).¹⁴

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(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*₆ 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: $\text{Mo}_2\text{P}_4\text{C}_{32}\text{H}_{72}$, orthorhombic, space group *Pnna* (No. 52), $a = 13.715$ (3) Å, $b = 17.055$ (3) Å, $c = 17.937$ (2) Å, $U = 4196.72$ (19) Å³, $D_c = 1.876$ g cm⁻³, $Z = 4$, $\lambda(\text{Mo K}\alpha) = 0.71069$ Å (graphite monochromator), $\mu(\text{Mo K}\alpha) = 11.5$ cm⁻¹. Methods: Patterson, difference Fourier, full matrix least squares. Refinement of 2232 observed, 4121 measured ($2^\circ < 2\theta < 50^\circ$) 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.; Tavaniapour, I.; Day, V. W. *Proc. Natl. Acad. Sci. U.S.A.* 1978, 75, 1056.