6538 *Inorg. Chem.* **1995**, *34*, 6538–6545

Synthesis and X-ray Crystal Structures of $\{Mo(CO)(Et_2PC_2H_4PEt_2)_2\}_2(\mu\text{-}N_2)$ with an End-On Bridging Dinitrogen Ligand and $Mo(CO)(Bu^i{}_2PC_2H_4PBu^i{}_2)_2$ Containing an Agostic Mo···H−C Interaction

Xiao-Liang Luo,* Gregory J. Kubas,* Carol J. Burns, Ray J. Butcher, and Jeffrey C. Bryan

Chemical Science and Technology Division, Mail Stop C346, Los Alamos National Laboratory,
Los Alamos, New Mexico 87545

Received May 19, 1995[®]

The compound formed by the reaction of *trans*-$Mo(N_2)_2(Et_2PC_2H_4PEt_2)_2$ with ethyl acetate in refluxing toluene under argon has been reformulated as the bridging dinitrogen complex $\{Mo(CO)(Et_2PC_2H_4PEt_2)_2\}_2(\mu\text{-}N_2)$ (**1**), in contrast with the previously proposed formulation of $Mo(CO)(Et_2PC_2H_4PEt_2)_2$ (**2**). In refluxing *p*-xylene and under argon, compound **1** eliminates the bridging dinitrogen ligand to form the nitrogen-free compound **2**. The reaction of *trans*-$Mo(N_2)_2(Bu^i{}_2PC_2H_4PBu^i{}_2)_2$ with ethyl acetate in refluxing toluene under argon gives directly the nitrogen-free compound $Mo(CO)(Bu^i{}_2PC_2H_4PBu^i{}_2)_2$ (**3**). The molecular structures of compounds **1** and **3** have been determined by single-crystal X-ray diffraction studies. Compound **1** contains an end-on bridging dinitrogen ligand. Compound **3** attains a formal 18-electron configuration by virtue of an agostic Mo···H−C interaction between the molybdenum atom and an aliphatic γ-C−H bond of the alkyldiphosphine ligand. On the basis of the agostic Mo···C and Mo···H distances, the agostic interaction in **3** appears to be stronger than that in the related compound $Mo(CO)(Ph_2PC_2H_4PPh_2)_2$ which involves an ortho aromatic C−H bond of the diphosphine ligand. Crystallographic data for **1**: monoclinic, space group $C2/c$, $a = 24.270(2)$ Å, $b = 44.233(4)$ Å, $c = 20.378(2)$ Å, $\beta = 90.725(9)°$, $V = 21875(3)$ Å^3, $Z = 16$, and $R = 0.048$. Crystallographic data for **3**: orthorhombic, space group $Pna2_1$, $a = 18.332(4)$ Å, $b = 22.066(4)$ Å, $c = 10.589(2)$ Å, $V = 4283(2)$ Å^3, $Z = 4$, and $R = 0.034$.

Introduction

We have previously reported the one-step synthesis of a series of formally coordinatively unsaturated molybdenum monocarbonyl complexes of the type $Mo(CO)(R_2PC_2H_4PR_2)_2$ (R = Ph, Et, Bu^i, CH_2Ph, $CH_2C_6H_4$-*m*-Me) by the reactions of bis(dinitrogen)molybdenum complexes *trans*-$Mo(N_2)_2(R_2PC_2H_4PR_2)_2$ with an ester such as ethyl acetate in refluxing benzene or toluene under argon.[1,2] The first compound, $Mo(CO)(Ph_2PC_2H_4PPh_2)_2$, of the series was originally prepared by Hidai and co-workers, who reacted *trans*-$Mo(N_2)_2(Ph_2PC_2H_4PPh_2)_2$ with *N,N*-dimethylformamide (DMF) to give *trans*-Mo(DMF)(CO)$(Ph_2PC_2H_4PPh_2)_2$, which was converted into *trans*-$Mo(N_2)(CO)(Ph_2PC_2H_4PPh_2)_2$ under dinitrogen and then into $Mo(CO)(Ph_2PC_2H_4PPh_2)_2$ under argon.[3] A single-crystal X-ray diffraction study of $Mo(CO)(Ph_2PC_2H_4PPh_2)_2$ revealed that the compound adopts a distorted octahedral structure, in which an ortho C−H bond of a phenyl ring on the diphosphine ligand takes up the otherwise vacant coordination site trans to the CO ligand, forming a weak agostic Mo···H−C interaction.[3] The variable-temperature ^1H NMR spectra of $Mo(CO)(R_2PC_2H_4PR_2)_2$ (R = CH_2Ph, $CH_2C_6H_4$-*m*-Me) indicate the presence of a similar agostic Mo···H−C interaction.[2]

Apparently, the weak agostic Mo···H−C interaction in $Mo(CO)(R_2PC_2H_4PR_2)_2$ can be readily displaced by donor molecules that are sufficiently slender to enter the sterically congested coordination sphere. Therefore, these apparently 16-electron complexes can form adducts with a wide variety of small molecules.[1-5] In particular, the reaction with H_2 [1-2] or a hydrosilane R_3SiH [5] gives either a nonclassical σ complex[6] $Mo(\eta^2\text{-}HX)(CO)(R_2PC_2H_4PR_2)_2$ (X = H, SiR_3) or a classical oxidative addition product $MoHX(CO)(R_2PC_2H_4PR_2)_2$ (X = H, SiR_3), with the outcome of the reaction being determined primarily by the basicity of the diphosphine ligand. Thus, the electronic control of σ bond coordination versus cleavage has been achieved in this molybdenum system. Furthermore, this represents the first system in which various types of σ bonds, *i.e.* C−H, H−H, and Si−H bonds, can be coordinated to the same metal fragment in a nonclassical η^2-fashion.[1,2,5]

Since the compounds $Mo(CO)(R_2PC_2H_4PR_2)_2$ display a rich and diverse reaction chemistry, including the coordination and activation of various types of σ bonds, full characterization of these complexes is warranted. In our previous work,[1] the compounds $Mo(CO)(R_2PC_2H_4PR_2)_2$ (R = Et, Bu^i) were not well-characterized because of the difficulty involved in purification. Aside from IR data, neither NMR spectroscopic data nor elemental analysis data were obtained for these compounds.[1] Thus, the exact nature of these compounds is unknown. Although it is established that the compounds $Mo(CO)(R_2PC_2H_4PR_2)_2$ (R = CH_2Ph,[2] $CH_2C_6H_4$-*m*-Me,[2] Ph[3]) contain an agostic Mo···H−C interaction between the molybdenum atom and an ortho aromatic C−H bond of the diphosphine ligand, there is the question of whether an aliphatic C−H bond of the alkyldiphosphine ligand in the compounds $Mo(CO)(R_2PC_2H_4PR_2)_2$ (R = Et, Bu^i) can also form a similar agostic Mo···H−C

[®] Abstract published in *Advance ACS Abstracts*, November 1, 1995.

(1) (a) Kubas, G. J.; Burns, C. J.; Eckert, J.; Johnson, S. W.; Larson, A. C.; Vergamini, P. J.; Unkefer, C. J.; Khalsa, G. R. K.; Jackson, S. A.; Eisenstein, O. *J. Am. Chem. Soc.* **1993**, *115*, 569. (b) Kubas, G. J.; Ryan, R. R.; Unkefer, C. J. *J. Am. Chem. Soc.* **1987**, *109*, 8113.

(2) Luo, X.-L.; Kubas, G. J.; Burns, C. J.; Eckert, J. *Inorg. Chem.* **1994**, *33*, 5219.

(3) Sato, M.; Tatsumi, T.; Kodama, T.; Hidai, M.; Uchida, T.; Uchida, Y. *J. Am. Chem. Soc.* **1978**, *100*, 4447.

(4) (a) Tatsumi, T.; Tominaga, H.; Hidai, M.; Uchida, Y. *J. Organomet. Chem.* **1980**, *199*, 63.

(5) (a) Luo, X.-L.; Kubas, G. J.; Bryan, J. C.; Burns, C. J.; Unkefer, C. J. *J. Am. Chem. Soc.* **1994**, *116*, 10312. (b) Luo, X.-L.; Kubas, G. J.; Burns, C. J.; Bryan, J. C.; Unkefer, C. J. *J. Am. Chem. Soc.* **1995**, *117*, 1159.

(6) (a) Kubas, G. J. *Acc. Chem. Res.* **1988**, *21*, 120. (b) Schubert, H. *Adv. Organomet. Chem.* **1990**, *30*, 151. (c) Crabtree, R. H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 789.

0020-1669/95/1334-6538$09.00/0

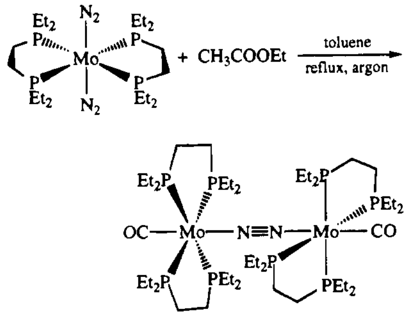
interaction. Even though examples of agostic M···H—C interactions between an aliphatic C—H bond of an alkylphosphine ligand and a metal atom are rather rare,[7,8] they were presumed to be present in $Mo(CO)(R_2PC_2H_4PR_2)_2$ (R = Et, Bu^i).[1]

In this paper, we report in detail the synthesis and characterization of the unusual bridging dinitrogen complex $\{Mo(CO)(Et_2PC_2H_4PEt_2)_2\}_2(\mu\text{-}N_2)$ (**1**) and the two agostic complexes $Mo(CO)(R_2PC_2H_4PR_2)_2$ (R = Et (**2**), Bu^i (**3**)). Contrary to the previous report,[1] the compound formed by the reaction of *trans*-$Mo(N_2)_2(Et_2PC_2H_4PEt_2)_2$ with ethyl acetate in refluxing toluene under argon has now been reformulated as compound **1** instead of compound **2**. Compound **1** eliminates the bridging dinitrogen ligand only at an elevated temperature to form the nitrogen-free compound **2**. The molecular structures of compounds **1** and **3** have been determined by single-crystal X-ray crystallography. Compound **1** has been shown to contain an end-on bridging dinitrogen ligand. To our knowledge, only one bridging dinitrogen complex of Mo(0), *i.e.* $\{Mo(\eta^6\text{-}C_6H_3Me_3)(Me_2PC_2H_4PMe_2)\}_2(\mu\text{-}N_2)$,[9] has been previously characterized by X-ray crystallography. The X-ray crystal structure of compound **3** reveals an agostic Mo···H—C interaction between the molybdenum atom and an aliphatic C—H bond of the alkyldiphosphine ligand.

Results and Discussion

Synthesis and and Spectroscopic Characterization of the Bridging Dinitrogen Complex $\{Mo(CO)(Et_2PC_2H_4PEt_2)_2\}_2(\mu\text{-}N_2)$ (1). It was previously reported[1] that the reaction of *trans*-$Mo(N_2)_2(Et_2PC_2H_4PEt_2)_2$ with ethyl acetate in refluxing toluene under argon gave a purple solution which turned red upon cooling. From the red solution, a new compound was isolated as a red solid which was tentatively formulated as $Mo(CO)(Et_2PC_2H_4PEt_2)_2$ since it reacted with H_2 and N_2 to form the dihydride complex $MoH_2(CO)(Et_2PC_2H_4PEt_2)_2$ and the dinitrogen complex *trans*-$Mo(N_2)(CO)(Et_2PC_2H_4PEt_2)_2$, respectively.[1] Peculiarly, the color of the new compound differs from those of the analogous compounds $Mo(CO)(R_2PC_2H_4PR_2)_2$ (R = CH_2Ph,[2] $CH_2C_6H_4$-*m*-Me,[2] Ph[3]) which are much more intensely colored, black or deep purple in the solid state and dark green or deep red in solution.

We have now found that the product formed by the reaction of *trans*-$Mo(N_2)_2(Et_2PC_2H_4PEt_2)_2$ with ethyl acetate under the conditions described above is, in fact, the bridging dinitrogen complex $\{Mo(CO)(Et_2PC_2H_4PEt_2)_2\}_2(\mu\text{-}N_2)$ (**1**) (eq 1), which is contrary to the previously proposed formulation of $Mo(CO)(Et_2PC_2H_4PEt_2)_2$ (**2**).[1]



1

(1)

Table 1. Crystallographic Data for $\{Mo(CO)(Et_2PC_2H_4PEt_2)_2\}_2(\mu\text{-}N_2)$ (**1**)

empirical formula	$C_{42}H_{96}Mo_2N_2O_2P_8$	*V*, Å^3	21875(3)
fw	1100.85	Z	16
crystal system	monoclinic	ρ(calcd), g cm^{-3}	1.337
space group	C2/c	μ(MoK_α), cm^{-1}	7.26
a, Å	24.270(2)	min/max transm coeff	0.76−0.93
b, Å	44.233(4)	T, K	173
c, Å	20.378(2)	R[a]	0.048
β, deg	90.725(9)	R_w[b]	0.112

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

As reported previously,[1] compound **1** is highly soluble even in alkane solvents. The previous yield of **1** by precipitation with cold nonane was low, and a pure product was difficult to obtain.[1] However, we have now found that the compound is only sparingly soluble in cold hexamethyldisiloxane ($Me_3SiOSiMe_3$). Thus, compound **1** can be isolated as a red solid in a significantly improved yield of 79% by precipitation of the product from cold hexamethyldisiloxane. In addition, the purity of the product is much higher, allowing meaningful NMR and elemental analysis. The presence of the bridging dinitrogen ligand has been confirmed by elemental analysis data (see the Experimental Section) and a single-crystal X-ray diffraction study (*vide infra*).

The ^1H NMR spectrum of **1** in $C_6D_5CD_3$ at 298 K displays several broad multiplet resonances in the region of δ 1.01−1.94 due to the diphosphine ligand. When the sample is cooled to 193 K, the resonances broaden into featureless lumps. The $^{31}P\{^1H\}$ NMR spectrum at 298 K shows a slightly broad resonance at δ 58.4, which collapses into two resonances of equal intensity at 193 K. The dynamic $^{31}P\{^1H\}$ NMR behavior can be accounted for by a staggered rotomeric relationship between the two MoP_4 fragments, as shown in eq 1, which results in two inequivalent sets of phosphorus nuclei. This staggered configuration has been confirmed by an X-ray crystallographic analysis of **1** (*vide infra*).

The IR spectrum of **1** in a Nujol mull shows a strong ν(CO) band at 1747 cm^{-1}. No band is observed which can be assigned to the ν(NN) stretching mode, because such a vibration mode in a symmetrically bridging dinitrogen complex is not IR active due to the lack of any dipole moment change associated with the vibration mode.

X-ray Crystal Structure of $\{Mo(CO)(Et_2PC_2H_4PEt_2)_2\}_2(\mu\text{-}N_2)$ (1). The formulation of **1** as a bridging dinitrogen complex has been confirmed by a single-crystal X-ray diffraction study. A summary of the crystallographic data of **1** is given in Table 1. The asymmetric unit consists of one complete and two half-molecules of **1** (see supplementary material). Each of the two half-molecules has two crystallographically imposed 2-fold axes perpendicularly bisecting the N−N triple bond of the bridging dinitrogen ligand, whereas the complete molecule has no crystallographically imposed symmetry. In all the molecules, some of the methyl groups on the diphosphine ligands are disordered over two positions. In addition to this disorder, there is a more extensive disorder in the complete molecule, where the two diphosphine ligands at one molybdenum center are disordered in a ratio of 69:31 over two orientations which are rotated by 90° about the Mo−N−N−Mo axis. Nevertheless, all the molecules in the asymmetric unit have very similar coordination geometries and bond lengths, so we have chosen the complete molecule for a more detailed discussion.

---

(7) (a) Wasserman, H. J.; Kubas, G. J.; Ryan, R. R. *J. Am. Chem. Soc.* **1986**, *108*, 2294. (b) Zhang, K.; Gonzalez, A. A.; Mukerjee, S. L.; Chou, S.-J.; Hoff, C. D.; Kubat-Martin, K. A.; Barnhart, D.; Kubas, G. J. *J. Am. Chem. Soc.* **1991**, *113*, 9170.

(8) Heinekey, D. M.; Schomber, B. M.; Radzewich, C. E. *J. Am. Chem. Soc.* **1994**, *116*, 4515.

(9) Forder, R. A.; Prout, K. *Acta Crystallogr.* **1974**, *B30*, 2778.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $\{Mo(CO)(Et_2PC_2H_4PEt_2)_2\}_2(\mu\text{-}N_2)$ (**1**)

	Bond Lengths		
Mo(3)−P(31a)	2.406(2)	Mo(3)−P(32)	2.426(1)
Mo(3)−P(33)	2.431(2)	Mo(3)−P(34)	2.435(2)
C(31)−O(31)	1.180(6)	C(41)−O(41)	1.179(7)
Mo(3)−N(31)	2.183(4)	Mo(4)−N(41)	2.160(4)
Mo(3)−C(31)	1.924(5)	Mo(4)−C(41)	1.926(6)
Mo(4)−P(41)	2.430(2)	Mo(4)−P(42)	2.426(1)
Mo(4)−P(43)	2.432(1)	Mo(4)−P(44)	2.435(2)
N(31)−N(41)	1.127(5)		
	Bond Angles		
P(31a)−Mo(3)−P(32)	81.4(1)	P(31a)−Mo(3)−P(33)	98.21(1)
P(31a)−Mo(3)−P(34)	168.7(1)	P(32)−Mo(3)−P(33)	173.7(1)
P(32)−Mo(3)−P(34)	92.2(6)	P(33)−Mo(3)−P(34)	87.1(1)
C(31)−Mo(3)−P(31a)	83.9(2)	C(31)−Mo(3)−P(32)	85.7(2)
C(31)−Mo(3)−P(33)	88.0(2)	C(31)−Mo(3)−P(34)	86.3(2)
N(31)−Mo(3)−P(31a)	95.2(1)	N(31)−Mo(3)−P(32)	92.2(1)
N(31)−Mo(3)−P(33)	94.1(1)	N(31)−Mo(3)−P(34)	94.4(1)
C(31)−Mo(3)−N(31)	177.8(2)	C(41)−Mo(4)−N(41)	177.7(2)
Mo(3)−C(31)−O(31)	179.2(5)	Mo(4)−C(41)−O(41)	179.1(6)
Mo(3)−N(31)−N(41)	179.1(4)	Mo(4)−N(41)−N(31)	179.1(4)
P(41)−Mo(4)−P(42)	81.7(1)	P(41)−Mo(4)−P(43)	98.7(1)
P(41)−Mo(4)−P(44)	175.2(1)	P(42)−Mo(4)−P(43)	175.5(1)
P(42)−Mo(4)−P(44)	98.3(1)	P(43)−Mo(4)−P(44)	81.0(1)
C(41)−Mo(4)−P(41)	86.6(2)	C(41)−Mo(4)−P(42)	86.9(2)
C(41)−Mo(4)−P(43)	88.6(2)	C(41)−Mo(4)−P(44)	88.6(2)
N(41)−Mo(4)−P(41)	92.1(1)	N(41)−Mo(4)−P(42)	91.1(1)
N(41)−Mo(4)−P(43)	93.4(1)	N(41)−Mo(4)−P(44)	92.7(1)

The selected bond lengths and angles for the complete molecule are given in Table 2. Figure 1 shows an ORTEP drawing of the complete molecule of **1**, with the minor component of the disorder omitted for clarity. In addition, an ORTEP drawing which shows the disorder in this molecule is given in Figure 2, where the view is obtained by looking down the Mo−N−N−Mo axis with the disordered end on top, and the minor component is outlined by open bonds as opposed to filled bonds.

The structure analysis confirms the dimeric nature of the molecule of **1** which contains an essentially linear Mo−N−N−Mo linkage with an end-on bridging dinitrogen ligand connecting the two molybdenum atoms. Both of the two Mo−N−N angles are 179.1(4)°. The coordination geometry about each molybdenum atom is best described as a slightly distorted octahedron, with the two diphosphine ligands lying on the equatorial plane, and the CO and the bridging dinitrogen ligands occupying the two trans apical positions. The two C−Mo−N linkages are nearly linear with C(31)−Mo(3)−N(31) and C(41)−Mo(4)−N(41) angles of 177.8(2) and 177.7(2)°, respectively.

The coordination octahedra of the pair of molybdenum atoms are rotated about the Mo−N−N−Mo axis with respect to each other so that the two MoP_4 fragments are in a staggered rather than an eclipsed rotameric relationship. This is most evident in the large P−Mo−Mo−P torsional angles which are listed in Table 3. This staggered conformation, which leads to an idealized point symmetry of D_{2d} for the molecule, is very likely a result of minimization of the steric repulsions between the ethyl groups of the diphosphine ligands. The staggered conformation found in the solid state is preserved in solution, as indicated by the observation of two resonances in the $^{31}P\{^1H\}$ NMR spectrum at low temperature (*vide supra*).

There is a small but systematic distortion of the diphosphine ligands in compound **1** away from the bridging dinitrogen ligand toward the two terminal CO ligands. Thus, all the N−Mo−P angles are slightly obtuse, ranging from 91.1(1) to 95.2° and averaging 93.2(1)°, whereas all the C−Mo−P angles are slightly acute, ranging from 83.9(2) to 88.6(2)° and averaging 86.8(2)°. The distortion from an idealized octahedral coordination geometry can be attributed to the steric repulsions between the diphosphine ligands on the two molybdenum centers. This is supported by the fact that analogous bridging dinitrogen complexes $\{Mo(CO)(R_2PC_2H_4PR_2)_2\}_2(\mu\text{-}N_2)$ (R = Bu^i, Ph, $CH_2C_6H_5$, $CH_2C_6H_4$-*m*-Me), which contain bulkier diphosphine ligands, cannot be synthesized probably as a result of the excessive steric repulsions between the diphosphine ligands.

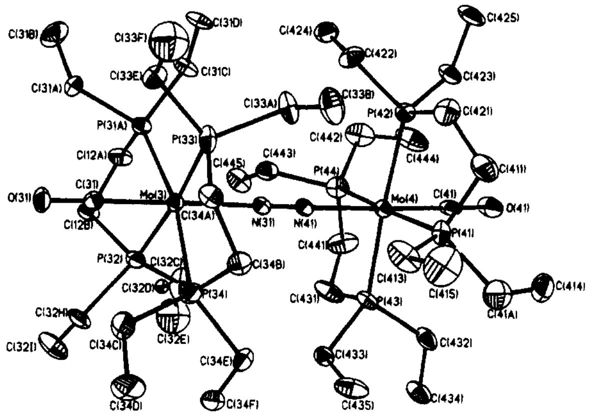


Figure 1. ORTEP drawing for the complete molecule in the crystal structure of $\{Mo(CO)(Et_2PC_2H_4PEt_2)_2\}_2(\mu\text{-}N_2)$ (**1**), with the minor component of the disorder omitted for clarity.

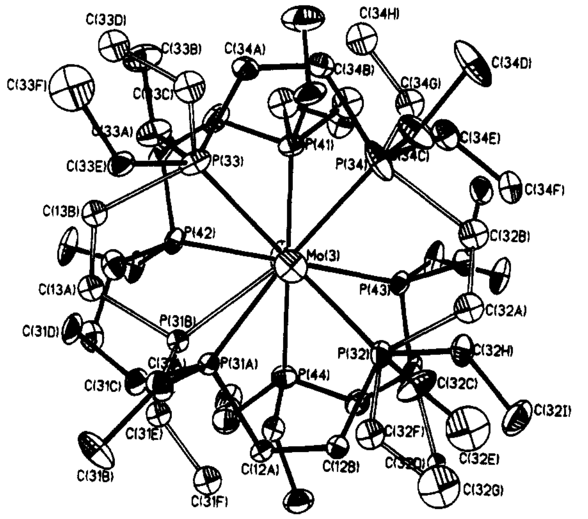


Figure 2. ORTEP drawing for the complete molecule in the crystal structure of $\{Mo(CO)(Et_2PC_2H_4PEt_2)_2\}_2(\mu\text{-}N_2)$ (**1**), showing the disorder in this molecule. The view is obtained by looking down the Mo−N−N−Mo axis with the disordered end on top. The minor component of the disorder is outlined by open bonds as opposed to filled bonds.

The N−N bond length of 1.127(5) Å in **1**, which is only slightly expanded from that of 1.0976 Å in free N_2,[10] lies at the lower end of the range of 1.12−1.36 Å [11] found for other end-on bridging dinitrogen complexes. In fact, the N−N distance in **1** is very close to that of 1.118(8) Å in the mononuclear Mo(0) dinitrogen complex *trans*-$Mo(N_2)_2(Ph_2PC_2H_4PPh_2)_2$.[12] The compound $\{Mo(\eta^6\text{-}C_6H_3Me_3)(Me_2PC_2H_4PMe_2)\}(\mu\text{-}N_2)$,[9] which is the only other crystallographically characterized bridging dinitrogen complex of Mo(0), shows a similarly short N−N bond length of 1.145(7) Å. Due to the high trans

---

(10) Wilkinson, P. G.; Houk, N. B. *J. Chem. Phys.* **1956**, *24*, 528.

(11) (a) Chatt, J.; Dilworth, J. R.; Richards, R. L. *Chem. Rev.* **1978**, *78*, 589. (b) Fryzuk, M. D.; Haddad, T. S.; Mylvaganam, M.; McConville, D. H.; Rettig, S. J. *J. Am. Chem. Soc.* **1993**, *115*, 2782.

(12) Uchida, T.; Uchida, Y.; Hidai, M.; Kodama, T. *Acta Crystallogr.* **1975**, *B31*, 1197.

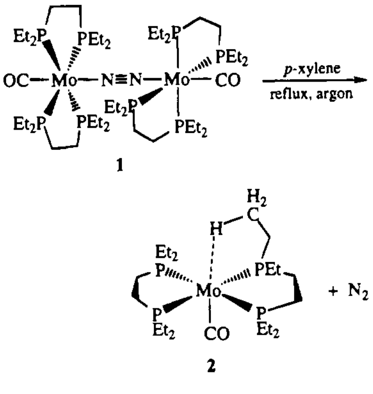
Table 3. Torsional Angles (deg) Showing Staggered Rotomeric Relationship between Two MoP$_4$ Fragments of {Mo(CO)(Et$_2$PC$_2$H$_4$PEt$_2$)$_2$}$_2$(μ-N$_2$) (**1**)

P(31a)−Mo(3)−Mo(4)−P(42)	63.1(1)	P(31a)−Mo(3)−Mo(4)−P(44)	−35.2(1)
P(32)−Mo(3)−Mo(4)−P(43)	−34.8(1)	P(32)−Mo(3)−Mo(4)−P(44)	46.3(1)
P(33)−Mo(3)−Mo(4)−P(41)	46.2(1)	P(33)−Mo(3)−Mo(4)−P(42)	−35.5(1)
P(34)−Mo(3)−Mo(4)−P(41)	−41.2(1)	P(34)−Mo(3)−Mo(4)−P(43)	57.6(1)

influence of the two CO ligands in **1**, the averaged Mo−N bond length of 2.172(4) Å is appreciably longer than that of 2.042(4) Å found in {Mo(η^6-C$_6$H$_3$Me$_3$)(Me$_2$PC$_2$H$_4$PMe$_2$)}(μ-N$_2$).[9]

The long Mo−N bond and short N−N bond in **1** clearly indicate that the bridging dinitrogen ligand is little reduced by coordination to the two molybdenum atoms and that the overall bonding situation within the Mo(μ-N$_2$)Mo unit is best represented by Mo−N≡N−Mo (with two Mo−N single bonds and a N≡N triple bond). It is of interest to note that the high oxidation state bridging dinitrogen complex {(η^5-C$_5$Me$_5$)MoMe$_3$}(μ-N$_2$), reported by Schrock and co-workers,[13] shows a relatively short averaged Mo−N distance of 1.890(2) Å (ca. 0.28 Å shorter than that in **1**), which is close to the Mo=N double bond distances observed in the molybdenum η^1-hydrazido(2−) complexes (Mo=N−NR$_2$).[14] In addition, the N−N distance of 1.236(3) Å in Schrock's compound is long compared to those in **1** and free N$_2$ and therefore indicates a partially reduced form of N$_2$. The short Mo−N distance and long N−N distance in Schrock's compound have been taken as suggesting that the bridging dinitrogen ligand behaves partially as a diimido group as represented by Mo=NN=Mo,[13] which is in sharp contrast with the bonding situation Mo−N≡N−Mo in **1**.

Synthesis and and Spectroscopic Characterization of Mo(CO)(Et$_2$PC$_2$H$_4$PEt$_2$)$_2$ (2). We have found that the bridging dinitrogen ligand in complex **1** can be eliminated at a higher temperature. Thus, when a red solution of {Mo(CO)(Et$_2$PC$_2$H$_4$PEt$_2$)$_2$}$_2$(μ-N$_2$) (**1**) in *p*-xylene is refluxed under argon, a deep blue solution is formed. After evaporation of the solvent, a dark red solid is obtained for which the microanalytical data are consistent with the formulation Mo(CO)(Et$_2$PC$_2$H$_4$PEt$_2$)$_2$ (**2**) (eq 2).



(2)

The absence of any dinitrogen ligand in **2** has been confirmed by an elemental analysis. Compound **2** is so reactive toward dinitrogen that both in solution and in the solid state it can scavenge traces of dinitrogen inside a glovebox operated under a helium atmosphere to revert to the bridging dinitrogen complex **1**. The intense color of compound **2** both in solution and in the solid state is reminiscent of those of other formally 16-electron complexes of M(0) (M = Cr, Mo, W)[1−3,7,15,16] and suggests the presence of an agostic Mo···H−C interaction analogous to that found for Mo(CO)(Bu$^i{}_2$PC$_2$H$_4$PBu$^i{}_2$)$_2$ by X-ray crystallography (*vide infra*). The agostic interaction in **2** is most likely formed by one of the β-C−H bonds of one ethyl group since such an interaction results in the formation of a favorable five-membered chelate ring. Attempts to grow crystals of **2** for X-ray diffraction have been thwarted by the fact that the compound is extremely soluble in all common organic solvents, even at low temperature.

The ^{1}H NMR spectrum of **2** in C$_6$D$_5$CD$_3$ at 298 K displays several overlapping multiplet resonances in the region of δ 0.64−1.98 due to the diphosphine ligand. When the sample is cooled to 193 K, the resonances broaden into featureless lumps. No high-field resonance for the agostic hydrogen is observed, suggesting that the agostic hydrogen undergoes rapid exchange with other methyl hydrogens. The fluxionality is also indicated by the variable-temperature ^{31}P{^{1}H} NMR spectra in which only a single resonance is observed in the temperature range of 193−298 K. The IR spectrum of **2** in toluene shows a strong ν(CO) band at 1721 cm^{-1}. No absorption is observed that may be assigned to an agostic Mo···H−C interaction. However, such absorptions are expected to be weak and accordingly are not a reliable criterion for agostic interactions.[17]

Reactions of {Mo(CO)(Et$_2$PC$_2$H$_4$PEt$_2$)$_2$}$_2$(μ-N$_2$) (1) and Mo(CO)(Et$_2$PC$_2$H$_4$PEt$_2$)$_2$ (2) with Small Molecules. Although complex **1** loses N$_2$ only at an elevated temperature under argon, the bridging dinitrogen ligand can be readily displaced at room temperature by small donor molecules L to give the monomeric adducts of the type Mo(L)(CO)(Et$_2$PC$_2$H$_4$PEt$_2$)$_2$ with concomitant evolution of dinitrogen (eq 3).

$$\underset{\mathbf{1}}{\{\mathrm{Mo(CO)(Et_2PC_2H_4PEt_2)_2}\}_2(\mu\text{-N}_2)} + \mathrm{L} \rightarrow \mathrm{Mo(L)(CO)(Et_2PC_2H_4PEt_2)_2} + \mathrm{N_2} \quad (3)$$

$$\underset{\mathbf{2}}{\mathrm{Mo(CO)(Et_2PC_2H_4PEt_2)_2}} + \mathrm{L} \rightarrow \mathrm{Mo(L)(CO)(Et_2PC_2H_4PEt_2)_2} \quad (4)$$

The same adducts can also be formed from the reactions of **2** with small molecules (eq 4). For example, both **1** and **2** react with H$_2$ or small silanes to give the dihydride complex MoH$_2$(CO)(Et$_2$PC$_2$H$_4$PEt$_2$)$_2$ [1] and the η^2-silane complexes *cis*-Mo(η^2-H-SiR$_3$)(CO)(Et$_2$PC$_2$H$_4$PEt$_2$)$_2$,[5] respectively. It was the similar reactivities of compounds **1** and **2** toward small molecules, in combination with the absence of the ν(NN) band in the IR spectrum of compound **1**, that led to the incorrect formulation of the bridging dinitrogen complex **1** as Mo(CO)(Et$_2$PC$_2$H$_4$PEt$_2$)$_2$ (**2**) in our previous work.[1]

Synthesis and Spectroscopic Characterization of Mo(CO)(Bu$^i{}_2$PC$_2$H$_4$PBu$^i{}_2$)$_2$ (3). The reaction of *trans*-Mo(N$_2$)$_2$(Bu$^i{}_2$PC$_2$H$_4$PBu$^i{}_2$)$_2$ with ethyl acetate in refluxing toluene under argon

---

(13) Schrock, R. R.; Kolodziej, R. M.; Liu, A. H.; Davis, W. M.; Vale, M. G. *J. Am. Chem. Soc.* **1990**, *112*, 4338.

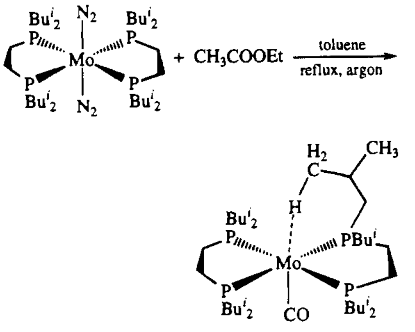
(14) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley: New York, 1988.

(15) Khalsa, G. R. K.; Kubas, G. J.; Unkefer, C. J.; Van Der Sluys, L. S.; Kubat-Martin, K. A. *J. Am. Chem. Soc.* **1990**, *112*, 3855.

(16) (a) Ishida, T.; Mizobe, Y.; Tanase, T.; Hidai, M. *J. Organomet. Chem.* **1991**, *409*, 355. (b) Ishida, T.; Mizobe, Y.; Tanase, T.; Hidai, M. *Chem. Lett.* **1988**, 441.

(17) (a) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395. (b) Brookhart, M.; Green, M. L. H.; Wong, L.-L. *Prog. Inorg. Chem.* **1988**, *36*, 1. (c) Crabtree, R. H.; Hamilton, D. G. *Adv. Organomet. Chem.* **1988**, *28*, 299.

gives a dark red solution from which a red-brown solid is isolated. The elemental analysis data for the solid are consistent with the formulation $Mo(CO)(Bu^{i}{}_2PC_2H_4PBu^{i}{}_2)_2$ (**3**) (eq 5). The



3

(5)

previous yield of **3** by precipitation with cold nonane was low due to its high solubility in alkane solvents.[1] However, the compound has now been found to be only slightly soluble in cold hexamethyldisiloxane and accordingly can be obtained in a significantly improved yield of 84% by precipitation of the product from cold hexamethyldisiloxane.

The ^1H NMR spectrum of **3** in $C_6D_5CD_3$ at 298 K displays several overlapping multiplet resonances in the region of δ 0.6–2.4 due to the diphosphine ligand. When the sample is cooled to 193 K, the resonances broaden into featureless lumps. No high-field resonance for the agostic hydrogen is observed, suggesting that the agostic hydrogen undergoes rapid exchange with the other methyl hydrogens. The fluxionality is also indicated by the variable-temperature $^{31}P\{^1H\}$ NMR spectra in which only a single resonance is observed in the temperature range 193–298 K.

The IR spectrum of **3** in Nujol show a strong ν(CO) band at 1721 cm^{-1}. Although no absorption is observed that may be attributed to an agostic C—H group, the presence of an agostic Mo···H—C interaction in **3** is suggested by its deep color, analogous to those observed for other agostic complexes of M(0) (M = Cr, Mo, W),[1-3,7,15,16] and has been confirmed by X-ray crystallography (*vide infra*). It is noteworthy that the ν(CO) stretching frequencies of compounds **1**–**3** and related compounds[1-5,16,18] are much lower than the range of 1850–2125 cm^{-1} typically found for neutral terminal carbonyl complexes and, in fact, fall within the range of 1700–1850 cm^{-1} commonly observed for neutral bridging carbonyl complexes.[19] It seems likely that these zero-valent group 6 metal monocarbonyl complexes containing weakly π-accepting phosphine coligands have exceedingly low ν(CO) stretching frequencies simply because the metal centers are highly π-basic.

Table 4. Crystallographic Data for $Mo(CO)(Bu^{i}{}_2PC_2H_4PBu^{i}{}_2)_2$ (**3**)

empirical formula	$C_{37}H_{80}MoOP_4$	Z	4
fw	760.83	ρ(calcd), g cm^{-3}	1.180
crystal system	orthorhombic	μ(MoK_α), cm^{-1}	4.81
space group	$Pna2_1$	min/max transm coeff	N/A
a, Å	18.332(4)	T, K	173
b, Å	22.066(4)	R[a]	0.034
c, Å	10.589(2)	R_w[b]	0.075
V, Å^3	4283(2)		

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o{}^2]^{1/2}$.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for *trans*-$Mo(CO)(Bu^{i}{}_2PC_2H_4PBu^{i}{}_2)_2$ (**3**)

	Bond Lengths		
Mo–P(1)	2.447(1)	Mo–P(2)	2.455(1)
Mo–P(3)	2.434(1)	Mo–P(4)	2.409(1)
Mo–C(1c)	1.886(4)	C(1c)–O(1c)	1.190(5)
Mo···C(423)	3.007(4)	Mo···H(42e)	2.20[a]
	Bond Angles		
P(1)–Mo–P(2)	80.21(4)	P(1)–Mo–P(3)	98.60(4)
P(1)–Mo–P(4)	177.69(4)	P(2)–Mo–P(3)	169.62(4)
P(2)–Mo–P(4)	101.38(4)	P(3)–Mo–P(4)	80.15(4)
C(1c)–Mo–P(1)	87.8(2)	C(1c)–Mo–P(2)	85.3(2)
C(1c)–Mo–P(3)	84.4(2)	C(1c)–Mo–P(4)	94.0(2)
Mo–C(1c)–O(1c)	179.1(6)	Mo–P(4)–C(421)	113.0(1)
Mo–P(4)–C(411)	128.5(2)	Mo–P(3)–C(311)	126.1(2)
Mo–P(3)–C(321)	118.7(1)	Mo–P(1)–C(121)	126.6(2)
Mo–P(1)–C(111)	115.0(2)	Mo–P(2)–C(211)	128.3(2)
Mo–P(2)–C(221)	116.6(1)	P(4)–C(421)–C(422)	114.9(3)
P(4)–C(411)–C(412)	118.2(3)	P(3)–C(311)–C(312)	119.0(3)
P(3)–C(321)–C(322)	120.5(3)	P(1)–C(121)–C(122)	116.7(3)
P(1)–C(111)–C(112)	119.4(3)	P(2)–C(211)–C(212)	121.2(3)
P(2)–C(221)–C(222)	122.5(3)	Mo···H(42e)–C(423)	140.8[a]
Mo···C(423)–H(42e)	26.8[a]	C(423)···Mo···H(42e)	12.4[a]
C(1c)–Mo···H(42e)	166.0[a]	P(1)–Mo···H(42e)	99.5[a]
P(2)–Mo···H(42e)	107.6[a]	P(3)–Mo···H(42e)	82.8[a]
P(4)–Mo···H(42e)	78.4[a]		

[a] Bond lengths and angles involving the agostic hydrogen H(42e) are based on idealized coordinates for this atom with *d*(C–H) = 0.96 Å.

X-ray Crystal Structure of $Mo(CO)(Bu^{i}{}_2PC_2H_4PBu^{i}{}_2)_2$ (3). Five-coordinate 16-electron species of M(0) (M = Cr, Mo, W) are often invoked as the intermediates in the dissociative substitution reactions of six-coordinate group 6 metal complexes.[20] Although the structures of such intermediates have been probed by low-temperature matrix-isolation studies,[21] none has been established by X-ray crystallography. Several ostensibly five-coordinate 16-electron complexes of M(0) (M = Cr, Mo, W) have been shown by ^1H NMR spectroscopy[2] or X-ray crystallography[3,7] to adopt a six-coordinate octahedral structure, in which a pendent C—H bond of a bound ligand is engaged in an agostic M···H—C interaction with the otherwise coordinatively unsaturated metal center, thus completing an 18-electron configuration.

We wondered whether compound **3** is a true five-coordinate 16-electron complex which is stabilized by a combination of the large steric bulk and high electron-donating ability of the alkyldiphosphine ligand $Bu^{i}{}_2PC_2H_4PBu^{i}{}_2$. We have therefore undertaken an X-ray crystallographic study on a single crystal of **3**. A summary of the crystallographic data is given in Table 4, and the selected bond lengths and angles are given in Table 5. An ORTEP drawing is shown in Figure 3. Clearly from close inspection of the bond distances and angles for this formally five-coordinate species, the coordination geometry around the molybdenum atom is better described as a slightly distorted octahedron. The two diphosphine ligands lie on the equatorial plane, and the CO ligand occupies one apical position. The remaining apical site trans to the CO ligand is occupied by an aliphatic γ-C—H bond of a diphosphine ligand. This looks particularly obvious in the crystal packing diagram

---

(18) Mizobe, Y.; Ishida, T.; Egawa, Y.; Ochi, K.; Tanase, T.; Hidai, M. *J. Coord. Chem.* **1991**, *23*, 57.

(19) (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*, 2nd ed.; University Science Books: Mill Valley, CA, 1987; pp 114–115. (b) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley: New York, 1988; p 1034.

(20) (a) Atwood, J. D. *Inorganic and Organometallic Reaction Mechanisms*; Brooks/Cole: Monterey, CA, 1985; Chapter 4. (b) Howell, J. A. S.; Burkinshaw, P. M. *Chem. Rev.* **1983**, *83*, 557. (c) Darensbourg, D. J. *Adv. Organomet. Chem.* **1982**, *21*, 113. (d) Graham, J. R.; Angelici, R. J. *Inorg. Chem.* **1967**, *6*, 2082. (e) Covey, W. D.; Brown, T. L. *Inorg. Chem.* **1973**, *12*, 2820.

(21) (a) Perutz, R. N.; Turner, J. J. *J. Am. Chem. Soc.* **1975**, *97*, 4791. (b) Burdett, J. K.; Perutz, R. N.; Poliakoff, M.; Turner, J. J. *J. Chem. Soc., Chem. Commun.* **1975**, 157. (c) Black, J. D.; Braterman, P. S. *J. Am. Chem. Soc.* **1975**, *97*, 2908.

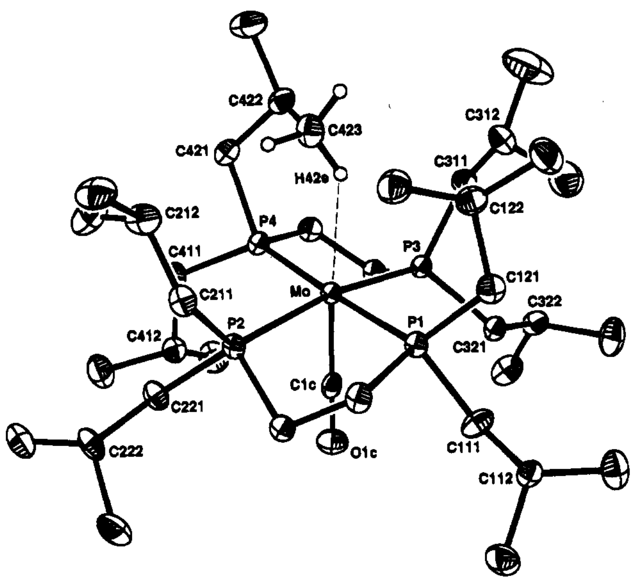


Figure 3. ORTEP drawing of Mo(CO)(Bu$^i_2$PC$_2$H$_4$PBu$^i_2$)$_2$ (**3**).

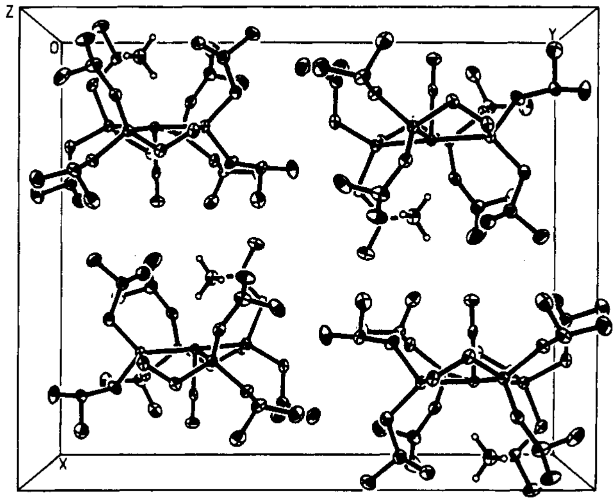


Figure 4. Unit cell packing diagram for Mo(CO)(Bu$^i_2$PC$_2$H$_4$PBu$^i_2$)$_2$ (**3**).

shown in Figure 4. The resulting three-center two-electron Mo···H—C interaction supplies the electrons necessary for the molybdenum center to formally attain an 18-electron configuration.

The agostic Mo···C(423) distance of 3.007(4) Å is much longer than the Mo—C single bond distances of 2.2–2.4 Å found in molybdenum alkyl complexes[22] but significantly shorter than the sum of the van der Waals radii (3.90 Å) of Mo and C atoms. This indicates a weak but not negligible attractive bonding interaction between Mo and C(423) atoms. For comparison, in the related compound Mo(CO)(Ph$_2$PC$_2$H$_4$PPh$_2$)$_2$,[3] the agostic Mo···C distance is 3.50(2) Å,[23] which is significantly longer than that in **3** and so suggests a weaker agostic Mo···H—C interaction than that in **3**.

The agostic hydrogen atom H(42e) in **3** was not located in the difference Fourier map, so its position is based upon the assumption of an idealized tetrahedral geometry about the agostic carbon atom C(423) and d(C—H) = 0.96 Å. The agostic hydrogen atom is opposite the CO group with respect to the equatorial plane defined by the molybdenum and four phosphorus atoms, the C(1c)—Mo···H(42e) angle being 166.0°. The calculated Mo···H(42e) separation of 2.20 Å is only 0.34 Å longer than the averaged bridging Mo—H distance of 1.860(4) Å in {(η^5-C$_5$H$_5$)Mo(CO)$_2$}$_2$(μ-H)(μ-PMe$_2$)[24] and so indicates a substantial bonding interaction. Previously reported agostic Mo···H distances cover a relatively wide range of 1.8–3.0 Å.[3,25] The compound Mo(CO)(Ph$_2$PC$_2$H$_4$PPh$_2$)$_2$ has an agostic Mo···H distance of 2.98(11) Å,[3] which is significantly longer than that calculated for **3** and so again suggests a weaker agostic Mo···H—C interaction than that in **3**.

The overall geometry of the agostic Mo···H—C fragment in **3** is similar to those in the compounds Mo{BEt$_2$(pz)$_2$}(η^3-CH$_2$CHXCH$_2$)(CO)$_2$ (pz = 1-pyrazolyl; X = H, Ph) reported by Cotton and co-workers.[26] The Mo···H(42e)—C(423) angle in **3** is 140.8°, while Cotton's compounds have Mo···H—C angles of 131(2) and 136(6)°. These M···H—C angles clearly fall at the upper end of the range commonly found for agostic complexes.[17,27] There seems to be a correlation between the M···H—C angle and the strength of the agostic interaction; *i.e.*, the agostic interaction is stronger with a smaller M···H—C angle.[27] The large Mo···H—C angle observed for **3** suggests a relatively weak agostic interaction.

Consistent with the presence of the agostic Mo···H—C interaction, there is a small but systematic distortion of P(1), P(2), and, to less extent, P(3) toward the CO group, with the three C(1c)—Mo—P angles being acute and ranging from 84.4(2) to 87.8(2)°. Such a distortion creates more room opposite to the CO group in order to accommodate the agostic C—H bond. Without the agostic Mo···H—C interaction, an opposite distortion away from the CO group toward the vacant site would occur on steric grounds. On the other hand, P(4) is distorted away from the CO group, C(1c)—Mo—P(4) being obtuse (94.0(2)°), in order to help place the agostic C—H bond in an ideal position for maximal interaction with the molybdenum center.

By virtue of the Mo···H interaction, a six-membered chelate ring is formed which includes Mo, P(4), three isobutyl carbon atoms, and H(42e). The P(4)—Mo···H(42e) angle, *i.e.* the "bite" angle of the chelate ring, is 78.4°, which turns out to be the smallest cis angle of the coordination octahedron about the molybdenum atom. Within the chelate ring, the Mo—P(4)—

---

(22) (a) Churchill, M. R. *Perspect. Struct. Chem.* **1971**, *3*, 91. (b) Kirtley, S. W. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, England, 1982; Vol. 3, Chapter 27.1. (c) Atwood, J. L.; Hunter, W. E.; Rogers, R. D.; Carmona, E.; Wilkinson, G. *J. Chem. Soc., Dalton. Trans.* **1979**, 1519. (d) Ko, J. J.; Bockman, T. M.; Kochi, J. K. *Organometallics* **1990**, *9*, 1833. (e) Prout, K.; Cameron, T. S.; Forder, R. A.; Critchley, S. R.; Denton, B.; Rees, G. V. *Acta Crystallogr.* **1974**, *B30*, 2290.

(23) The agostic Mo···C distance in Mo(CO)(Ph$_2$PC$_2$H$_4$PPh$_2$)$_2$ is calculated from the reported positional parameters of the Mo and agostic carbon atoms.[3]

(24) Petersen, J. L.; Dahl, L. F.; Williams, J. M. *J. Am. Chem. Soc.* **1974**, *96*, 6610.

(25) (a) Cotton, F. A.; Luck, R. L. *Inorg. Chem.* **1989**, *28*, 3210. (b) Cotton, F. A.; LaCour, T.; Stanislowski, A. G. *J. Am. Chem. Soc.* **1974**, *96*, 754. (c) Cotton, F. A.; Daw, V. W. *J. Chem. Soc., Chem. Commun.* **1974**, 415. (d) Bourner, D. G.; Brammer, L.; Green, M.; Moran, G.; Orpen, A. G.; Reeve, C.; Schaverien, C. J. *J. Chem. Soc., Chem. Commun.* **1985**, 1409. (e) Brammer, L.; Dunne, B. J.; Green, M.; Moran, G.; Orpen, A. G.; Reeve, C.; Schaverien, C. J. *J. Chem. Soc., Dalton Trans.* **1993**, 1747. (f) Green, M.; Norman, N. C.; Orpen, A. G. *J. Am. Chem. Soc.* **1981**, *103*, 1269. (g) Contreras, L.; Monge, A.; Pizzano, A.; Ruiz, C.; Sànchez, L.; Carmona, E. *Organometallics* **1992**, *11*, 3971. (h) Carmona, E.; Sànchez, L.; Marin, J. M.; Poveda, M. L.; Atwood, J. L.; Priester, R. D.; Rogers, R. D. *J. Am. Chem. Soc.* **1984**, *106*, 3214. (i) Bott, S. G.; Brammer, L.; Connelly, N. G.; Green, M.; Orpen, A. G.; Paxton, J. F.; Schaverien, C. J.; Bristow, S.; Norman, N. C. *J. Chem. Soc., Dalton Trans.* **1990**, 1957. (j) Green, M.; Norman, N. C.; Orpen, A. G.; Schaverien, C. J. *J. Chem. Soc., Dalton Trans.* **1984**, 2455.

(26) (a) Cotton, F. A.; LaCour, T.; Stanislowski, A. G. *J. Am. Chem. Soc.* **1974**, *96*, 754. (b) Cotton, F. A.; Luck, R. L. *Inorg. Chem.* **1989**, *28*, 3210.

(27) Crabtree, R. H.; Holt, E. M.; Lavin, M.; Morehouse, S. M. *Inorg. Chem.* **1985**, *24*, 1986.

C(421) angle of 113.0(1)° is considerably contracted relative to the other Mo−P−C angles of the same type, which range from 115.0(2) to 128.5(2)° and average 122.8(2)°. Similar contraction has previously been observed for agostic interactions involving a monodentate alkylphosphine ligand.[7,8] The strongly distorted geometry about P(4) is apparently a result of the formation of the six-membered chelate ring and provides evidence for a substantial attractive interaction between the atoms Mo and H(42e). In addition, the P(4)−C(421)−C(422) angle of 114.9(3)° is also contracted, although to less extent, relative to the other P−C−C angles of the same type which range from 116.7(3) to 122.5(3)° and average 119.6(3)°. It is interesting to note that the diphosphine ligands in the related compound $Mo(CO)(Ph_2PC_2H_4PPh_2)_2$ apparently have normal undistorted geometries,[3] probably because the agostic Mo···H−C interaction in this compound is much weaker than that in **3**, as evidenced by much longer Mo···H and Mo···C distances.

Another interesting structural feature of **3** caused by the agostic Mo···H−C interaction is the difference in the Mo−P bond lengths. The Mo−P(4) distance of 2.409(1) Å is slightly shorter than all the other Mo−P distances which range from 2.434(1) to 2.455(1) Å and average 2.445(1) Å. This observation does not seem to be incidental because the related compounds $Mo(CO)(Ph_2PC_2H_4PPh_2)_2$ [3] and $M(CO)_3(PR_3)_2$ (M = Cr, W)[7] show rather similar behavior. A plausible explanation is that the chelate effect imposed by the Mo···H−C interaction strengthens the Mo−P(4) bond, resulting in a shortening in the Mo−P(4) distance.

Conclusion

In summary, the compound formed by the reaction of *trans*-$Mo(N_2)_2(Et_2PC_2H_4PEt_2)_2$ with ethyl acetate in refluxing toluene under argon should be reformulated as $\{Mo(CO)(Et_2PC_2H_4PEt_2)_2\}_2(\mu\text{-}N_2)$ (**1**), which has been shown by X-ray crystallography to contain an end-on bridging dinitrogen ligand. Only at an elevated temperature and under argon does compound **1** eliminate the bridging dinitrogen ligand to form the nitrogen-free compound $Mo(CO)(Et_2PC_2H_4PEt_2)_2$ (**2**). In contrast, the reaction of *trans*-$Mo(N_2)_2(Bu^i_2PC_2H_4PBu^i_2)_2$ with ethyl acetate in refluxing toluene under argon gives directly the nitrogen-free compound $Mo(CO)(Bu^i_2PC_2H_4PBu^i_2)_2$ (**3**). The X-ray crystal structure of **3** reveals an agostic Mo···H−C interaction between the molybdenum atom and an aliphatic γ-C−H bond of the alkyldiphosphine ligand. This agostic interaction relieves the coordinative unsaturation at the molybdenum center and allows compound **3** to attain an octahedral coordination geometry with a formal 18-electron configuration. As judged by the agostic Mo···C and Mo···H distances, the agostic interaction in compound **3** appears to be stronger than that in the related compound $Mo(CO)(Ph_2PC_2H_4PPh_2)_2$, which involves an ortho aromatic C−H bond of the diphosphine ligand.

Experimental Section

General Procedures. All manipulations were performed either under a helium atmosphere in a Vacuum Atmospheres glovebox or under an argon atmosphere using standard Schlenk techniques. Solvents were distilled from sodium benzophenone ketyl and stored in a glovebox under helium. The bis(dinitrogen)molybdenum complexes *trans*-$Mo(N_2)_2(R_2PC_2H_4PR_2)_2$ (R = Et, Bu^i) were prepared as described previously.[1a]

^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker AF-250 spectrometer at 250.13 and 101.26 MHz, respectively; ^1H chemical shifts were referenced to the residual solvent resonance relative to TMS; ^{31}P chemical shifts were referenced to external 85% H_3PO_4. Infrared spectra were recorded on a BioRad FTS-40 FT-IR spectrometer. Elemental analyses were performed using a Perkin-Elmer PE2400 CHN elemental analyzer.

Synthesis of $\{Mo(CO)(Et_2PC_2H_4PEt_2)_2\}_2(\mu\text{-}N_2)$ (1). *trans*-$Mo(N_2)_2(Et_2PC_2H_4PEt_2)_2$ (0.80 g, 1.42 mmol) and ethyl acetate (1.50 g, 17.0 mmol) in toluene (15 mL) were refluxed for 40 min with a stream of argon (ultra high purity) sweeping through the reaction flask (50 mL, with side arm) and exiting through the reflux condenser. The resulting purple solution turned red upon cooling to room temperature and was evaporated in vacuo to dryness, giving a dark red residue which was triturated with 5 mL of hexamethyldisiloxane. Chilling of the mixture at −38 °C in a freezer for 15 min followed by filtration gave **1** as a red solid; yield 0.67 g (79%). Anal. Calcd for $C_{42}H_{96}Mo_2N_2O_2P_8$: C, 45.82; H, 8.79; N, 2.54. Found: C, 45.26; H, 8.66; N, 2.39. IR (Nujol): ν(CO) 1747 cm^{-1}. ^1H NMR ($C_6D_5CD_3$, 298 K): δ 1.93 (m), 1.63 (m), 1.40 (br), 1.14 (br m), 1.06 (br m). $^{31}P\{^1H\}$ NMR ($C_6D_5CD_3$, 298 K): δ 58.4. $^{31}P\{^1H\}$ NMR ($C_6D_5CD_3$, 193 K): δ 56.1 (br s), 55.1 (br s).

Synthesis of $Mo(CO)(Et_2PC_2H_4PEt_2)_2$ (2). A solution of compound **1** (0.20 g) in *p*-xylene (5 mL) was refluxed for 40 min with a stream of argon (ultrahigh purity) sweeping through the reaction flask (50 mL, with side arm) and exiting through the reflux condenser. The resulting deep blue solution was cooled to room temperature and evaporated in vacuo to dryness, giving **2** as a slightly tacky dark red solid which was contaminated with a small amount of the high-boiling *p*-xylene. The solid was dried at 60 °C in vacuo for 8 h and then scraped off the bottom and wall of the reaction flask; yield 0.15 g (77%). Anal. Calcd for $C_{21}H_{48}MoOP_4$: C, 47.02; H, 9.02; N, 0.00 Found: C, 46.96; H, 9.02; N, 0.17. IR (toluene): ν(CO) 1721 cm^{-1}. ^1H NMR ($C_6D_5CD_3$, 298 K): δ 1.98 (m), 1.57 (m), 1.17 (m), 0.64 (m). $^{31}P\{^1H\}$ NMR ($C_6D_5CD_3$, 298 K): δ 70.6.

Synthesis of $Mo(CO)(Bu^i_2PC_2H_4PBu^i_2)_2$ (3). *trans*-$Mo(N_2)_2(Bu^i_2PC_2H_4PBu^i_2)_2$ (0.88 g, 1.12 mmol) and ethyl acetate (1.20 g, 13.6 mmol) in toluene (15 mL) were refluxed for 1 h with a stream of argon (ultrahigh purity) sweeping through the reaction flask (50 mL, with side arm) and exiting through the reflux condenser. The resulting dark red solution was cooled to room temperature and evaporated in vacuo to dryness. The residue was triturated with 5 mL of hexamethyldisiloxane. Chilling of the mixture at −38 °C in a freezer for 15 min followed by filtration gave **3** as a red-brown solid; yield 0.71 g (84%). Anal. Calcd for $C_{37}H_{80}MoOP_4$: C, 58.40; H, 10.60; N, 0.00. Found: C, 57.93; H, 10.59; N, 0.25. IR (Nujol): ν(CO) 1724 cm^{-1}. ^1H NMR ($C_6D_5CD_3$, 298 K): δ 0.6–2.4 (m). $^{31}P\{^1H\}$ NMR ($C_6D_5CD_3$, 298 K): δ 55.0.

X-ray Crystallographic Analysis of $\{Mo(CO)(Et_2PC_2H_4PEt_2)_2\}_2(\mu\text{-}N_2)$ (1). Red crystals of **1** suitable for X-ray diffraction measurements were grown by slowly cooling a saturated solution of **1** in hot hexane. A crystal of approximate dimensions 0.43 × 0.37 × 0.24 mm was selected, mounted on a glass fiber with Apiezon "H" grease under an argon stream, and quickly transferred to the goniostat cooled to −100 °C with a cold nitrogen stream. Data were collected on a Siemens P4S diffractometer with graphite monochromated Mo Kα radiation (λ = 0.710 73 Å). Cell constants and an orientation matrix were obtained by least-squares refinement of the setting angles of 25 randomly selected reflections. Accurate cell constants and an improved orientation matrix were obtained from the least-squares refinement of the setting angles of the 50 strongest reflections found in the thin shell between 12.0 and 13.0° in θ. Although there was one relatively long axis (b = 44.233(4) Å), no unusual precautions were necessary to prevent overlapping data due to the fact this was a C-centered cell. A total of 21 324 reflections were collected ($-1 \le h \le +28$, $-1 \le k \le +52$, $-24 \le l \le +24$) in the range $4.20° < 2\theta < 50.00°$ with 19 257 being unique (R_{int} = 2.13%). The collected data set was analyzed for intense high χ (above 80°) reflections over a range of 2θ values, which were then scanned to provide the basis for an empirical absorption correction with the transmission coefficient ranging from 0.67 to 0.82. No crystal decay was observed during the data collection.

The structure was solved by the automatic Patterson routine in the SHELXTL[28] software which gave a partial solution that could be expanded by a combination of least-squares refinement using the

---

[28] SHELXTL; Siemens Analytical X-Ray Instruments, Inc.: Madison, WI, 1993.

SHELX-93[29] software and difference Fourier syntheses. It was found that in the asymmetric unit there are two half molecules with two crystallographically imposed 2-fold axes perpendicularly bisecting the N−N triple bonds of each molecule, as well as one complete molecule with no crystallographically imposed symmetry. In the course of this procedure it was found that several methyl groups of the diphosphine ligands were disordered over two positions for all the molecules. The sum of the multiplicities of the two sites were refined and constrained to be unity and their temperature factors were refined and constrained to be equal. In addition to this disorder, there was a more extensive disorder of the complete molecule. Here the two diphosphine ligands at one end of the molecule were disordered over two orientations rotated by 90° about the Mo−N−N−Mo axis in a ratio of 69:31. This disorder was successfully modeled using the extensive variable parameters available for disordered groups found in SHELX-93.[29] The calculated positions of the hydrogen atoms on nondisordered carbon atoms (C−H fixed at 0.96 Å) were added to the structure factor calculations but were not refined. The final residuals for the full-matrix least-squares refinement based on F^2 were $R = 4.80\%$, $R_w = 11.23\%$, and GOF = 1.057 for 1238 variable parameters and 14 357 reflections ($F > 4.0\sigma(F)$).

X-ray Crystallographic Analysis of $Mo(CO)(Bu^i_2PC_2H_4PBu^i_2)_2$ (3). Dark red crystals of **3** suitable for X-ray diffraction measurements were grown from Et_2O/hexamethyldisiloxane. A crystal of approximate dimensions of 0.40 × 0.37 × 0.16 mm was selected, mounted on a glass fiber with Apiezon "H" grease under an argon stream, and quickly transferred to the goniostat cooled to −100 °C with a cold nitrogen stream. Data were collected on an Enraf-Nonius CAD4 diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å). Cell constants and an orientation matrix were obtained by least-squares refinement of the setting angles of 25 randomly selected reflections. There are two possible space groups, *Pna*2$_1$ and *Pnma*. The former was shown to be correct by subsequent solution and refinement, and attempted refinement in the latter was unsuccessful. Accurate cell constants and an improved orientation matrix were obtained from the least-squares refinement of the setting angles of the 25 strongest reflections found in the thin shell between 12.0 and 13.0° in θ. A total of 9292 reflections (two quadrants) were collected ($-24 \le h \le 0$, $-26 \le k \le +29$, $0 \le l \le +13$) in the range $4.26° < 2\theta < 55.94°$ with 5416 being unique ($R_{int} = 3.79\%$). No absorption correction was carried out as preliminary ψ scans showed very little variation in absorption with angle. No crystal decay was evident during the data collection.

The structure was solved by the automatic Patterson routine in the SHELXTL[28] software, which gave a partial solution that could be expanded by a combination of least-squares refinement using the SHELX-93[29] software and difference Fourier syntheses. The enantiomer was shown to be correct by the fact that the Flack parameter was found to be −0.01(4). The calculated positions of the hydrogen atoms (C−H fixed at 0.96 Å) were added to the structure factor calculations but were not refined. The final residuals for the full-matrix least-squares refinement based on F^2 were $R = 3.39\%$, $R_w = 7.52\%$, and GOF = 0.996 for 485 variable parameters and 4212 reflections ($F > 4.0\sigma(F)$).

Acknowledgment. This work was performed under the auspices of the Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research, U.S. Department of Energy.

Supporting Information Available: Tables of crystallographic data, positional and thermal parameters, bond lengths and angles, and atomic parameters of hydrogen atoms and figures of ORTEP drawings and unit cells for **1** and **3** (29 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

IC9506116

---

(29) SHELX-93; Siemens Analytical X-Ray Instruments, Inc.: Madison, WI, 1993.