Preparation, Structures, and Some Reactivities of Five-Coordinate Alkyne Complexes of Mo with Tetraphosphine or Diphosphine Coligand [Mo(RC≡CR′){*meso-o*-C_6H_4($PPhCH_2CH_2PPh_2$)$_2$}] and [Mo(RC≡CR′)($Ph_2PCH_2CH_2PPh_2$)$_2$]

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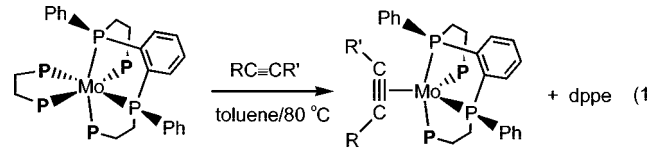
The five-coordinate alkyne complexes [Mo(η^2-RC≡CR′)(κ^4-**P4**)] (**3**; **P4** = *meso-o*-C_6H_4-($PPhCH_2CH_2PPh_2$)$_2$) were synthesized by treatment of the Mo(0) tetraphosphine complex [Mo(κ^4-**P4**)(dppe)] (**1**; dppe = $Ph_2PCH_2CH_2PPh_2$) with internal alkynes RC≡CR′. The X-ray analysis of **3a** (R = Me, R′ = COOMe) and **3b** (R = R′ = Ph) has disclosed their trigonal-bipyramidal geometry in a solid state, whereas their fluxional feature in solution has been demonstrated by the VT-NMR study. New closely relating diphosphine complexes [Mo(η^2-RC≡CR′)(dppe)$_2$] (**4**) have also been obtained analogously from the reactions of *trans*-[Mo$(N_2)_2$(dppe)$_2$] with RC≡CR′, and their trigonal-bipyramidal structures have been confirmed by the X-ray diffraction for **4a** (R = Me, R′ = COOMe). Complexes **3a**, **3b**, **4a**, and **4b** were allowed to react with aqueous HCl in THF to give hydrogenation products from coordinated alkynes including *cis*/*trans*-alkenes and/or alkanes, the yields of which depend upon the nature of the alkyne complexes and the amounts of acid. From the reactions of **3a** with $HBF_4 \cdot Et_2O$ under the controlled conditions, two intermediate complexes were isolated, namely, a hydridoalkyne complex [MoH(η^2-MeC≡CCOOMe)(κ^4-**P4**)][BF_4] and an η^3-allyl complex [Mo(η^3-$CH_2CHCHCOOMe$-κO)(κ^4-**P4**)][BF_4], and the mechanism for the formations of hydrogenation products of alkynes via these intermediate stages has been proposed. Reaction of **3a** with H_2S gas also resulted in the hydrogenation of the coordinated alkyne to the alkene, which was further converted to the H_2S adduct smoothly under the reaction conditions. Oxidation of **3a** by I_2 yielding a cationic alkyne complex [MoI(η^2-MeC≡CCOOMe)(κ^4-**P4**)]I is also described.

Introduction

Since the isolation of the zerovalent Mo complex containing a new tetraphosphine coligand [Mo(κ^4-**P4**)(dppe)] (**1**; **P4** = *meso-o*-C_6H_4($PPhCH_2CH_2PPh_2$)$_2$, dppe = $Ph_2PCH_2CH_2PPh_2$) from the reaction of *trans*-[Mo$(N_2)_2$(dppe)$_2$] (**2**) with dppe via the condensation of two dppe ligands to form **P4** under forcing conditions,[1] we have been investigating the reactivities of **1** toward a series of small molecules. These studies have disclosed already the reactivities distinctively displayed by this {Mo(**P4**)} site, which include the formations of zerovalent **P4** complexes having one, two, and/or three CO, nitrile, isocyanide,[2] and N_2[1b] ligands as well as the cleavages of the C=O bond in CO_2, the C=S bond in RNCS,[3] and C−X bonds in $PhCH_2X$ (X = Cl, Br)[4] in the coordination sphere of Mo. Now, we have found that the reactions of **1** with internal alkynes RC≡CR′ afford the five-coordinate alkyne complexes [Mo(η^2-RC≡CR′)(κ^4-**P4**)] (**3**). In this paper, we wish to describe in detail the characterization of **3**, together with their analogues consisting of bidentate dppe ligands [Mo(η^2-RC≡CR′)(dppe)$_2$] (**4**) newly prepared from **2**. Protonation of the coordinated alkynes in **3** and **4** to give hydrogenation products is also reported.

Results and Discussion

Preparation of 3 from 1. When treated with alkynes RC≡CR′ in toluene at 80 °C, **1** was converted into **3a** (R = Me, R′ = COOMe) and **3b** (R = R′ = Ph), which are isolable as analytically pure crystals in satisfactory yields (eq 1). For MeC≡CPh, the similar product **3c** (R = Me, R′ = Ph) was obtained, as was confirmed by the X-ray analysis and spectroscopic data, but isolation in a pure form was unsuccessful due to the contamination by dppe. Although **3** were also produced for RC≡CR′ (R, R′ = Me or primary alkyl groups), isolations failed because of their lower stabilities than **3a**−**3c** in addition to the difficulty in separation from free dppe. The alkynes having bulky substituents such as Bu′C≡CMe and $Me_3SiC{\equiv}CSiMe_3$ did not react with **1** under these conditions.



1 **3a**: R = Me, R' = COOMe; **3b**: R = R' = Ph; **3c**: R = Me, R' = Ph

P = PPh_2

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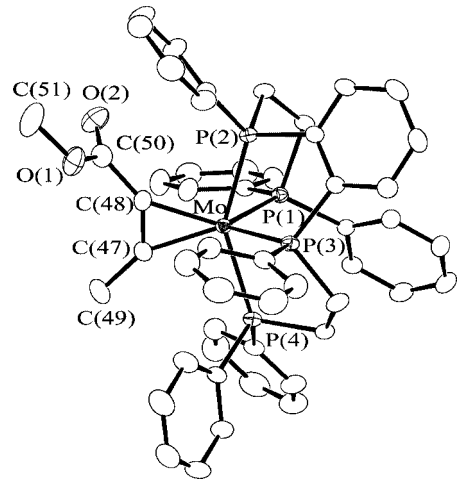
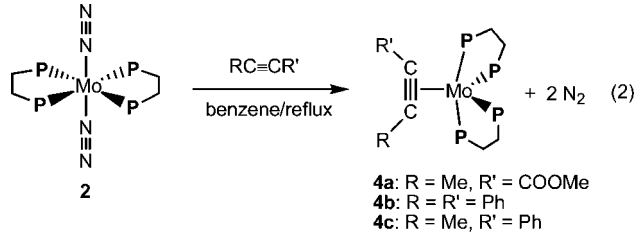


Figure 1. An ORTEP drawing for **3a** at 30% probability level. Hydrogen atoms are omitted for clarity.

Preparation of 4 from 2. For comparison of the structures and properties, synthesis of the dppe analogues **4** from **2** was also attempted, and we have found that the corresponding alkyne complexes **4a**−**4c** are isolable by treatment of **2** with RC≡CR′ in benzene at reflux, as shown in eq 2. Under these conditions, reactions with the alkynes having Bu^t and Me_3Si groups did not occur also for **2**. Two complexes of this type, [Mo(η^2-HC≡CH)(dppe)$_2$] (**4d**)[5] and [Mo(η^2-MeC≡CMe)(dppe)$_2$] (**4e**),[6] are precedented, the former of which was obtained in 32% yield from the reaction of **2** with excess HC≡CLi · $H_2NCH_2CH_2NH_2$ and the latter in 2−5% yields from [$MoCl_4$(dppe)], dppe, and MeC≡CMe under reductive conditions. The reactions reported here demonstrate a convenient and reliable method to prepare **4**, although the analogues containing terminal alkynes are not available by this procedure due to the facile formations of bis(alkyne) complexes [Mo(η^2-RC≡CH)$_2$(dppe)$_2$] (R = Me[7] and Ph[8]) or the products resulting from the alkynic C−H bond cleavage.[8]



Structures of 3 and 4. The single-crystal X-ray analysis has been undertaken for **3a** and **3b** to clarify their structures in detail. Figures 1 and 2 depict the ORTEP drawings for **3a** and **3b**, respectively, while Table 1 lists the selected bond distances and angles therein. The structure of **3c** was also confirmed by the X-ray crystallography, which is included in Supporting Information.

The structures of **3a** and **3b** are essentially identical. Thus, complexes **3** have a distorted trigonal-bipyramidal structure with one inner P atom, P(2), and one outer P atom, P(4), in **P4** at the axial positions. The η^2-alkynes are ligating to the Mo center in a manner that the alkynic C−C bond is oriented perpendicularly to the triangular equatorial plane defined by P(1), P(3), and the midpoint of the alkynic C−C bond. The P(2)−Mo−P(4) linkages are bent toward the direction opposite to the alkynes, with the P−Mo−P angles at 148.20(2) and 147.72(2)° for **3a** and **3b**, respectively. As for the structures of coordinated alkynes, the C≡C−C arrays are bent significantly with the substituents R and R′ directed away from the Mo centers, where the observed C≡C−C angles of 132.6(2)−137.2(2)° are rather closer to those of the sp^2 C atoms than the sp C atoms. Consistently, the alkynic C−C bond lengths are elongated to 1.312(3) and 1.316(3) Å for **3a** and **3b**, which are comparable to those of the typical C−C double bonds. The distances of alkynic C atoms from Mo at 2.062(2)−2.081(2) Å fall in the range of the 4e-donating alkynes (1.93−2.09 Å) and are

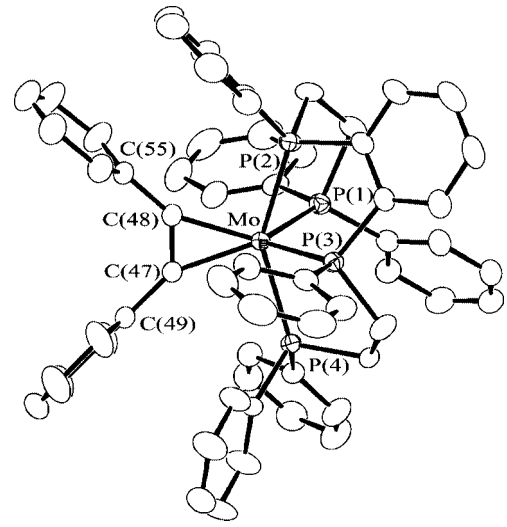


Figure 2. An ORTEP drawing for **3b** at 30% probability level. Hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Distances (Å) and Angles (°) in 3a and 3b

3a

(a) Bond Distance

Mo−P(1)	2.3801(6)	Mo−P(2)	2.4093(5)
Mo−P(3)	2.3627(6)	Mo−P(4)	2.4392(5)
Mo−C(47)	2.075(2)	Mo−C(48)	2.062(2)
C(47)−C(48)	1.312(3)		

(b) Bond Angle

P(1)−Mo−P(2)	77.57(2)	P(1)−Mo−P(3)	101.66(2)
P(1)−Mo−P(4)	88.80(2)	P(2)−Mo−P(3)	77.80(2)
P(2)−Mo−P(4)	148.20(2)	P(3)−Mo−P(4)	77.04(2)
C(47)−Mo−C(48)	36.99(9)	Mo−C(47)−C(48)	71.0(1)
Mo−C(47)−C(49)	154.2(2)	C(48)−C(47)−C(49)	134.8(2)
Mo−C(48)−C(47)	72.1(1)	Mo−C(48)−C(50)	149.7(2)
C(47)−C(48)−C(50)	137.2(2)		

3b

(a) Bond Distance

Mo−P(1)	2.4016(8)	Mo−P(2)	2.4202(6)
Mo−P(3)	2.3452(7)	Mo−P(4)	2.4506(5)
Mo−C(47)	2.081(2)	Mo−C(48)	2.069(2)
C(47)−C(48)	1.316(3)		

(b) Bond Angle

P(1)−Mo−P(2)	77.04(2)	P(1)−Mo−P(3)	102.61(2)
P(1)−Mo−P(4)	89.38(2)	P(2)−Mo−P(3)	77.09(2)
P(2)−Mo−P(4)	147.72(2)	P(3)−Mo−P(4)	77.56(2)
C(47) −Mo−C(48)	36.98(9)	Mo−C(47)−C(48)	71.0(1)
Mo−C(47)−C(49)	155.1(2)	C(48)−C(47)−C(49)	133.1(2)
Mo−C(48)−C(47)	72.0(1)	Mo−C(48)−C(55)	155.4(2)
C(47)−C(48)−C(55)	132.6(2)		

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Table 2. Selected Bond Distances (Å) and Angles (°) in 4a

	molecule 1	molecule 2
(a) Bond Distances		
Mo(1)−P(1)	2.428(1)	2.418(1)
Mo(1)−P(2)	2.483(1)	2.473(1)
Mo(1)−P(3)	2.415(1)	2.427(1)
Mo(1)−P(4)	2.449(1)	2.449(1)
Mo(1)−C(53)	2.065(3)	2.070(3)
Mo(1)−C(54)	2.060(3)	2.068(4)
C(53)−C(54)	1.314(5)	1.318(6)
(b) Bond Angles		
P(1)−Mo(1)−P(2)	78.18(3)	78.41(3)
P(1)−Mo(1)−P(3)	107.09(3)	103.84(3)
P(1)−Mo(1)−P(4)	87.96(3)	88.10(3)
P(2)−Mo(1)−P(3)	86.80(3)	87.77(3)
P(2)−Mo(1)−P(4)	155.80(3)	157.90(3)
P(3)−Mo(1)−P(4)	78.35(3)	78.48(3)
C(53) −Mo(1)−C(54)	37.1(1)	37.2(2)
Mo(1) −C(53) −C(54)	71.2(2)	71.3(2)
Mo(1)−C(53) −C(55)	156.4(3)	155.7(3)
C(54) −C(53)−C(55)	132.4(3)	132.9(3)
Mo(1)−C(54) −C(53)	71.6(2)	71.5(2)
Mo(1)−C(54)−C(56)	153.5(3)	147.5(5)[a]
C(53)−C(54)−C(56)	134.6(3)	138.2(5)[a]

[a] Data for the COOMe group in the predominant disordered molecule.

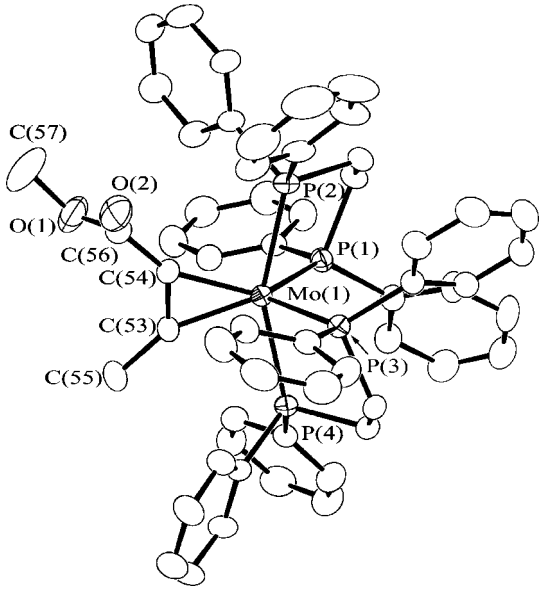

Figure 3. An ORTEP drawing for one of the two crystallographically independent molecules of **4a** (30% probability level). All hydrogen atoms and the solvating benzene are omitted for clarity.

significantly shorter than those of the 2e-donating alkynes (2.13−2.24 Å),[9] which is in good agreement with the fact that the electron count of the Mo center in **3** becomes 18 by assuming the donation of 4 electrons from the coordinated alkyne.

To compare the structures in detail, the X-ray analysis has also been carried out for the diphosphine complex **4a**. The single crystal of **4a** contained two crystallographically independent molecules with essentially identical structures. Selected bond distances and angles are listed in Table 2, while the ORTEP drawing is depicted in Figure 3 for only one of the two molecules. As observed for the previously reported **4d**[5] and **4e**,[6] **4a** has a distorted trigonal-prismatic geometry, analogous to **3a**,

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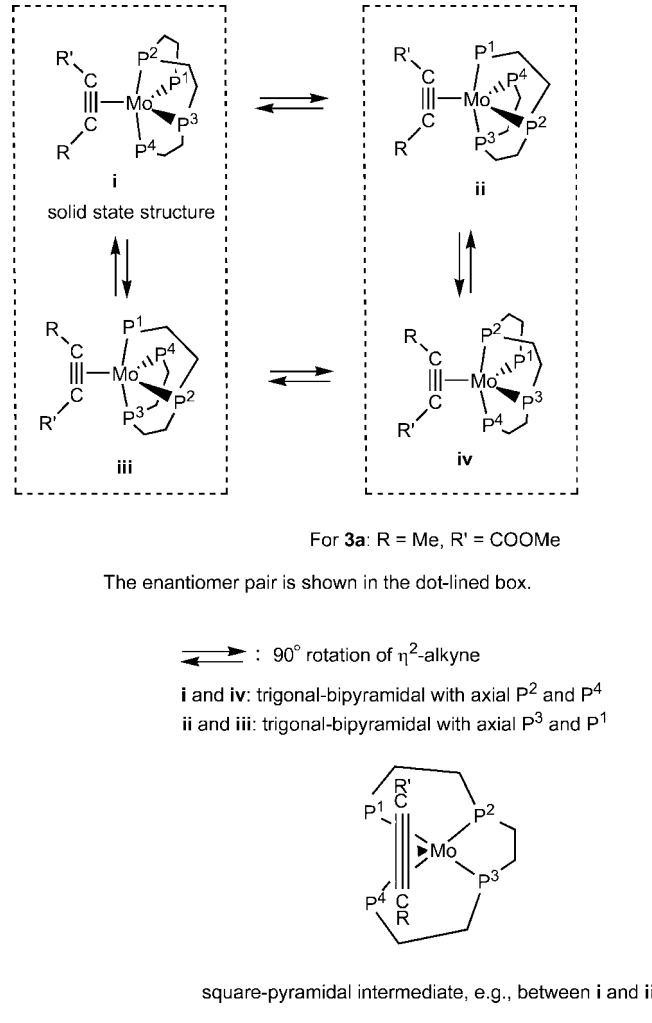
Scheme 1



with the alkyne molecule binding in parallel to the axial P(2)−P(4) vector. It is noteworthy that the P(2)−Mo−P(4) angles in **4a** at 155.80(3) and 157.90(3)° are considerably larger than that in **3a** (148.20(2)°). However, this difference does not affect the bonding parameters associated with the alkyne, that is, the Mo−C bond distances (2.060(3)−2.070(3) Å) as well as the alkynic C−C bond lengths (1.314(5) and 1.318(6) Å) and bent C≡C−C angles (132.4(3)−138.2(5)°) in **4a** are almost comparable to those in **3a** described above. On the other hand, in the unsubstituted alkyne complex **4d**,[5] the axial P−Mo−P angle is wider (161.28(5)°), while the Mo−C distances at 2.071(5) and 2.061(5) Å are analogous to those in **3a** and **4a**, although the alkynic C−C bond length of 1.265(7) Å is slightly shorter.

Fluxional Feature in Solution. The X-ray analysis of **3a** has disclosed the coordination of the alkyne parallel to the P(2)−P(4) vector, where the COOMe substituent points to the direction of the inner P(2) atom exclusively (**i** in Scheme 1). However, as for the ^{1}H NMR resonances of the ligated alkyne in **3a** at 20 °C, one somewhat broadened signal was observed for the COOMe protons, but the resonance due to the CMe protons was not assignable. On the other hand, the ^{31}P{^{1}H} NMR spectrum of **3a** at 20 °C showed two sets of four broad multiplets. Since these findings seemed to suggest the fluxional feature of **3a** in solution, the VT-NMR study has been carried out. As shown in Figure 4, the ^{31}P{^{1}H} NMR spectrum recorded at −20 °C showed eight multiplets, indicating clearly the presence of two isomers each consisting of four inequivalent P

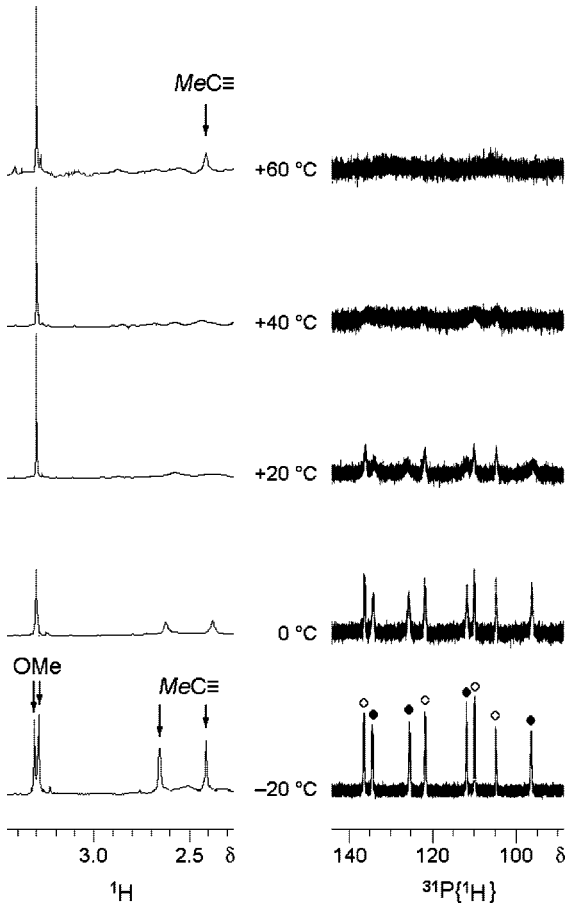


Figure 4. VT-NMR spectra of **3a** in toluene-d_8.

atoms. The ^{1}H NMR spectrum at the same temperature exhibited two sets of two singlets due to COOMe and CMe protons, showing also the presence of two isomers, the ratio of which was 0.53:0.47. The ^{13}C{^{1}H} NMR spectum at this temperature is consistent with these findings, displaying the signals suggesting the presence of two isomers in a ratio of approximately 1:1. As the recording temperatures were raised in a stepwise manner up to 60 °C, the ^{31}P{^{1}H} NMR signals broadened gradually and coalesced, while the ^{1}H NMR signals were converted finally to one singlet for COOMe protons and one broad peak for CMe protons. The ^{13}C{^{1}H} NMR spectrum at 40 °C also exhibited only one set of broad signals assignable to the alkynic C atoms. These spectral features may be interpreted in terms of the presence of two isomers containing the alkynes with different orientations, which may interconvert in the NMR time scale as shown in Scheme 1. Thus, upon starting from the solid-state structure **i**, rotation of the alkyne ligand around the Mo−alkyne bonding axis by 90° forms two isomers **ii** and **iii**, where **iii** corresponds to the enantiomer of **i**. This process also exchanges the axial and equatorial P atoms probably via the Berry mechanism involving a square-pyramidal intermediate since the orientation of the alkyne ligand parallel to the equatorial plane is energetically disfavored, as confirmed previously by the EHMO calculation using the model [Mo(η^2-HC≡CH)(PH$_3$)$_4$].[5] These reversible interconversions totally give two enantiomer pairs (**i**, **iii**) and (**ii**, **iv**) in equilibrium that are separable as two species from NMR criteria under appropriate conditions.

In contrast to the tetraphosphine complex **3a** with inequivalent axial P atoms, similar isomerization by the orientation of the alkyne does not occur in the case of the diphosphine complex

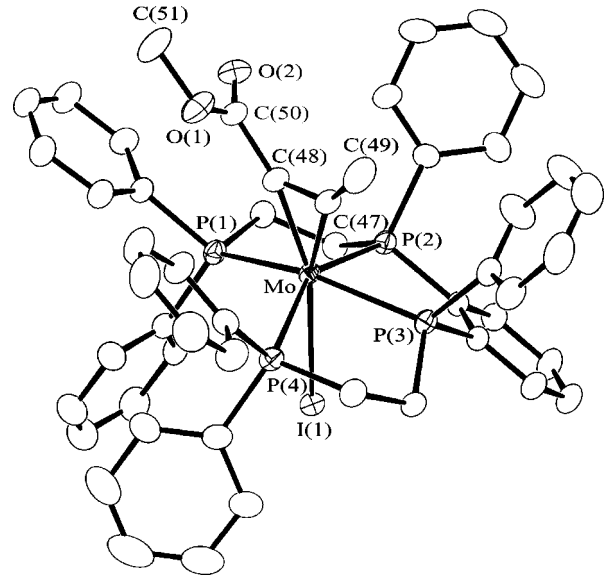


Figure 5. An ORTEP drawing for the cation in **5** at 30% probability level. Hydrogen atoms are omitted for clarity.

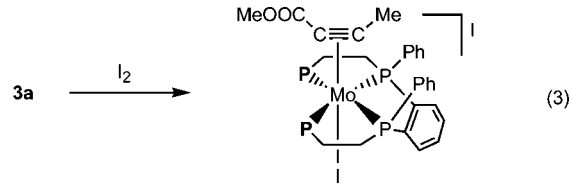
Table 3. Selected Bond Distances (Å) and Angles (°) in 5

(a) Bond Distance			
Mo−P(1)	2.581(1)	Mo−P(2)	2.478(1)
Mo−P(3)	2.487(1)	Mo−P(4)	2.547(1)
Mo−I	2.873(5)	Mo−C(47)	1.997(5)
Mo−C(48)	2.002(5)	C(47)−C(48)	1.328(7)
(b) Bond Angle			
P(1)−Mo−P(2)	79.76(4)	P(1)−Mo−P(3)	150.05(4)
P(1)−Mo−P(4)	113.71(4)	P(1)−Mo−I	78.32(3)
P(2)−Mo−P(3)	77.52(4)	P(2)−Mo−P(4)	150.83(4)
P(2)−Mo−I	78.78(3)	P(3)−Mo−P(4)	79.68(4)
P(3)−Mo−I	78.33(3)	P(4)−Mo−I	78.98(3)
C(47)−Mo−C(48)	38.8(2)	Mo−C(47)−C(48)	70.8(3)
Mo−C(47)−C(49)	155.1(4)	C(48)−C(47)−C(49)	133.5(5)
Mo−C(48)−C(47)	70.4(3)	Mo−C(48)−C(50)	157.2(4)
C(47)−C(48)−C(50)	132.3(5)		

4a. Thus, the ^{1}H NMR signals of the alkyne ligand in **4a** were resolved well in the whole temperature range of recording. However, the site exchange of P atoms exists. The ^{31}P{^{1}H} NMR spectra of **4a** at room temperature showed only one set of three slightly broadened resonances with the intensity ratio of 2:1:1 due to four essentially inequivalent P atoms, where two signals may be accidentally overlapping, which broadened further upon the increase in the recording temperature and were finally recorded as one broad signal at +80 °C. This indicates that the pseudorotation of alkyne is also occurring in **4a**. The observed coalescence temperature is lower for **3a** than that for **4a** probably because the square-pyramidal intermediate is more readily accessible for **3a** with the tetradentate ligand. Accordingly, from the NMR criteria, all three complexes **3** are highly fluxional, and their features are almost similar, whereas those of **4** clearly depend on the nature of the alkyne with the fluxionality decreasing in the order **4b** > **4c** > **4a**.

Reaction of 3a with Iodine. We have found that the reaction of **3a** with 1 equiv of I_2 in toluene at 0 °C affords the Mo(II)−alkyne complex [MoI(η^2-MeC≡CCOOMe)(κ^4-**P4**)]I (**5**) in moderate yield (eq 3). For comparison with the Mo(0)−alkyne complexes **3**, the structure of **5** has been determined by the X-ray diffraction as shown in Figure 5. Selected bond distances and angles are summarized in Table 3. It is worth noting that the related alkyne complexes [MoCl(η^2-RC≡CR′)(κ^4-**P4**)]Cl (R = Ph, R′ = H; R = *p*-tolyl, R′ = H; R = Me, R′ = Ph) were

isolated recently from the reactions of [$MoCl_2(\kappa^4$-**P4**)] (**6**) with RC≡CR′, but their X-ray structures were not available.[10]



(3)

5

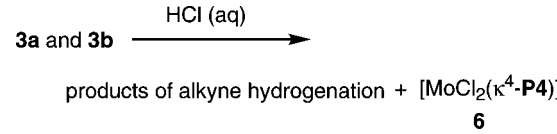
Complex **5** consists of a discrete cation of an octahedral structure with the linear tetraphosphine ligand at the equatorial four sites. One axial site is occupied by the alkyne π-bonded in the direction parallel to the Mo−P(1) bond, whereby the two C and two O atoms in the COOMe group oriented toward the P(1) atom are almost coplanar and this plane is twisted so that the π-stacking interaction is available with the phenyl group attached to P(1). At the trans site of the alkyne, the iodide ligand is present, and the phenylene group in **P4** is directed to this side of the equatorial plane.

The Mo−P bond lengths in the range of 2.47−2.59 Å for **5** are significantly longer than those in **3a** (2.36−2.44 Å), whereas the Mo−C distances at 1.997(5) and 2.002(5) Å in the former are considerably shorter than those in the latter at 2.075(2) and 2.062(2) Å. However, bonding parameters associated with the C−C≡C−C arrays of the coordinated MeC≡CCOOMe are almost comparable between **5** and **3a**, being consistent with the feature of the 4e-donating alkyne.[9b]

The $^{31}P\{^1H\}$ NMR spectra of **5** at room temperature showed two multiplets with the same intensity at δ 41.1 and 88.0 due to the outer and inner P atoms of **P4**, while the ^1H NMR spectrum at room temperature exhibited two sharp singlets at δ 1.20 and 3.13 assignable to CMe and OMe protons, respectively. These findings indicate that the orientation of the binding alkyne in **5** is not rigid in solution, which results in the equivalent feature of the two inner P atoms as well as the two outer P atoms on the NMR time scale.

Reactions of 3 and 4 with Acids. As for the reactivity of the coordinated alkyne toward acid,[11] Davies and co-workers reported briefly that the reaction of **4e** with HCl in THF at 25 °C gave predominantly [$MoCl_2(dppe)_2$] with the concomitant formation of 1-butene (69%) and *cis*-2-butene (10%) together with the liberation of 2-butyne (21%) and [$MoH_2Cl_2(dppe)_2$].[6] On the other hand, the reaction of **4d** with excess $HBF_4 \cdot OEt_2$ was reported to give the Mo(II) alkyne complex *trans*-[$MoF(\eta^2$-HC≡CH)$(dppe)_2$][BF_4] and H_2.[5] Now, we have studied the reactions of the tetraphosphine complexes **3a** and **3b** with aqueous hydrochloric acid, and these results have been compared with those of the reaction of the diphosphine complexes **4a** and **4b** conducted under the same conditions.

When the diphenylacetylene complex **3b** was treated with 2 equiv of concentrated HCl(aq) in THF at 0 °C for 1 h, *trans*-PhCH=CHPh was obtained in 62% yield as the major product together with $PhCH_2CH_2Ph$ (10%) and free diphenylacetylene (12%). Formation of *cis*-PhCH=CHPh was almost negligible. Presence of the dichloro complex **6** in the reaction mixture as the predominant Mo-containing product was confirmed by the $^{31}P\{^1H\}$ NMR spectroscopy (eq 4).[4] An increase in the amount of hydrochloric acid to 3 equiv afforded essentially the same results with respect to the yields of the products originating from the alkyne. On the other hand, similar treatment of **4b** with 2 equiv of HCl also resulted in the formation of *trans*-PhCH=CHPh as the predominant product, but its yield was much lower (31%). Concomitant formations of *cis*-PhCH=CHPh and $PhCH_2CH_2Ph$ in 8 and 4% yields, respectively, were observed together with the liberation of 20% of coordinated diphenylacetylene. It is to be noted that in the case of **4b**, the yields of the hydrogenation products become nearly comparable to those from **3b** by increasing the amount of HCl to 3 equiv, namely, *trans*-PhCH=CHPh, 52%; *cis*-PhCH=CHPh, 6%; $PhCH_2CH_2Ph$, 6%; and PhC≡CPh, 15%. Presence of [$MoH_2Cl_2(dppe)_2$][12] or [$MoCl_2(dppe)_2$][13] in these reaction mixtures was demonstrated by their NMR spectra. The related reactions converting coordinated alkynes into alkenes by treatment with protic acid have been reported for several transition-metal complexes of, for example, Mo,[14] W,[15] V,[16] Nb,[17] Ti,[18] Zr,[19] and Pt,[20] where preferential formation of *E*-isomers observed here was reported only for the Pt system.[20]



(4)

Interestingly, as shown in Table 4, the reaction of **3a** with 2 equiv of hydrochloric acid under analogous conditions gives a significant amount of the terminal alkene CH_2=$CHCH_2COOMe$ (10%) in addition to the expected inner alkenes *trans*-CH_3CH=CHCOOMe (36%) and *cis*-CH_3CH=CHCOOMe (4%) as well as the alkane $CH_3CH_2CH_2COOMe$ (13%), although the combined yield of these four was 63%. When the amount of HCl was increased, only the yield of CH_2=$CHCH_2COOMe$ increased, and it reached 44% by treatment with 4 equiv of HCl, where the total yield of these four compounds was 98%. The results for the reactions of **4a** with 2 and 12 equiv of hydrochloric acid under the analogous conditions are also shown in Table 4, indicating much lower combined yields of these four hydrogenated products than those from **3a**. From the reaction mixtures, [$MoH_2Cl_2(dppe)_2$][12] and [$MoCl(\eta^2$-MeC≡CCOOMe)$(dppe)_2$]Cl were isolated as the Mo-containing products. These findings may suggest that **4a** is more amenable to double protonation at the Mo center than **3a** and the generated dihydrido species [$MoH_2(\eta^2$-MeC≡CCOOMe)$(dppe)_2$]$^{2+}$ does not produce hydrogenated alkynes but releases alkyne or H_2 to give [$MoH_2Cl_2(dppe)_2$] and [$MoCl(\eta^2$-MeC≡CCOOMe)-$(dppe)_2$]Cl, respectively. It is also interesting to note that the reaction of the bis(alkyne) complex *trans*-[$Mo(\eta^2$-MeC≡CH$)_2(dppe)_2$] with excess HCl gas is known to give no free

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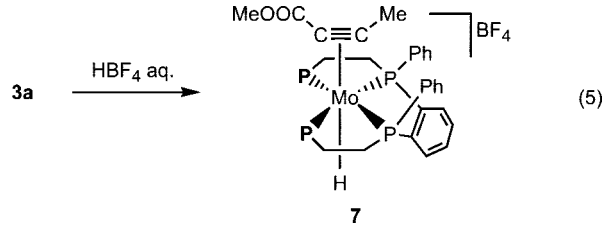
Table 4. Yields of Hydrogenation Products from the Reactions of 3a and 4a with Hydrochloric Acid

complex	HCl (equiv)	yields (%)					
							total
3a	2	36	4	10	13	0	63
3a	3	32	4	28	14	0	78
3a	4	30	7	44	17	0	98
4a	2	8	3	13	6	16	46
4a	3	10	6	14	4	16	50
4a	12	15	10	15	4	15	59

alkenes or alkanes but the vinyl species *trans*-[MoCl(CH-CHMe)(dppe)$_2$] together with 1 equiv of free MeC≡CH.[7]

Mechanism for the Hydrogenation of Coordinated Alkyne. When the reaction of **3a** with hydrochloric acid was monitored by the use of NMR spectroscopy, it was verified that the reaction mixture at the initial stages contained the species showing the characteristic hydride resonance at δ −4.13, which then disappeared with concurrent generation of the signals due to the alkenes. An analogous species was also detected for the reaction of **3b** with hydrochloric acid, which showed the hydride resonance at δ −3.80 as a triplet of triplets (J_{P-H} = 44 and 42 Hz) and two signals at δ 78.5 and 101.1 with the same intensities in the ^{1}H or ^{31}P{^{1}H} NMR spectrum, respectively. Attempts have been made to characterize these intermediates unambiguously, and it has turned out that careful treatment of **3a** with 1 equiv of HBF$_4$·Et$_2$O results in the isolation of the hydridoalkyne complex [MoH(η^2-MeC≡CCOOMe)(κ^4-**P4**)][BF$_4$] (**7**) as the possible initial intermediate for the hydrogenation reaction of the MeC≡CCOOMe complex **3a** (eq 6). The ^{31}P{^{1}H} NMR spectrum showing two broad signals with the same intensities at 20 °C as well as the ^{1}H NMR spectrum exhibiting the hydride resonance at δ −4.13 as a triplet of triplets is consistent with this proposed structure that is closely related to the X-ray analyzed structure of **5**.



Upon standing the solution overnight at room temperature, **7** has proved to be converted into the oxapentadienyl complex [Mo(η^3-CH$_2$CHCHCOOMe-κO)(κ^4-**P4**)][BF$_4$] (**8**) (eq 6), which was fully characterized by the X-ray crystallography. An ORTEP drawing is depicted in Figure 6, while selected bond distances and angles are listed in Table 5. As shown in Figure 6, **8** has an η^3-allyl group with the COOMe substituent at the anti position, where the carbonyl O atom is also binding to the Mo center. Four P atoms coordinate to the Mo center from the other side, comprising a basal plane. Three allyl C atoms C(48)−C(50) and the acyl O atom O(2) are almost coplanar, but the acyl C atom C(47) having no bonding interaction with Mo deviates by 0.26 Å from the least-squares plane defined by the above four atoms. The acyl-κO-η^3-allyl type ligand observed here was previously demonstrated, to the best of our knowledge,

Table 5. Selected Bond Distances (Å) and Angles (°) in 8

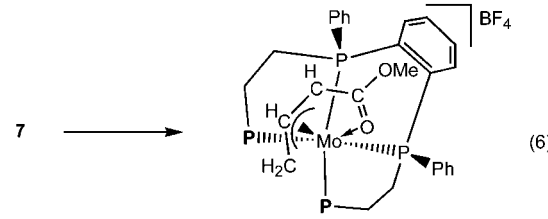
(a) Bond Distance

Mo−P(1)	2.4638(5)	Mo−P(2)	2.4226(4)
Mo−P(3)	2.4363(7)	Mo−P(4)	2.5523(6)
Mo−O(2)	2.306(1)	Mo−C(48)	2.329(3)
Mo−C(49)	2.320(3)	Mo−C(50)	2.334(2)
O(2)−C(47)	1.242(3)	C(47)−C(48)	1.445(4)
C(48)−C(49)	1.409(3)	C(49)−C(50)	1.373(4)
cf. Mo···C(47)	2.522(2)		

(b) Bond Angle

P(1)−Mo−P(2)	76.69(2)	P(1)−Mo−P(3)	104.23(2)
P(1)−Mo−P(4)	89.77(2)	P(2)−Mo−P(3)	75.89(2)
P(2)−Mo−P(4)	144.38(2)	P(3)−Mo−P(4)	75.84(2)
O(1)−C(47)−O(2)	123.2(2)	O(1)−C(47)−C(48)	114.2(2)
O(2)−C(47)−C(48)	122.6(2)	C(47)−C(48)−C(49)	123.8(2)
C(48)−C(49)−C(50)	122.8(2)		

for the Mn complex [Mn(PhCH$_2$CHCHCHCONMe$_2$)(CO)$_3$].[21] Analogous nonplanar η^5-oxapentadienyl ligands observed in certain Mn[22] and Rh[23] complexes were also interpreted in terms of the contribution of this acyl-κO-η^3-allyl structure. On the other hand, planar η^5-oxapentadienyl ligands were found in some Mn,[24] Re,[25] and Ru[26] complexes, in which the π-electrons are presumed to delocalize over three C—C and one C—O bonds. As for this Mn complex,[24] the bonding parameters associated with the oxametallacycle can rather be interpreted by the dienolate structure [Mn{CH$_2$=CHCH=C(Me)O}(CO)$_3$].



In consideration of these findings, the mechanism for the hydrogenation of alkynes might be proposed as follows (Scheme 2). After the migration of the hydride in the hydridoalkyne complexes (e.g., **7**) to the coordinated alkyne, the generated η^2-

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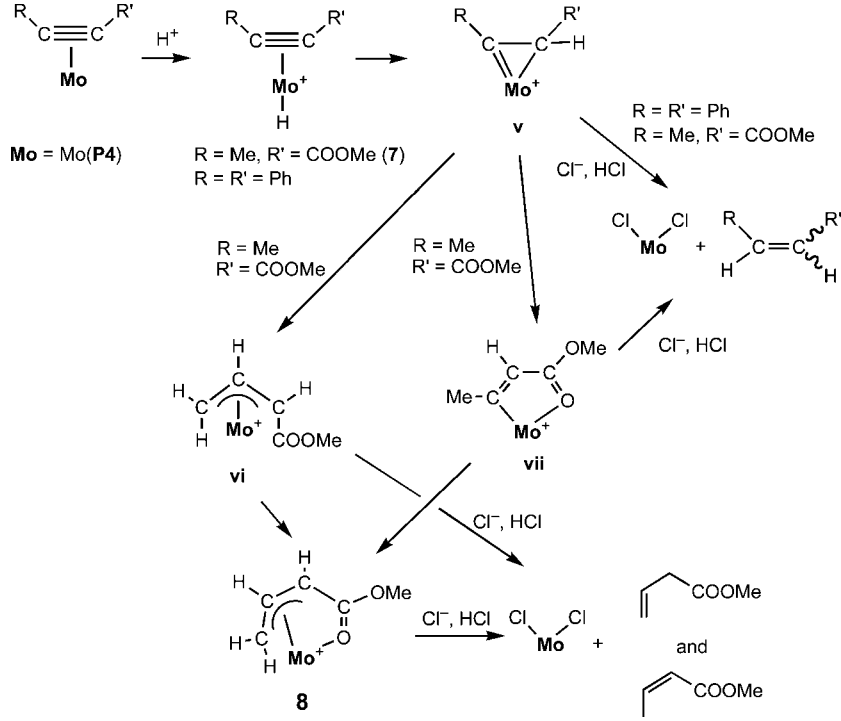
Scheme 2



vinyl species **v** affords cis- and trans-inner alkenes upon facile second protonation. On the other hand, in the case of MeC≡CCOOMe, a significant amount of **v** presumably isomerizes to the η^3-allyl species **vi** and **8**, which may produce predominantly the terminal alkene by the following second protonation. Due to the considerable stability of **8**, an excess amount of acid seems to be required to liberate the alkene from the Mo site of **8**.

Two intermediate stages may be considered further in the pathways from **v** (R = Me, R′ = COOMe) to **8**; one is the η^3-allyl {Mo(η^3-$CH_2CHCH-COOMe$)} species **vi** via the internal H-shift, which corresponds to the intermediate proposed previously for the reaction of **4e** with HX to give the inner and terminal alkenes (vide supra).[6] Transformations of η^2-vinyl complexes[27] to η^3-allyl species through H migration have been observed previously for the other Mo(II)[28] and W(II)[29] complexes. It might also be possible that the intermediate **vi** directly affords the alkene mixture in the presence of an excess amount of HCl. The other intermediate to **8** is the κ^2-*C*,*O*-vinyl {Mo(MeC═CHCOOMe)} species **vii**, and the complexes of this type are precedented, which include $[MoH_2(HC{=}CHCOOR)(dppe)_2][BF_4]$[30] together with some related Mo complexes.[31] Although these complexes were derived through the different reaction courses, formation of the κ^2-*C*,*O*-vinyl {M(HC═CHCOOMe)} complex from the hydrido complex with HC≡CCOOMe was demonstrated for M = Fe.[32]

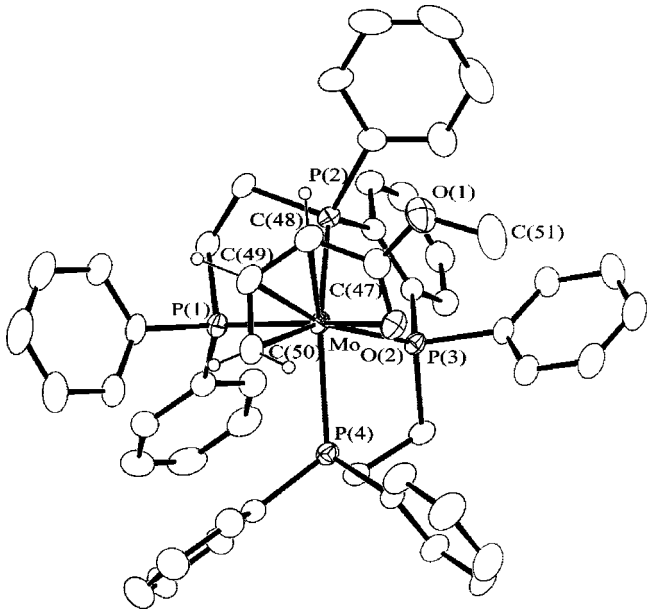


Figure 6. An ORTEP drawing for the cation in **8** at 30% probability level. Hydrogen atoms except for those of the allyl group are omitted for clarity.

Reactions of 3a and 3b with H_2S Gas. When **3a** dissolved in THF was treated with excess H_2S gas at room temperature, formation of $MeCH(SH)CH_2COOMe$ in 54% yield was observed in the reaction mixture. This thiol is presumably produced through the addition of H_2S to the hydrogenated product $CH_2{=}CHCH_2COOMe$. This was confirmed independently by treating this alkene with H_2S gas in THF, although this conversion into the thiol was considerably slower than its formation from **3a** and H_2S gas. On the other hand, the reaction of MeCH═CHCOOMe with H_2S did not proceed under these conditions. As the Mo-containing product, the expected bis(hy-

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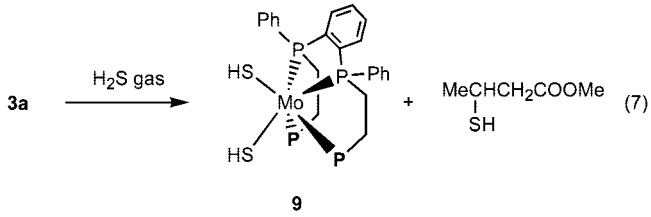
drosulfido) complex [Mo(SH)$_2$(κ^4-**P4**)] (**9**), having the trigonal-prismatic structure analogous to the dichloro complex **6**,[4] was isolated in 46% yield (eq 7). It has already been found separately by us that **9** can be obtained directly from the reaction of **1** with H_2S gas, and its structure has been determined in detail by the X-ray analysis, which will be reported elsewhere.[33] From the reaction of **3b** with H_2S gas, a mixture of *trans*- and *cis*-PhCH=CHPh (26 and 23% yields, respectively) was produced in addition to $PhCH_2CH_2Ph$ (12%) and free PhC≡CPh (2%), which presents a sharp contrast to the reactions of **3b** with 2 or 3 equiv of hydrochloric acid described above to give no *cis*-stilbene.



9

Conclusion

A series of Mo(0) tetraphosphine complexes [Mo(RC≡CR′)(**P4**)] (**3**) and their diphosphine analogues [Mo(RC≡CR′)(dppe)$_2$] (**4**) have been prepared and their trigonal-bipyramidal structures in a solid state fully characterized. These demonstrate the new candidates of the still rare five-coordinate Mo(0) complexes. In **3** and **4**, the alkynes occupying one equatorial site bind to the Mo center parallel to the axial P—P vector. The VT-NMR study has disclosed that these complexes are fluxional in solutions, where the rotation of the alkynes takes place probably via the square-pyramidal intermediates. Reactions of **3** and **4** with HCl(aq) in THF gave the mixtures of alkenes, alkanes, and liberated alkynes, the ratio of which sharply depends upon the nature of the alkynes, phosphines, and the ratio of HCl to the complex; for example, the **P4** comlexes **3** tend to give alkenes in higher yields than the dppe complexes **4**. Two new **P4** complexes **7** and **8** have been isolated as the intermediate stages in the hydrogenation reactions of coordinated alkyne in the MeC≡CCOOMe complex **3a**, and the mechanism for this hydrogenation reaction including **7** and **8** has been proposed.

Experimental Section

General. All manipulations were carried out under N_2 using standard Schlenk techniques. Solvents were dried by common methods and distilled under N_2 before use. Complexes **1**[1] and **2**[34] were prepared according to the literature methods, while other chemicals were obtained commercially and used as received.

NMR and IR spectra were measured on a JEOL alpha-400 or a JASCO FT/IR-420 spectrometer. The NMR data described below were obtained at 20 °C, except for those stated otherwise. For the ^{1}H NMR data, the signals due to phenyl, phenylene, and methylene groups are omitted. GC-MS analyses used Shimadzu GCMS QP5050 equipped with a CBP10 capillary column, while quantitative GLC analyses were by Shimadzu GC14B with a CBP1 or CBP10 capillary column. Elemental analyses were done with a Perkin-Elmer 2400 series II CHN analyzer.

Preparation of 3a. To a suspension of **1**·C_6H_6 (645 mg, 0.500 mmol) in toluene (20 mL) was added MeC≡CCOOMe (150 μL, 1.5 mmol), and a mixture was stirred for 4 h at 80 °C. A resultant red solution was concentrated, and hexane was added. Title compound **3a**·0.5$C_6H_5CH_3$ was obtained as red crystals (416 mg, 87% yield). ^{1}H NMR (C_6D_6): δ 3.33 (s, 3H, COOMe). The CMe protons could not be assigned (see text). ^{31}P{^{1}H} NMR (C_6D_6): δ 103.7 (m), 109.2 (m), 121.0 (m), and 135.2 (m) for the major isomer and 95.2 (m), 111.0 (m), 125.1 (m), and 133.2 (m) for the minor isomer. ^{13}C{^{1}H} NMR (THF-d_8, 40 °C): δ 19.2 (br, *Me*C), 26.3, 31.4 (br, PCH_2), 50.4 (s, OMe), 125−150 (m, aromatic), 172−178 (vbr, *C*CO_2Me), 180.5 (vbr, C=O), 186−192 (vbr, Me*C*). ^{13}C{^{1}H} NMR (THF-d_8, −20 °C): δ 18.8 (br d, J = 5 Hz, *Me*C), 20.3 (br d, J = 7 Hz, *Me*C), 24−34 (m, PCH_2), 50.4, 50.8 (s, OMe), 125−150 (m, aromatic), 173.9 (br d, J_{CP} = 20 Hz, *C*CO_2Me), 178.3 (br dd, J_{CP} = 20, 2 Hz, *C*CO_2Me), 179.7 (br d, J_{CP} = 7 Hz, C=O), 181.6 (br d, J_{CP} = 4 Hz, C=O), 186.0 (br dd, J_{CP} = 25, 8 Hz, Me*C*), 189.7 (br d, J_{CP} = 23 Hz, Me*C*). The ratio of the major and the minor isomers was about 1:1. IR (KBr): ν(C≡C), 1626; ν(C=O), 1675 cm^{-1}. Anal. Calcd for $C_{54.5}H_{52}MoO_2P_4$: C, 68.27; H, 5.47. Found: C, 68.34; H, 5.28.

Preparation of 3b. This product was obtained from the analogous reaction of **1**·C_6H_6 (648 mg, 0.502 mmol) and PhC≡CPh (267 mg, 1.50 mmol) in toluene (20 mL) at 80 °C for 6 h. The evaporated reaction mixture residue was extracted with ether, and after addition of hexane to the concentrated extract, **3b** was isolated as red crystals (418 mg, 84% yield). ^{31}P{^{1}H} NMR (C_6D_6): δ 101, 108, 125, 133 (br, 1P each). ^{13}C{^{1}H} NMR (THF-d_8, 40 °C): δ 26.8 (br t, J_{CP} = 19 Hz, PCH_2), 31.6 (br t, J_{CP} = 21 Hz, PCH_2), 122.9 (s, *p*-C of C*Ph*), 125.4 (br, *o*- or *m*-C of C*Ph*), 149.0 (s, *ipso*-C of C*Ph*), 126−154 (m, aromatic), 186−191 (vbr, C≡C). IR (KBr): ν(C≡C), 1633 cm^{-1}. Anal. Calcd for $C_{60}H_{52}MoP_4$: C, 72.58; H, 5.28. Found: C, 72.74; H, 5.57.

Preparation of 3c. This product was obtained from the analogous reaction of **1**·C_6H_6 (129 mg, 0.100 mmol) and PhC≡CMe (38 μL, 0.30 mmol) in toluene (5 mL) at 80 °C for 2 h. The evaporated reaction mixture residue was extracted with ether, and **3c** was obtained as red crystals after the storage of the concentrated extract at −20 °C for a week. However, crystals of **3c** deposited as a mixture with dppe and could not be purified despite repeated trials. ^{1}H NMR (THF-d_8, 40 °C): δ 2.18 (br s, MeC). ^{31}P{^{1}H} NMR (C_6D_6): δ 104, 110, 122, 134 (br, 1P each). ^{13}C{^{1}H} NMR (THF-d_8, 40 °C): δ 19.3 (br s, *Me*C), 26.3, 31.7 (br, PCH_2), 122.5 (s, *p*-C of C*Ph*), 124.8 (s, *o*- or *m*-C of C*Ph*), 149.9 (s, *ipso*-C of C*Ph*), 126−153 (m, aromatic), 184.3, 185.8 (br, C≡C). IR (KBr): ν(C≡C), 1643 cm^{-1}. Satisfactory analytical data were not available.

Preparation of 4a. A solution of **2** (495 mg, 0.522 mmol) and MeC≡CCOOMe (150 μL, 1.5 mmol) in benzene (20 mL) was refluxed for 3 h with stirring. The resultant dark red solution was filtered, and hexane was added to the concentrated filtrate to give **4a**·0.5C_6H_6 as red crystals (428 mg, 80% yield). ^{1}H NMR (C_6D_6): δ 2.70 (s, 3H, CMe), 3.18 (s, 3H, COOMe). ^{31}P{^{1}H} NMR (C_6D_6): δ 86.1 (m, 1P), 94.6 (m, 1P), 108.1 (m, 2P). ^{13}C{^{1}H} NMR (THF-d_8): δ 21.1 (br d, J_{CP} = 5 Hz, *Me*C), 33.5−34.5, 35−36 (m, PCH_2), 50.5 (s, OMe), 126−152 (m, Ph), 177.5 (br d, J_{CP} = 27 Hz, *C*CO_2Me), 180.5 (s, C=O), 189.9 (br d, J_{CP} = 33 Hz, Me*C*). IR (KBr): ν(C≡C), 1622; ν(C=O), 1683 cm^{-1}. Anal. Calcd for $C_{60}H_{57}MoO_2P_4$: C, 69.97; H, 5.58. Found: C, 69.86; H, 5.55.

Preparation of 4b. A solution of **2** (478 mg, 0.504 mmol) and PhC≡CPh (268 mg, 1.50 mmol) in benzene (25 mL) was refluxed for 3 h with stirring, and then, the resultant red suspension was filtered off. The red brown solid of **4b** was washed with benzene and dried in vacuo (318 mg). An additional amount of **4b** was obtained by refluxing the filtrate further for 3 h and concentrating the resultant mixture (45 mg). The combined yield was 67%. ^{31}P{^{1}H} NMR (THF-d_8): δ 90−95, 101−106 (br, 2P each). ^{13}C{^{1}H} NMR (THF-d_8): δ 123.0 (s, *p*-C of C*Ph*), 126.0, 127.0 (s, *o*- and *m*-C of C*Ph*), 149.7 (s, *ipso*-C of C*Ph*), 190.6 (m, C≡C); other signals were not assignable due to severe broadening. IR (KBr):

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Table 6. Crystal Data for $3a \cdot 0.5C_6H_5CH_3$, 3b, $4a \cdot 0.5C_6H_6$, $5 \cdot 3CH_2Cl_2$, and $8 \cdot 0.75Et_2O \cdot 0.25CH_2Cl_2$

	3a·0.5$C_6H_5CH_3$	**3b**	**4a**·0.5C_6H_6	**5**·3CH_2Cl_2	**8**·0.75Et_2O·0.25CH_2Cl_2
formula	$C_{54.5}H_{52}MoO_2P_4$	$C_{60}H_{52}MoP_4$	$C_{60}H_{57}MoO_2P_4$	$C_{54}H_{54}Cl_6I_2MoO_2P_4$	$C_{54.25}H_{57}BCl_{0.5}F_4MoO_{2.75}P_4$
fw	958.84	992.91	1029.94	1421.38	1077.41
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)
a, Å	11.649(1)	12.564(1)	13.615(2)	14.207(2)	12.972(2)
b, Å	13.909(1)	12.9979(3)	18.151(3)	26.132(3)	14.103(2)
c, Å	17.279(1)	17.618(2)	21.636(4)	15.818(2)	16.393(2)
α, deg	97.083(6)	94.064(6)	94.861(3)	90	65.491(4)
β, deg	105.394(6)	102.6552(3)	91.653(2)	90.2654(5)	73.284(5)
γ, deg	114.742(6)	115.018(5)	102.108(3)	90	81.146(6)
V, Å^3	2361.8(3)	2499.9(4)	5203(2)	5873(1)	2611.4(6)
Z	2	2	4	4	2
ρ_{calcd}, g cm^{-3}	1.348	1.319	1.315	1.607	1.370
crystal size, mm^3	0.40 × 0.30 × 0.30	0.40 × 0.30 × 0.15	0.40 × 0.40 × 0.30	0.50 × 0.30 × 0.10	0.50 × 0.35 × 0.15
no. of unique reflns	11192	11326	23508	13907	12381
no. of data ($I > 2\sigma(I)$)	9107	8822	16035	9081	9881
no. of variables	612	638	1354	683	755
transmn factor	0.678−0.873	0.719−0.938	0.674−0.882	0.547−0.844	0.688−0.934
*R*1[a]	0.036	0.036	0.063	0.054	0.038
*wR*2[b]	0.107	0.108	0.167	0.151	0.110
GOF[c]	1.005	1.009	1.020	1.043	1.029

[a] $R1 = \Sigma||F_o| - |Fc||/\Sigma|F_o|$ ($I > 2\sigma(I)$). [b] $wR2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma w(F_o^2)^2]^{1/2}$ (all data). [c] GOF = $[\Sigma w(|F_o| - |F_c|)^2/\{$(no. observed) − (no. variables)$\}]^{1/2}$.

ν(C≡C), 1607 cm^{-1}. Anal. Calcd for $C_{66}H_{58}MoP_4$: C, 74.02; H, 5.46. Found: C, 73.84; H, 5.41.

Preparation of 4c. This complex was obtained from **2** (474 mg, 0.500 mmol) and PhC≡CMe (190 μL, 1.5 mmol) in benzene (25 mL) in 40% yield (204 mg) by the procedure analogous to that for **4a**. ^{1}H NMR (C_6D_6): δ 2.60 (s, 3H, CMe). ^{31}P{^{1}H} NMR (C_6D_6): δ 88.3 (br, 1P), 94.6 (br, 1P), 98.8 (br, 1P), 102.8 (br, 1P). ^{13}C{^{1}H} NMR (THF-d_8): δ 21.0 (s, *Me*C), 33−37 (m, PCH_2), 123.0 (s, *p*-C of C*Ph*), 125.7, 127.5 (s, *o*- and *m*-C of C*Ph*), 150.5 (s, *ipso*-C of C*Ph*), 126−152 (m, PPh), 186.2 (br t, J_{CP} = 13 Hz, C≡C), 187.8 (br t, J_{CP} = 16 Hz, C≡C). IR (KBr): ν(C≡C), 1608 cm^{-1}. Anal. Calcd for $C_{61}H_{56}MoP_4$: C, 72.62; H, 5.59. Found: C, 72.78; H, 5.70.

Preparation of 5. Into a stirred solution of **3a**·0.5$C_6H_5CH_3$ (94 mg, 0.098 mmol) in toluene (2 mL) was added a solution of I_2 (25 mg, 0.10 mmol) in toluene (3 mL) through canulei at 0 °C. The mixture was continuously stirred at 0 °C for 3 h and then filtered off. Crystallization of the remaining solid from CH_2Cl_2−ether afforded **5**·3CH_2Cl_2 as green crystals. Several crystals were collected and sealed immediately in glass capillaries for the X-ray diffraction study. Other crystals were filtered off and dried thoroughly under vacuum, which were formulated as **5**·0.25CH_2Cl_2 from the ^{1}H NMR spectrum (62 mg, 53% yield). ^{1}H NMR ($CDCl_3$): δ 1.10 (s, 3H, CMe), 3.13 (s, 3H, COOMe), 5.30 (s, 0.5H, CH_2Cl_2). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 41.2, 88.0 (2P each); AA′XX′ pattern with $J_{A-X} + J_{A-X'}$ = 93 Hz. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 21.7 (s, *Me*C), 27.4 (br d, J_{CP} = 30 Hz, PCH_2), 33.9 (dd, J_{CP} = 31, 13 Hz, PCH_2), 52.5 (s, OMe), 127−150 (m, PPh), 172.8 (br t, J_{CP} = 5 Hz, C═O), 222.0 (dd, J_{CP} = 15, 6 Hz, ≡*C*COOMe), 236.7 (dd, J_{CP} = 13, 9 Hz, Me*C*≡). IR (KBr): ν(C═O), 1708 cm^{-1}. ν(C≡C), not assignable. Anal. Calcd for $C_{51.25}H_{48.5}Cl_{0.5}I_2MoO_2P_4$: C, 51.82; H, 4.12. Found: C, 51.25; H, 4.01.

Reactions of Alkyne Complexes with Aqueous HCl. Typical procedures are as follows. Aqueous HCl (35%) was added to a solution of **3** or **4** (0.10 mmol) in THF (4 mL) at 0 °C, and the mixture was stirred at this temperature for 1 h. Organic compounds produced were analyzed by GLC and GC-MS methods, where the yields were determined by the use of naphthalene (for **3a** and **4a**) or biphenyl (for **3b** and **4b**) as the internal standard.

Isolation of [MoCl(MeC≡CCOOMe)(dppe)$_2$]Cl. Into a stirred THF solution (4 mL) of **4a** (105 mg, 0.102 mmol) was added aqueous HCl (35%, 18 μL, 0.21 mmol) at 0 °C. After 1 h at 0 °C, the mixture was evaporated to dryness under reduced pressure, and the green residue was washed with ether. The residual solid was extracted with benzene (10 mL), and the remaining solid was crystallized from CH_2Cl_2−ether to afford [MoCl(MeC≡C-COOMe)(dppe)$_2$]Cl as green crystals (17 mg, 16% yield). The benzene extract was dried up, and the residue was crystallized from THF−ether, giving [MoH_2Cl_2(dppe)$_2$] as orange crystals (8 mg, 8% yield). Although the isolation was unsuccessful, the presence of *trans*-[$MoCl_2$(dppe)$_2$] in the reaction mixture was confirmed by its characteristic, paramagnetically shifted signals in the ^{1}H NMR spectrum. Data for [MoCl(MeC≡CCOOMe)(dppe)$_2$]Cl: ^{1}H NMR (CD_2Cl_2): δ 1.70 (s, 3H, CMe), 2.84 (s, 3H, OMe). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 40−43 (m). IR (KBr): ν(C═O), 1701 cm^{-1}. Satisfactory analysis data were not available even after repeated crystallization.

Preparation of 7. To a solution of **3a**·0.5$C_6H_5CH_3$ (95 mg, 0.099 mmol) in THF (3 mL) was added 54% HBF_4·Et_2O (14 μL, 0.10 mmol) at 0 °C. After stirring at this temperature for 40 min, ether (10 mL) was added slowly with stirring, and the mixture was filtered. The filtrate was dried up in vacuo at 0 °C, and the residual solid was washed repeatedly with ether. The yield of **7** as a purple solid was 47 mg (∼47%). Since **7** was thermally unstable and contained small amounts of impurities even after recrystallization, satisfactory analysis data were not available. ^{1}H NMR (CD_2Cl_2): δ −4.13 (tt, J_{P-H} = 45 and 41 Hz, 1H, MoH), 2.17 (s, 3H, CMe), 3.25 (s, 3H, COOMe). ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 81.7 (br, 2P), 99.7 (m, 2P). IR (KBr): ν(C═O), 1698 cm^{-1}.

Isolation of 8. Complex **7** (40 mg, ∼0.040 mmol) was dissolved in CH_2Cl_2 (2 mL), and ether (17 mL) was layered on it. After being kept at room temperature for 10 days, dark red crystals grown were collected by filtration. The filtrate was dried up in vacuo, and the residue was subjected to the same procedure two more times, affording **8**·0.75Et_2O·0.25CH_2Cl_2 in 56% combined yield (24 mg). From the NMR criteria, existence of two isomers in a ratio of 5:3 in equiribrium was confirmed at 0 °C, and significant broadening of the signals due to the exchange between these two was observed at the temperatures higher than 20 °C. ^{1}H NMR (CD_2Cl_2, 0 °C): δ 2.09 (s, OMe of the major isomer), 2.57 (s, OMe of the minor isomer), 1.12 (t, 4.5H, Et_2O), 3.40 (q, 3H, Et_2O), 5.31 (s, 0.5H, CH_2Cl_2). The signals due to π-allyl group were not assignable because of their overlapping with those of PCH_2 in the range δ 0.3−3.8. ^{31}P{^{1}H} NMR (CD_2Cl_2, 0 °C): δ 58.3 (ddd, J = 26, 25, 14 Hz), 77.6 (ddd, J = 31, 25, 10 Hz), 110.1 (ddd, J = 52, 26, 10 Hz), 119.1 (ddd, J = 52, 31, 14 Hz) for the major isomer and 49.8, 65.7, 120.2, 130.4 (m) for the minor isomer. IR (KBr): ν(C═O), 1549 cm^{-1}. Anal. Calcd for $C_{54.25}H_{57}BCl_{0.5}F_4MoO_{2.75}P_4$: C, 60.48; H, 5.33. Found: C, 60.52; H, 5.38.

Reactions of 3a with H_2S Gas. (1) Through a solution of **3a**·0.5$C_6H_5CH_3$ (96 mg, 0.10 mmol) in THF (3 mL), H_2S gas was bubbled for 10 min at 0 °C, and the mixture was stirred at room

temperature for 24 h. Complex **9** precipitated as a green solid, which was filtered off, washed with ether, and dried in vacuo (41 mg, 47% yield). Complex **9** was identified by comparing its ^{1}H and ^{31}P{^{1}H} NMR spectra with those of the authenticated complex.[33]

(2) After the analogous treatment of a solution of **3a**·0.5$C_6H_5CH_3$ (55 mg, 0.057 mmol) in THF-d_8 (2 mL), the yield of MeCH(SH)CH_2COOMe[35] was determined to be 54% by recording the ^{1}H NMR spectrum of the liquid phase using triphenylmethane as an internal standard. δ 1.32 (d, J = 6.8 Hz, 3H, MeC), 2.12 (d, J = 6.8 Hz, 1H, SH), 2.52 (dd, J = 16.0, 7.7 Hz, 1H, CH_2), 2.59 (dd, 1H, J = 16.0, 6.5 Hz, 1H, CH_2), 3.28 (m, 1H, MeC*H*), 3.62 (s, 3H, OMe). Formations of trace amounts of methyl tetrolate and its hydrogenation products were also observed.

X-ray Crystallography. Single crystals of **3a**·0.5$C_6H_5CH_3$, **3b**, **4a**·0.5C_6H_6, **5**·3CH_2Cl_2, and **8**·0.75Et_2O·0.25CH_2Cl_2 were sealed in glass capillaries under argon and mounted on a Rigaku mercury-CCD diffractometer equipped with a graphite-monochromatized Mo Kα source. All diffraction studies were done at 23 °C, whose details are listed in Table 6. The X-ray analysis was carried out also for **3c**, whose data are added in Supporting Information. Data collection were performed by using the CrystalClear program package.[36] All data were corrected for Lorentz and polarization effects as well as for absorption.

Structure solution and refinements were conducted by using the CrystalStructure program package.[37] The positions of non-hydrogen atoms were determined by Patterson methods (PATTY)[38] and subsequent Fourier synthesis (DIRDIF99).[39] These were refined with anisotropic thermal parameters by full-matrix least-squares techniques, while all hydrogens were placed at the calculated positions, except for those stated otherwise, and included at the final stages of the refinements.

In the crystal of **3a**·0.5C_6H_5Me, the solvating toluene was present at the center of symmetry, and the Me group was disordered over two positions with the same occupancies. The crystal of **4a**·0.5C_6H_6 contained two crystallographically independent molecules, in one of which the COOMe group was disordered over two positions with a 6:4 occupancy ratio. In **5**·3CH_2Cl_2, one Cl atom in one of the three solvating CH_2Cl_2 molecules was disordered over two positions in a ratio of 3:1. In the crystal of **8**·0.75Et_2O·0.25CH_2Cl_2, the position of solvating molecule was occupied by disordered Et_2O or CH_2Cl_2 in a ratio of 3:1. Hydrogen atoms in these molecules were not placed for calculation. Four H atoms in the allyl group were found from the Fourier map and refined isotropically.

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Supporting Information Available: Details of VT-NMR data for **3** and **4** and crystallographic data of **3a**·0.5$C_6H_5CH_3$, **3b**, **3c**, **4a**·0.5C_6H_6, **5**·3CH_2Cl_2, and **8**·0.75Et_2O·0.25CH_2Cl_2 in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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