Reactivity of *trans*-[M(CO)(DMF)($Ph_2PCH_2CH_2PPh_2$)$_2$] (M=Mo, W) toward Terminal Alkynes: Synthesis of Alkynylhydrido and Vinylidene Complexes

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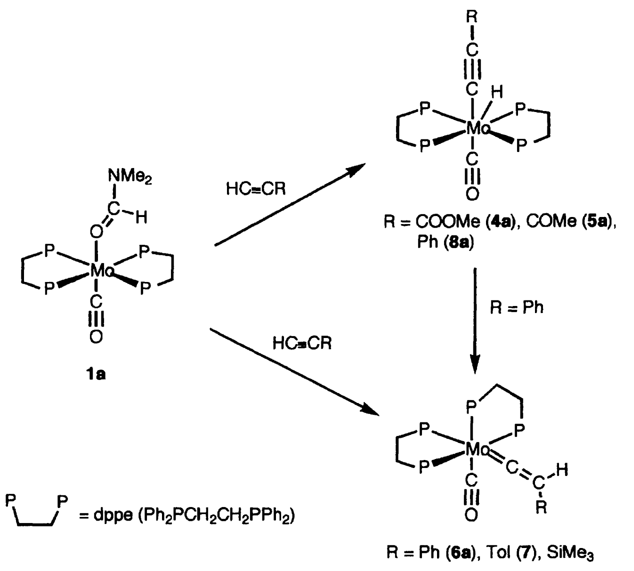
Treatment of *trans*-[Mo(CO)(DMF)(dppe)$_2$] (**1a**; dppe = $Ph_2PCH_2CH_2PPh_2$) with HC≡CCOOMe in benzene at room temperature or at reflux afforded an alkynylhydrido complex [Mo(C≡CCOOMe)H(CO)(dppe)$_2$] (**4a**), whereas the reactions of **1a** with arylacetylenes HC≡CR in benzene at reflux resulted in the formation of vinylidene complexes *cis*-[Mo(=C=CHR)(CO)(dppe)$_2$] (R = Ph (**6a**) or 4-MeC_6H_4). The W analogue *trans*-[W(CO)(DMF)(dppe)$_2$] (**1b**) gave only alkynylhydrido complexes [W(C≡CR)H(CO)(dppe)$_2$] (R = COOMe (**4b**) or Ph) by treatment with either HC≡CCOOMe or HC≡CPh. From the Mo vinylidene complex **6a** was obtained an alkylidyne complex *cis*-[Mo(≡CCH_2Ph)(CO)(dppe)$_2$]-[BF_4] (**9a**) upon treatment with aqueous HBF_4, whereas the reactions of Mo and W alkynylhydrido complexes **4** with HBF_4·Et_2O also resulted in the formation of the alkylidyne complexes *cis*-[M(≡CCH_2COOMe)(CO)(dppe)$_2$][BF_4] (**10**). The vinylidene complexes *cis*-[M(=C=CHCOOMe)(CO)(dppe)$_2$] (**11**) were readily derived from **10** by the reactions with NaOMe; these were not accessible from direct treatment of **1** with HC≡CCOOMe. The detailed structures of **4a**, **4b**, **9a**, and **11b** (M = W) have been established by single-crystal X-ray analyses.

We have previously reported that a Mo dinitrogen complex *trans*-[Mo(N_2)$_2$(dppe)$_2$] (dppe = $Ph_2PCH_2CH_2PPh_2$) reacts with excess DMF to give *trans*-[Mo(CO)(DMF)(dppe)$_2$] (**1a**).[1—3] Due to the labile nature of the DMF ligand, **1a** is readily converted to *trans*-[Mo(CO)(N_2)(dppe)$_2$] (**2a**) when kept under N_2 in a solution state without excess DMF. From **2a**, a coordinatively unsaturated complex [Mo(CO)(dppe)$_2$] (**3a**) is available by bubbling Ar gas into its solution.[1] Importantly, complex **3a** is highly reactive toward numerous substrates (L), e.g. amines, amides, olefins, nitriles, CO, N_2,[1,4] H_2,[5] and SiH_4,[6] to afford a wide range of zero-valent Mo complexes [Mo(CO)(L)(dppe)$_2$], including novel η^2-dihydrogen and η^2-silane complexes. The corresponding W complexes *trans*-[W(CO)(DMF)(dppe)$_2$] (**1b**), *trans*-[W(CO)(N_2)(dppe)$_2$] (**2b**), and [W(CO)(dppe)$_2$] (**3b**) are also accessible in essentially the same manner from *trans*-[W(N_2)$_2$(dppe)$_2$].[7] These W complexes have also proved to display interesting reactivities, which lead to the formation of a dihydrido complex [W(H)$_2$(CO)(dppe)$_2$] rather than a dihydrogen complex from the reaction of **3b** with H_2[7] and synthesis of a carbonatohydrido or carbamatohydrido complex [W(Y)H(CO)(dppe)$_2$] (Y = η^1-OCOOMe or η^2-O_2CNRR') by treatment of **2b** with CO_2 in the presence of MeOH or secondary amines, respectively.[8] It is noteworthy that a carbon dioxide complex *trans*-[W(CO)(η^2-CO_2)(dppe)$_2$] has successfully been derived from the carbamatohydrido complex.

In the course of our study on the reactivities displayed at the apparently vacant site in the isolated or in situ-generated complexes [M(CO)(dppe)$_2$], we have now investigated the reactions of **1a** and **1b** with terminal alkynes. This paper describes the formation of either alkynylhydrido or vinylidene complexes depending on the nature of the alkynes and metals. Both vinylidene and alkynyl complexes are currently attracting significant attention as useful synthons derived from alkynes in organic and organometallic syntheses.[9]

Results and Discussion

Reactions of 1a with Terminal Alkynes. When reacted with an equimolar amount of HC≡CCOOMe in benzene at room temperature, **1a** afforded an alkynylhydrido complex [Mo(C≡CCOOMe)H(CO)(dppe)$_2$] (**4a**) in 82% yield (Scheme 1). The reaction in refluxing benzene also gave **4a** as the only isolable product. For **4a**, the X-ray analysis has been undertaken to confirm the structure; results show the monocapped octahedral geometry with the CO and alkynyl ligands in mutually trans disposition (vide infra). IR data for **4a** are consistent with this structure, showing the ν(C≡C), ν(C≡O), and ν(C=O) bands at 2024, 1786, and 1655 cm^{-1}, respectively, although the ν(Mo–H) band was not assignable. In the ^1H NMR spectrum, the hydride proton appears at −5.28 ppm as a quintet with J_{P-H} = 42 Hz at room temperature, which is essentially unaltered even in the spectrum recorded at −85 °C. This indicates the non-rigid nature of **4a** in a solution state, as commonly observed for the related seven-coordinate hydrido complexes of Mo and W.[7,8,10] Reaction of **1a** with HC≡CCOMe proceeded similarly at room temperature to give an alkynylhydrido complex [Mo(C≡CCOMe)H(CO)(dppe)$_2$] (**5a**), whose IR and ^1H NMR



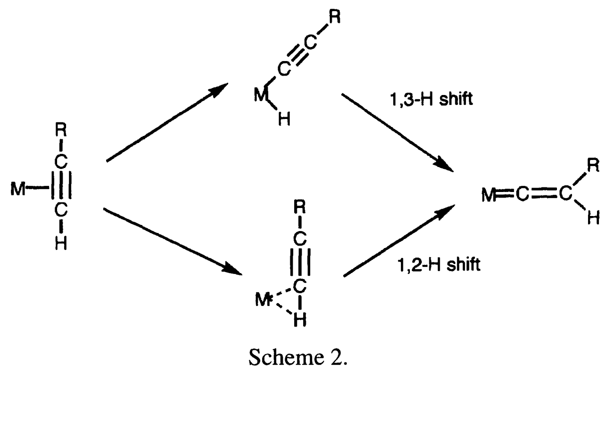
Scheme 1.

data (e.g. ν(C≡C), 2024 and 1991 cm^{-1};[11] ν(C≡O), 1806 cm^{-1}; δ(MoH) = −5.25 (quin)) are comparable to those of **4a**.

In contrast, treatment of **1a** with an equimolar amount of HC≡CPh or HC≡CTol (Tol = 4-MeC$_6$H$_4$) in benzene at reflux resulted in the formation of vinylidene complexes *cis*-[Mo(=C=CHR)(CO)(dppe)$_2$] (R = Ph (**6a**), Tol (**7**)) in moderate yields (Scheme 1). IR spectra of **6a** and **7** show strong ν(C=C) bands at 1509 and 1503 cm^{-1}, together with strong ν(C≡O) bands at 1809 and 1780 cm^{-1}, respectively. In the ^{1}H NMR spectra, the multiplet characteristic of the vinylidene proton appears at δ = 5.49 for both **6a** and **7**. Assignment of the vinylidene carbons was also attempted by using the ^{13}C NMR spectroscopy, but this was not successful owing to the low solubility or significant decomposition of these complexes in the common NMR solvents. *Cis* configuration of these vinylidene complexes is suggested by the ^{31}P NMR spectrum of **6a**, exhibiting four resonances at δ = 63.3, 57.6, 36.4, and 35.5. To confirm the structure, the X-ray crystallography was attempted by using single crystals of **6a**. However, due to the poor quality of the crystals, solution and refinements of its structure were unsuccessful. Formation of the *cis* complex in preference to the trans species may be interpreted in terms of a strong electron-withdrawing nature of the vinylidene ligand,[9,12] which favors the presence of the phosphine ligand rather than the CO in its *trans* position. The product from the reaction of **1a** with HC≡CSiMe$_3$ in benzene at reflux was unable to be isolated in an analytically pure form, but was characterized spectroscopically as a vinylidene complex *cis*-[Mo(=C=CHSiMe$_3$)(CO)(dppe)$_2$]. On the other hand, 1-octyne did not react with **1a** either at room temperature or under refluxing conditions in benzene.

Isomerization of terminal alkynes into vinylidene ligands is known to be facilitated by a significant number of coordinatively unsaturated metal moieties[9] and it is considered that this transformation proceeds via initial formation of the η^2-alkyne complex, followed by either a direct 1,2-hydrogen shift in the coordinated alkyne[13] or a 1,3-hydrogen shift via the alkynylhydrido intermediate (Scheme 2).[14] To get some insight into the reaction pathway toward the vinylidene complexes from **1a**, the reaction of **1a** with HC≡CPh was carried out under less forcing conditions, i.e. at 40 °C, and monitored by the ^{1}H NMR spectroscopy. Thus, the ^{1}H NMR spectrum of the reaction mixture recorded after 1 h clearly showed the presence of both the vinylidene complex **6a** and the alkynylhydrido complex [Mo(C≡CPh)H(CO)(dppe)$_2$] (**8a**), although the latter was characterized only spectroscopically.[15] The **6a**/**8a** ratio after 1 h estimated from the intensities of the vinylidene (Mo=C=C*H*Ph) and hydrido (Mo–*H*) signals was about 0.17; this increased to 1.6 and then to 2.3 after 20 and 53 h, respectively. This finding indicates that, in the reaction of **1a** with this alkyne, the alkynylhydrido complex **8a** initially formed is subsequently converted into the vinylidene complex **6a** (Scheme 1). On the other hand, the alkynylhydrido complex **4a** was not transformed into the corresponding vinylidene complex even under the refluxing conditions in benzene as described above. In the present reaction as well as all the other reactions reported herein, no η^2-alkyne complexes have been isolated or detected.

It is quite interesting that the fate of the terminal alkyne after interacting with the {Mo(CO)(dppe)$_2$} site is highly affected by the nature of the alkyne substituent. Recently Bianchini et al. have demonstrated the sequential transformation of terminal alkynes: {M(η^2-HC≡CR)} → {M(C≡CR)H} → {M(=C=CHR)}, at the [Co{(Ph$_2$PCH$_2$CH$_2$)$_3$P}]$^+$ site.[14] In this reaction, the vinylidene species is presumed to be produced through a 1,3-hydrogen shift from the alkynylhydrido species which is thermodynamically disfavored over the vinylidene species. With respect to this tautomerization, the stability of the alkynylhydrido form decreases in the order SiMe$_3$ > Ph > H > alkyls for the substituent R. Thus the product selectivity, viz. alkynylhydrido versus vinylidene, or the temperature at which the isomerization from the former to the latter occurs correlates to this order.[14] The present isolation of the alkynylhydrido complex **4a** as the sole product from the reaction with HC≡CCOOMe even at reflux in benzene suggests the high stability of the alkynylhydrido form, preventing its transformation into the vinylidene ligand. In contrast, the alkynylhydrido species generated from the reaction with HC≡CPh has been shown to be converted more readily into the vinylidene complex **6a**.

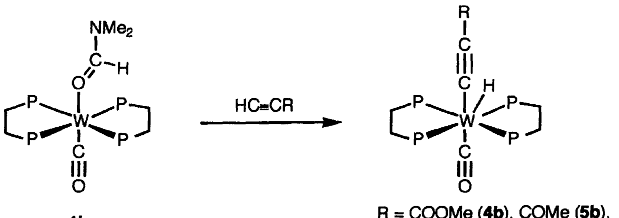


Scheme 2.

As for the Ir complexes, similar thermal rearrangement of the alkynylhydrido species $[IrCl(C{\equiv}CR)H(PPr^i_3)_2]$ into the vinylidene species $[IrCl(=C=CHR)(PPr^i_3)_2]$ has been observed ($R=SiMe_3$, Me, COOMe).[16] In the case of the Rh analogues, the alkynylhydrido species $[RhCl(C{\equiv}CR)H(PPr^i_3)_2]$ (R = H, Me, Ph) present in equilibrium with the alkyne complexes $[RhCl(\eta^2\text{-}HC{\equiv}CR)(PPr^i_3)_2]$ at room temperature have been shown to be quantitatively converted to the vinylidene complexes at higher temperatures.[17] For the formations of these Ir and Rh vinylidene complexes, an intermolecular process has been proposed for the hydrogen shift.

As a related work, it has previously been reported that the reactions of HC≡CR (R = Ph, COOMe, COOEt) with *trans*-$[M(N_2)_2(dppe)_2]$ (M = Mo, W) afford alkynyl complexes $[M(C{\equiv}CR)_2(H)_2(dppe)_2]$ and $[M(C{\equiv}CR)_2(dppe)_2]$.[18] A possible intermediate *trans*-$[M(HC{\equiv}CR)_2(dppe)_2]$ was isolable in the case of molybdenum. In these reactions at the $\{M(dppe)_2\}$ site, intermediary bis(alkyne) species may be formed in the first step; however, it does not lead to the formation of either monoalkynyl–monohydrido or vinylidene complexes. This is in a marked contrast to the reactions at the $\{Mo(CO)(dppe)_2\}$ site reported here.

Reactions of 1b with Terminal Alkynes. To compare the reactivities of the $\{Mo(CO)(dppe)_2\}$ site described above with those of the W analogue, the reactions of **1b** with HC≡CCOOMe, HC≡CCOMe, and HC≡CPh have also been investigated. Now we have found that treatment of **1b** with these alkynes gives the alkynylhydrido complexes $[W(C{\equiv}CR)H(CO)(dppe)_2]$ (R = COOMe (**4b**), COMe (**5b**), Ph (**8b**)) exclusively (Eq. 1).



1b

R = COOMe (**4b**), COMe (**5b**), Ph (**8b**)

(1)

Formation of the vinylidene species was not observed even in the reaction with HC≡CPh in hot benzene. These products were characterized spectroscpically, and for **4b** by the X-ray crystallography (vide infra). The IR spectra show the characteristic ν(C≡C) bands (**4b**: 2018, **5b**: 2029, 1991, **8b**: 2066 cm^{-1}) as well as the ν(C≡O) bands (**4b**: 1777, **5b**: 1813, **8b**: 1779 cm^{-1}). For **4b** and **5b**, the ν(C=O) bands due to the COOMe and COMe groups appear at 1649 and 1597 cm^{-1}, respectively. Frequencies of these characteristic bands observed for **4b** and **5b** differ only slightly from those of the Mo analogues **4a** and **5a**. The ^1H NMR spectra of **4b**, **5b**, and **8b** in C_6D_6 clearly indicate the presence of the hydrido ligands, although these high-field signals were recorded as the unresolvable broad singlets both at room temperature and at 60 °C.[19]

It is noteworthy that a vinylidene ligand is not formed at the $\{W(CO)(dppe)_2\}$ site even in the reaction with HC≡CPh. A comparable difference in reactivities of terminal alkynes toward the congenerous metals was previously manifested for the Co complex shown above and the related Rh complexes $[Rh\{(Ph_2PCH_2CH_2)_3P\}]^+$ and $[Rh\{Ph_2PCH_2CH_2)_3N\}]^+$. Thus, in the case of the Co complex, a series of vinylidene complexes is obtained from the corresponding alkynylhydrido complexes through tautomerization, whereas the Rh complexes give only alkynylhydrido complexes that are not convertible to vinylidene species under the similar conditions.[14,20] Formation of a stronger metal–hydride bond for Rh than for Co has been invoked to account for this difference.[14]

Reactions of terminal alkynes at the corresponding unsaturated group 6 and group 7 metal centers with the d^6 electronic configuration have been reported previously. These include the $\{W(CO)_3(dppe)\}$ and $\{ReCl(dppe)_2\}$ sites generated in situ from *fac*-$[W(CO)_3(dppe)(THF)]$ and *trans*-$[ReCl(N_2)(dppe)_2]$, respectively, and the isolated complexes $[TcCl(dppe)_2]$ and $[Re\{MeC(CH_2PPh_2)_3\}(CO)_2]^+$. However, all of these reactions led to the formation of the vinylidene complexes, i.e. *mer*-$[W(=C=CHR)(CO)_3(dppe)]$ (R = COOMe, Ph),[21] *trans*-$[ReCl(=C=CHR)(dppe)_2]$ (R = Et, Ph, COOMe, $SiMe_3$, etc.),[22] *trans*-$[TcCl(=C=CHR)(dppe)_2]$ (R = Me, Ph, ^{t}Bu),[23] and $[Re(=C=CHR)\{MeC(CH_2PPh_2)_3\}(CO)_2]^+$ (R = Ph, COOEt, C_6H_{13}).[24] Exclusive formation of the vinylidene ligand from both HC≡CCOOMe and HC≡CPh at the $\{W(CO)_3(dppe)\}$ site stands in an interesting contrast to the reaction at the $\{W(CO)(dppe)_2\}$ site reported here.

X-ray Structures of 4a and 4b. The X-ray analyses have been undertaken for both **4a** and **4b** to determine the detailed structures of these alkynylhydrido complexes. It is to be noted that, although numerous alkynyl complexes have been characterized by X-ray crystallography, the structures established for the alkynylhydrido complexes are still limited.[9c] Selected bond lengths and angles in **4** are listed in Table 1, while the ORTEP drawing and the atom numbering scheme for **4b** are shown in Fig. 1.

The structures of **4a** and **4b** are essentially identical and the corresponding bonding parameters in these two complexes are in good agreement with each other. Although the position of the hydrido ligand could not be located in the final difference Fourier maps for both complexes, the remaining six ligands constitute a distorted octahedron, with the alkynyl and the CO ligands occupying the mutually trans positions. As for the basal plane including four P atoms, two bite angles of the dppe ligands P(1)–M–P(2) and P(3)–M–P(4) are normal(76—79°). However, the P(2)–M–P(3) angles are significantly wider by ca. 20° than the P(1)–M–P(4) angles, indicating that the hydrido ligands are presumably present on the faces of the octahedron containing the P(2)–P(3) vector as one edge.

In the alkynyl moieties, the M–C(2)–C(3) and C(2)–C(3)–C(4) linkages are all essentially linear (173—175°), as commonly observed in the metal–alkynyl complexes. The C(2)–C(3) distance in **4b** at 1.160(6) Å is slightly shorter than those in most of the alkynyl complexes reported previously (the mean C≡C distance: 1.20 Å),[9c] but not unusual. The

Table 1. Selected Bond Distances and Angles in **4a** and **4b**

	4a (M=Mo)	**4b** (M=W)
(a) Bond distance (Å)		
M–P(1)	2.549(5)	2.541(1)
M–P(2)	2.458(5)	2.467(1)
M–P(3)	2.443(4)	2.441(1)
M–P(4)	2.513(4)	2.509(1)
M–C(1)	1.95(2)	1.971(5)
M–C(2)	2.23(2)	2.185(4)
C(1)–O(1)	1.17(1)	1.155(5)
C(2)–C(3)	1.21(2)	1.160(6)
C(3)–C(4)	1.42(2)	1.421(6)
C(4)–O(2)	1.22(2)	1.230(6)
C(4)–O(3)	1.27(2)	1.349(7)
O(3)–C(5)	1.39(2)	1.429(6)
(b) Bond angle (°)		
P(1)–M–P(2)	76.7(2)	76.88(5)
P(1)–M–P(3)	171.5(2)	170.83(4)
P(1)–M–P(4)	93.8(1)	93.34(4)
P(1)–M–C(1)	97.8(4)	98.0(1)
P(1)–M–C(2)	80.2(4)	81.4(1)
P(2)–M–P(3)	111.3(2)	112.05(4)
P(2)–M–P(4)	170.5(2)	170.15(5)
P(2)–M–C(1)	93.7(5)	92.7(1)
P(2)–M–C(2)	85.3(4)	86.0(1)
P(3)–M–P(4)	78.2(1)	77.77(4)
P(3)–M–C(1)	84.6(5)	84.0(1)
P(3)–M–C(2)	97.5(4)	96.8(1)
P(4)–M–C(1)	87.6(5)	87.5(1)
P(4)–M–C(2)	93.1(4)	93.8(1)
C(1)–M–C(2)	177.9(6)	178.6(2)
M–C(1)–O(1)	178(1)	177.4(4)
M–C(2)–C(3)	174(1)	174.4(4)
C(2)–C(3)–C(4)	173(1)	173.4(6)
C(3)–C(4)–O(2)	121(1)	125.9(6)
C(3)–C(4)–O(3)	112(1)	113.6(5)
O(2)–C(4)–O(3)	126(2)	120.5(6)
C(4)–O(3)–C(5)	116(1)	117.3(6)

C(2)–C(3) distance in the Mo complex **4a** (1.21(2) Å) is considerably longer than that in the W complex **4b**, but this feature is not discussed here further because of the fairly large estimated standard deviation for **4a** (0.02 Å).

Preparation and X-Ray Structure of an Alkylidyne Complex *cis*-[Mo(≡CCH$_2$Ph)(CO)(dppe)$_2$][BF$_4$] (9a). Treatment of the vinylidene complex **6a** with a slightly excess amount of an aqueous HBF$_4$ solution in THF smoothly afforded a cationic alkylidyne complex **9a** in moderate yield (Eq. 2), whose structure has been established unequivocally by the X-ray crystallography.

6a **9a**

(2)

The structure of the cation in **9a** is shown in Fig. 2, while

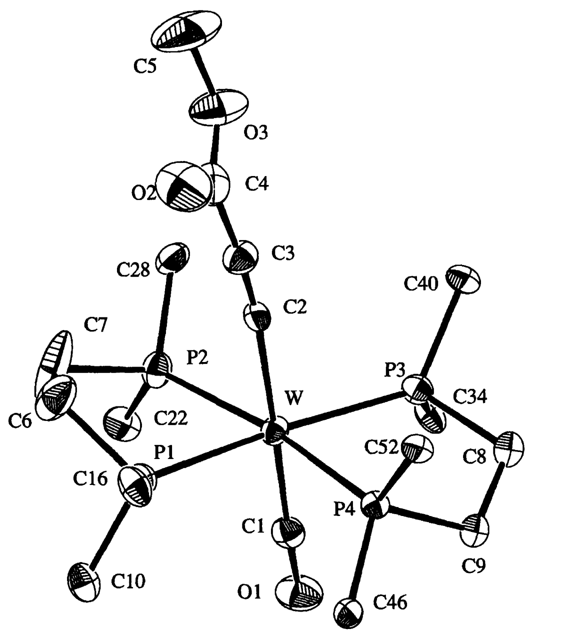


Fig. 1. Molecular structure of **4b**. Only the ipso-carbon atoms are shown for the phenyl groups in the dppe ligand.

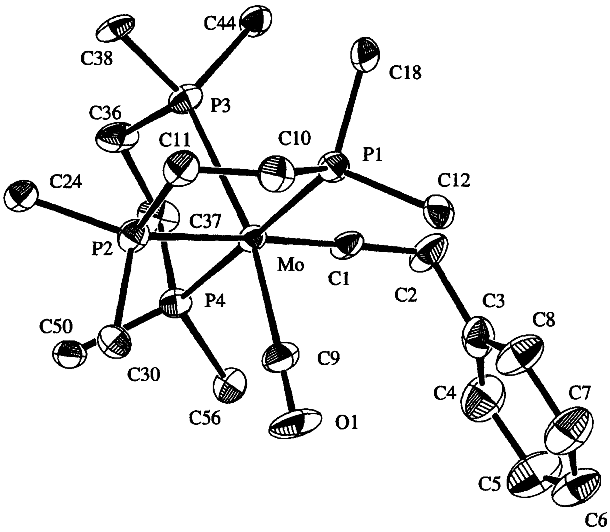


Fig. 2. Structure of the cation in **9a**. Only the ipso-carbon atoms are shown for the phenyl groups in the dppe ligand.

important bond lengths and angles are collected in Table 2.

The cation in **9a** has an octahedral structure, in which the alkylidyne and CO ligands occupy the mutually *cis* positions. The Mo–C(1)–C(2) linkage of the alkylidyne moiety is almost linear, with the angle of 177.5(7)°, and the quite short Mo–C(1) distance of 1.768(8) Å is diagnostic of the Mo–C triple bond. This Mo–C bond length is comparable to those in the other Mo(IV) alkylidyne complexes such as [MoCl(≡CPh) {P(OMe)$_3$}$_4$] (1.793(8) Å)[25] and [{Mo(≡CNEt$_2$)(CO)$_3$(μ-I)}$_2$] (1.795(18) Å).[26] It is to be noted that the Mo–P distances *trans* to the alkylidyne and CO ligands at 2.747(2) and 2.624(2) Å, respectively, are significantly longer than those for the mutually *trans* P atoms (2.501(3) and 2.508(2) Å). The difference between the former two Mo–P bond

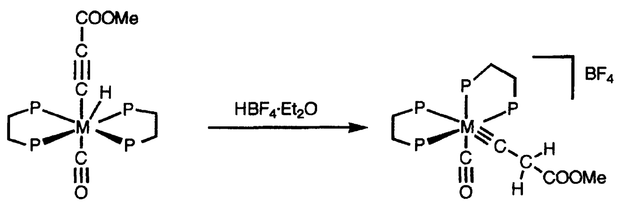
Table 2. Selected Bond Distances and Angles in **9a**

(a) Bond distance (Å)			
Mo–P(1)	2.501(3)	Mo–P(2)	2.747(2)
Mo–P(3)	2.624(2)	Mo–P(4)	2.508(2)
Mo–C(1)	1.768(8)	Mo–C(9)	2.030(8)
C(1)–C(2)	1.481(10)	C(2)–C(3)	1.52(1)
C(9)–O(1)	1.118(8)		
(b)Bond angle (°)			
P(1)–Mo–P(2)	77.95(8)	P(1)–Mo–P(3)	98.83(8)
P(1)–Mo–P(4)	176.28(9)	P(1)–Mo–C(1)	90.1(3)
P(1)–Mo–C(9)	90.2(2)	P(2)–Mo–P(3)	91.26(7)
P(2)–Mo–P(4)	104.85(8)	P(2)–Mo–C(1)	165.2(3)
P(2)–Mo–C(9)	83.4(3)	P(3)–Mo–P(4)	78.77(8)
P(3)–Mo–C(1)	99.2(2)	P(3)–Mo–C(9)	168.4(3)
P(4)–Mo–C(1)	87.5(3)	P(4)–Mo–C(9)	92.6(2)
C(1)–Mo–C(9)	88.0(3)		
Mo–C(1)–C(2)	177.5(7)	C(1)–C(2)–C(3)	115.9(7)
Mo–C(9)–O(1)	177.5(8)		

lengths reflects the stronger *trans* influence of the alkylidyne ligand than that of the CO ligand, as previously demonstrated for, e.g. *mer*-[W(≡CCH$_2$Ph)(dppe)(CO)$_3$][BF$_4$].[27]

Protonation of the vinylidene complex at the β-carbon atom affording the alkylidyne complex has previously been reported for the Mo and W complexes such as [MoBr(=C=CHPh)Cp{P(OMe)$_3$}$_2$],[28] [W(=C=CRR′)(CO)$_5$] (R=Bu^t, R′=Me, Et),[29] and [W(=C=CHPh)(CO)$_3$(dppe)].[21]

Preparation of Alkylidyne Complexes *cis*-[M(≡CCH$_2$COOMe)(CO)(dppe)$_2$][BF$_4$] (10) from Alkynylhydrido Complexes 4. Protonation of both Mo and W complexes **4** with a stoichiometric amount of HBF$_4$·Et$_2$O in THF resulted in the formation of alkylidyne complexes **10** in moderate to high yields (Eq. 3).



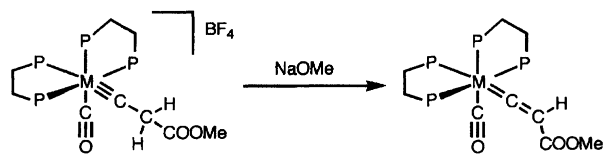
4 **10**

(3)

No intermediate stages have been isolated or detected. However, since it has been demonstrated well that the alkynyl ligand is susceptible to protonation at the β-carbon to give the vinylidene ligand,[9a)] the alkylidyne complexes **10** probably result from the initial formation of the hydridovinylidene intermediate [M(=C=CHCOOMe)H(CO)(dppe)$_2$][BF$_4$] followed by the rapid tautomerization. Formation of alkylidyne complexes from alkylhydrido complexes has rarely been observed; conversion of [W(C≡CCOOMe)$_2$(H)$_2$(dppe)$_2$] into [W(≡CCH$_2$COOMe)F(dppe)$_2$] by treatment with HBF$_4$·Et$_2$O is, to our knowledge, the only precedented example.[18] A hydridovinylidene intermediate was proposed also for this reaction, although no experimental evidence was available.[18] Up to now, only a few hydridovinylidene complexes have been isolated in a well-defined manner; these are, however, known to be converted into not the alkylidyne but rather the vinyl complexes, e.g. [Ta(=C=CH$_2$)(Cp*)$_2$H] into [Ta(CH=CH$_2$)(Cp*)$_2$(CO)] upon treatment with CO (Cp*=η^5-C$_5$Me$_5$)[30] and [Os(=C=CHCy)ClH(CO)(PPr$^i_3$)$_2$] into [Os(CH=CHCy)Cl(CO)(PPr$^i_3$)$_2$] (Cy=cyclohexyl).[31]

The ^{13}C NMR spectra showed the low-field resonances at 298 and 288 ppm for **10a** and **10b**, respectively, which are diagnostic of the alkylidyne carbon, whereas the ^{31}P NMR spectra exhibited four signals at 56.3, 53.1, 42.5, and 16.5 ppm for **10a** and 45.8, 42.2, 38.7, and 10.3 ppm for **10b**, indicating the cis structure for **10**. It is noteworthy that despite the presence of the alkynyl ligand trans to the CO ligand in **4**, the alkylidyne ligands in **10** occupy the cis position with respect to the CO ligand.

Preparation of Vinylidene Complexes *cis*-[M(=C=CHCOOMe)(CO)(dppe)$_2$] (11) from Alkylidyne Complexes 10 and X-Ray Structure of 11b (M=W). The vinylidene complexes **11**, which are not available directly from the reactions of HC≡CCOOMe with **1** because of the exclusive formation of the alkynylhydrido complexes **4**, have now been obtained through deprotonation of the alkylidyne complexes **10** with a base. Thus, when reacted with excess NaOMe in benzene, **10** were readily converted into **11** through the removal of one methylene proton in the alkylidyne ligand (Eq. 4).



10 **11**

(4)

The alkynylhydrido complexes **4** were not at all present in these reaction mixtures. Furthermore, **11b** was confirmed to be stable and recovered quantiatively even after heating at 90 °C for 1 h in toluene. These findings suggest that, not only the alkynylhydrido complexes **4** as described already, but also the vinylidene complexes **11** are thermally stable and the interconversion between these two tautomers requires a considerably energy.

For **11b**, single crystals suitable for X-ray analysis were obtained as the two C$_6$H$_6$ solvates and the structure has been determined in detail. The ORTEP drawing is shown in Fig. 3 and the important bonding parameters are listed in Table 3. The molecule has a distorted octahedral structure with the CO and vinylidene ligands in mutually cis positions. The W–C and C$_\alpha$–C$_\beta$ bond lengths in the vinylidene ligand are 1.88(1) and 1.36(1) Å, respectively, and the W–C–C angle is essentially linear with 171.2(9)°. These values are comparable to those in [W(=C=CHCOOMe)(CO)$_3$(dppe)] at 1.98(1) Å, 1.30(1) Å, and 173(1)°, respectively,[21] being in accordance with the expected W=C=C linkage. Six non-hydrogen atoms in the vinylidene ligand are almost coplanar with the largest deviation from the least-squares plane defined by these six

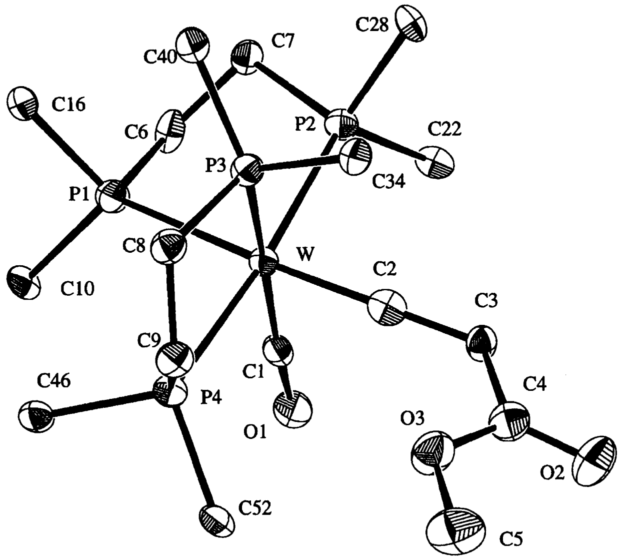


Fig. 3. Molecular structure of **11b**. Only the ipso-carbon atoms are shown for the phenyl groups in the dppe ligand. Solvating C_6H_6 molecules are also omitted.

Table 3. Selected Bond Distances and Angles in **11b**·$2C_6H_6$

a) Bond distance (Å)			
W–P(1)	2.604(3)	W–P(2)	2.482(3)
W–P(3)	2.561(3)	W–P(4)	2.477(3)
W–C(1)	1.89(1)	W–C(2)	1.88(1)
O(1)–C(1)	1.23(1)	C(2)–C(3)	1.36(1)
C(3)–C(4)	1.42(1)	C(4)–O(2)	1.25(1)
C(4)–O(3)	1.37(1)	O(3)–C(5)	1.43(1)
b) Bond angle (°)			
P(1)–W–P(2)	78.96(10)	P(1)–W–P(3)	103.11(9)
P(1)–W–P(4)	95.86(10)	P(1)–W–C(1)	83.6(3)
P(1)–W–C(2)	166.8(3)	P(2)–W–P(3)	97.98(10)
P(2)–W–P(4)	174.5(1)	P(2)–W–C(1)	91.1(3)
P(2)–W–C(2)	91.7(3)	P(3)–W–P(4)	81.21(10)
P(3)–W–C(1)	169.6(3)	P(3)–W–C(2)	87.4(3)
P(4)–W–C(1)	90.3(3)	P(4)–W–C(2)	93.7(3)
C(1)–W–C(2)	87.2(2)	W–C(1)–O(1)	176.2(9)
W–C(2)–C(3)	171.2(9)	C(2)–C(3)–C(4)	127(1)
C(3)–C(4)–O(2)	127(1)	C(3)–C(4)–O(3)	114(1)
O(2)–C(4)–O(3)	118(1)	C(4)–O(3)–C(5)	117(1)

atoms of 0.060(10) Å observed for C(3). As for the W–P distances, the W–P(1) bond distance trans to the vinylidene ligand at 2.604(3) Å is longer than the W–P(3) bond distance trans to the CO ligand (2.561(3) Å). As demonstrated for the alkylidyne ligand in **9a**, this result also implicates the stronger trans influence associated with the vinylidene ligand than that of the CO ligand.[21]

A vinylidene complex *cis*-[W(=C=CHPh)(CO)(dppe)$_2$] (**6b**) was also able to be synthesized by following this route. Thus, treatment of the alkynylhydrido complex **8b** with HBF_4·Et_2O afforded an alkylidyne complex *cis*-[W(≡CCH$_2$Ph)(CO)(dppe)$_2$][BF$_4$] (**9b**), which was further converted into the vinylidene complex **6b** upon deprotonation by NaOMe.

Experimental

All manipulations were carried out under N_2 using Schlenk tube techniques. Solvents were dried and distilled under N_2. Complexes **1a**[1] and **1b**[7] were prepared as previously described. Alkynes were obtained commercially and degassed before use, while aqueous HBF_4 (42%) and HBF_4·Et_2O (85%) were used as received. IR and NMR spectra were recorded on Shimadzu DR-8000 and JEOL EX-270 spectrometers, respectively. For the ^{1}H NMR data below, resonances due to the phenyl protons are omitted. Chemical shifts of the ^{31}P NMR spectra were referred to external 85% H_3PO_4. Elemental analyses were performed by a Perkin–Elmer 2400II CHN analyzer.

Preparation of [Mo(C≡CCOOMe)H(CO)(dppe)$_2$] (4a). To a dark red solution of **1a** (302 mg, 0.304 mmol) in benzene (15 ml) was added HC≡CCOOMe (0.029 ml, 0.32 mmol), and the mixture was stirred at room temperature for 24 h. Addition of hexane (100 ml) to the resultant brown solution deposited a brown solid, which was collected by filtration and recrystallized from benzene/hexane (250 mg, 82%). Found: C, 67.78; H, 5.18%. Calcd for $C_{57}H_{52}O_3P_4Mo$: C, 68.13; H, 5.22%. IR (KBr), ν(C≡C), 2024; ν(C≡O), 1786; ν(C=O), 1655 cm^{-1}; ^{1}H NMR (C_6D_6) δ=3.55 (s, 3H, COOMe), 2.52—2.32 (br m, 8H, PCH$_2$), −5.28 (quin, 1H, J_{P-H}=42 Hz, MoH).

Preparation of [Mo(C≡CCOMe)H(CO)(dppe)$_2$] (5a). After HC≡CCOMe (0.007 ml, 0.09 mmol) was added to **1a** (88.6 mg, 0.0891 mmol) in benzene (5 ml), the mixture was stirred at room temperature for 20 h. The resultant brown solution was dried up in vacuo and the residue was crystallized from THF/hexane, yielding the brown crystals of the title compound as mono THF solvate (43.6 mg, 46%). Found: C, 69.23; H, 5.34%. Calcd for $C_{57}H_{52}O_2P_4W$·C_4H_8O: C, 69.06; H, 5.70%. IR(KBr) ν(C≡C), 2024, 1991; ν(C≡O), 1806; ν(C=O), 1613 cm^{-1}; ^{1}H NMR (C_6D_6) δ=1.88 (s, 3H, COMe), 2.0—2.7 (br m, 8H, PCH$_2$), −5.25 (quin, J_{P-H}=30 Hz, 1H, MoH), 1.42 and 3.57 (m, THF).

Preparation of *cis*-[Mo(=C=CHPh)(CO)(dppe)$_2$] (6a). To a solution of **1a** (1.51 g, 1.52 mmol) in benzene (80 ml) was added HC≡CPh (0.18 ml, 1.59 mmol), and the mixture was stirred at reflux for 3 h. After cooling to room temperature, hexane (200 ml) was added to the resultant brown solution. A brown crystalline solid which precipitated was filtered off, washed with hexane, and then dried in vacuo, affording **6a**·$2C_6H_6$ (1.04 g, 74%). The presence of solvating C_6H_6 molecules was confirmed by the ^{1}H NMR spectrum of its THF-d_8 solution. Found: C, 74.00; H, 5.71%. Calcd for $C_{61}H_{54}OP_4Mo$·$2C_6H_6$: C, 74.36; H, 5.64%. IR(KBr) ν(C≡O), 1809; ν(C=C), 1509 cm^{-1}; ^{1}H NMR (C_6D_6) δ=5.49 (m, 1H, C=C*H*Ph), 2.79—1.83 (br m, 8H, PCH$_2$); ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$) δ=34.4 (d, J_{P-P}=24 Hz, 1P), 35.0 (d, J_{P-P}=24 Hz, 1P), 56.3 (dd, J_{P-P}=24 and 83 Hz, 1P), 63.1 (dd, J_{P-P}=24 and 83 Hz, 1P); the smaller P–P couplings could not be resolved.

Preparation of *cis*-[Mo(=C=CHTol)(CO)(dppe)$_2$] (7). This complex was prepared by essentially the same method as that for **6a** and characterized spectroscopically. Yield, 85%. IR (KBr), ν(C≡O), 1780; ν(C=C), 1503 cm^{-1}. ^{1}H NMR (C_6D_6) δ=5.49 (m, 1H, C=C*H*Tol), 2.81—1.86 (br m, 8H, PCH$_2$), 2.21 (s, 3H, Me in Tol).

Preparation of *cis*-[Mo(=C=CHSiMe$_3$)(CO)(dppe)$_2$]. A solution containing **1a** (733 mg, 0.727 mmol) and HC≡CSiMe$_3$ (0.20 ml, 1.4 mmol) in benzene (10 ml) was refluxed for 6 h. After cooling, the resultant solution was concentrated in vacuo. Addition of hexane deposited the orange solid, which was washed with hexane and dried (622 mg, 82%). Elemental analysis data of this product were unsatisfactory and the attempts at purification by

Table 4. X-Ray Crystallographic Data for **4a**, **4b**, **9a**, and **11b**·$2C_6H_6$

	4a	**4b**	**9a**	**11b**·$2C_6H_6$
(a) Crystal data				
Empirical formula	$C_{57}H_{52}O_3P_4Mo$	$C_{57}H_{52}O_3P_4W$	$C_{61}H_{55}OBF_4P_4Mo$	$C_{57}H_{55}O_3P_4W\cdot 2C_6H_6$
Formular weight	1004.9	1092.8	1110.7	1249.0
Crystal color	Yellow	Yellow	Yellow	Orange
Crystal dimension/mm	0.1×0.1×0.3	0.3×0.4×0.5	0.3×0.3×0.5	0.15×0.20×0.35
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$(No.14)	$P2_1/n$(No.14)	$P2_1/n$(No.14)	$P2_1/c$(No.14)
a/Å	16.983(3)	16.973(1)	12.145(4)	12.304(4)
b/Å	17.131(3)	17.099(2)	22.829(8)	18.306(3)
c/Å	17.307(3)	17.334(1)	19.773(3)	26.696(4)
β/deg	103.84(1)	103.85(1)	104.74(2)	99.89(2)
Vol/Å^3	4888(1)	4884.5(6)	5031(2)	5923(2)
Z	4	4	4	4
d(calcd)/g cm^{-3}	1.365	1.486	1.391	1.400
F(000)/electron	2080	2208	2288	2544
μ(Mo $K\alpha$)/cm^{-1}	4.43	25.43	4.24	21.07
(b) Data collection				
Radiation		Mo $K\alpha$(λ=0.7107Å)		
Monochromator		Graphite		
Temperature		Room temperature		
Scan method		ω–2θ		
Scan rate/deg min^{-1}		16		
$2\theta_{max}$/deg		55		
No. of unique reflections	9157	11603	9600	14025
Transmission factors	0.903 — 1.00	0.854 — 0.999	0.742 — 1.00	0.859 — 1.00
(c) Structure solution and refinements				
No. of data used	2757($I>2.5\sigma(I)$)	7285 ($I>3.0\sigma(I)$)	4854 ($I>3.0\sigma(I)$)	5679 ($I>3.0\sigma(I)$)
No. of variables	586	586	649	694
R, R_w	0.076, 0.042	0.036, 0.022	0.062, 0.037	0.056, 0.039
Max residual/electron Å^{-3}	0.69	1.05	0.93	1.50

recystallization resulted in the decomposition of the compound. IR (KBr) ν(CO), 1790; ν(C=C), 1516 cm^{-1}; δ(SiMe)=1238; ^{1}H NMR (C_6D_6) δ=0.1 (s, 9H, SiMe), 1.6—2.9 (br m, 8H, PCH_2), 4.09 (m, 1H, CHSi); ^{31}P{^{1}H} NMR (C_6D_6) δ=36.3 (dd, J_{P-P}=7 and 23 Hz, 1P), 38.8 (dd, J_{P-P}=7 and 24 Hz, 1P), 60.3 (dd, J_{P-P}=24 and 86 Hz, 1P), 64.0 (dd, J_{P-P}=23 and 85 Hz, 1P); the smaller P–P coupling could not be resolved.

Preparation of [W(C≡CCOOMe)H(CO)(dppe)$_2$] (4b). A benzene solution (10 ml) of **1b** (249 mg, 0.230 mmol) and HC≡CCOOMe (0.019 ml, 0.23 mmol) was stirred at 60 °C for 4 h and a resultant brown solution was concentrated in vacuo. Addition of hexane afforded **4b** as yellow crystals (158 mg, 63%). Found: C, 62.55; H, 5.09%. Calcd for $C_{57}H_{52}O_3P_4W$: C, 62.65; H, 4.80%. IR (KBr disk) ν(C≡C), 2018; ν(C≡O), 1777; ν(C=O), 1649 cm^{-1}; ^{1}H NMR (C_6D_6, 60°C) δ=−3.0 (br s, 1H, WH), 2.2—2.6 (br m, 8H, PCH_2), 3.6 (s, 3H, COOMe); see also Ref. 19.

Preparation of [W(C≡CCOMe)H(CO)(dppe)$_2$] (5b). After HC≡CCOMe (0.056 ml) was added into a solution of **1b** (728 mg, 0.714 mmol) in benzene (30 ml), the mixture was stirred at room temperature for 20 h. The resulting solution was dried up in vacuo and the brown residue was crystallized from THF/hexane. The title compond was isolated as monoTHF solvate (467 mg, 61%). Found: C, 64.18; H, 5.39%. Calcd for $C_{57}H_{52}O_2P_4W\cdot C_4H_8O$: C, 63.77; H, 5.39%. IR (KBr) ν(C≡C), 2029, 1991; ν(C≡O), 1813; ν(C=O), 1597 cm^{-1}; ^{1}H NMR (C_6D_6, 70 °C) δ=1.89 (s, 3H, COMe), 2.2—3.0 (br m, 8H, PCH_2), −4.0 (br s, WH), 1.63 and 3.74 (m, 4H each, THF).

Preparation of [W(C≡CPh)H(CO)(dppe)$_2$] (8b). Into a solution of **1b** (95.2 mg, 0.0880 mmol) in benzene (2 ml) was added HC≡CPh (0.010 ml, 0.10 mmol) and the mixture was stirred at room temperature for 1 h. The resultant brown solution was concentrated and hexane was added, yielding brown crystals of **8b** (86.6 mg, 89%). Found: C, 65.58; H, 5.31%. Calcd for $C_{61}H_{54}OP_4W$: C, 65.96; H, 4.90%. IR (KBr) ν(C≡C), 2066; ν(C≡O), 1779 cm^{-1}. ^{1}H NMR (C_6D_6, 60°C) δ=−4.1 (br s, 1H, WH), 2.2—2.7 (br m, 8H, PCH_2).

Preparation of *cis*-[Mo(≡CCH$_2$Ph)(CO)(dppe)$_2$][BF$_4$] (9a). Into a dark red solution of **6a** (1.16 g, 1.13 mmol) in THF (80 ml) was added aqueous HBF_4 (0.20 ml, 1.19 mmol), and the mixture was stirred at −78 °C for 1 h. The resulting yellow soluiton was evaporated to dryness in vacuo and the residue was crystallized from CH_2Cl_2/hexane. The yellow crystals obtained were filtered off, washed with hexane, and then dried in vacuo (650 mg, 52%). Found: C, 65.57; H, 5.23%. Calcd for $C_{61}H_{55}OBF_4P_4Mo$: C, 65.96; H, 4.99%. IR (KBr) ν(C≡O), 1910 cm^{-1}. ^{1}H NMR (CD_2Cl_2) δ=3.19 (s, 2H, CH_2Ph), 2.5—1.9 (br m, 8H, PCH_2). ^{13}C{^{1}H} NMR (CD_2Cl_2) δ=312 (Mo≡C), 251 (Mo–CO).

Preparation of *cis*-[Mo(≡CCH$_2$COOMe)(CO)(dppe)$_2$][BF$_4$] (10a). Into a solution of **4a** (123 mg, 0.122 mmol) in THF (5 ml) was added an equimolar amount of $HBF_4\cdot Et_2O$ (0.019 ml) at −78 °C, and the mixture was stirred at room temperature for 1 h. The resultant yellow suspension was filtered off and the remaining yellow precipitate was dissolved in CH_2Cl_2. Addition of hexane to this solution afforded **10a** as yellow crystals (66.4 mg, 54%). Found:

Table 5. Atomic Coordinates and Equivalent Temperature Factors for Non-Hydrogen Atoms in **4a**

Atom	*x*	*y*	*z*	*B*(eq)
Mo	0.22177 (9)	0.18225 (9)	-0.00958(8)	2.42 (3)
P(1)	0.3143 (3)	0.0647 (3)	-0.0072(3)	3.6 (1)
P(2)	0.3128 (3)	0.1881 (3)	0.1241 (3)	3.6 (1)
P(3)	0.1282 (3)	0.2927 (2)	-0.0332(2)	2.9 (1)
P(4)	0.1419 (2)	0.1565 (2)	-0.1493(2)	2.5 (1)
O(1)	0.0829 (6)	0.0992 (6)	0.0483(7)	4.7 (4)
O(2)	0.4930 (8)	0.2668 (8)	-0.120(1)	8.8 (6)
O(3)	0.4758 (8)	0.3635 (8)	-0.0399(8)	7.0 (5)
C(1)	0.136 (1)	0.1295 (8)	0.027 (1)	3.5 (5)
C(2)	0.323 (1)	0.2389 (8)	-0.0500(9)	3.3 (5)
C(3)	0.382 (1)	0.270 (1)	-0.065(1)	4.0 (5)
C(4)	0.456 (1)	0.300 (1)	-0.077(1)	4.4 (6)
C(5)	0.550 (1)	0.396 (1)	-0.045(1)	10.7 (9)
C(6)	0.408 (1)	0.085 (1)	0.061 (1)	7.2 (7)
C(7)	0.400 (1)	0.125 (1)	0.126 (1)	10.4 (7)
C(8)	0.0481 (8)	0.2839 (8)	-0.1269(8)	2.6 (4)
C(9)	0.0401 (8)	0.1970 (8)	-0.1553(8)	3.1 (4)
C(10)	0.290 (1)	-0.030(1)	0.030 (1)	3.6 (5)
C(11)	0.212 (1)	-0.049(1)	0.034 (1)	5.5(6)
C(12)	0.192 (1)	-0.120(1)	0.060 (1)	10 (1)
C(13)	0.250 (2)	-0.172(1)	0.082 (1)	8.7 (8)
C(14)	0.328 (1)	-0.162(1)	0.079 (1)	6.9 (8)
C(15)	0.347 (1)	-0.088(1)	0.050 (1)	5.0 (6)
C(16)	0.349 (1)	0.035 (1)	-0.095(1)	3.4 (5)
C(17)	0.316 (1)	-0.027(1)	-0.142(1)	5.4 (6)
C(18)	0.341 (1)	-0.046(1)	-0.212(1)	7.5 (7)
C(19)	0.404 (2)	-0.009(2)	-0.228(1)	9 (1)
C(20)	0.435 (1)	0.054 (1)	-0.183(2)	9 (1)
C(21)	0.411 (1)	0.075 (1)	-0.118(1)	7.0 (7)
C(22)	0.281 (1)	0.150 (1)	0.213 (1)	3.8 (5)
C(23)	0.332 (1)	0.118 (1)	0.275 (1)	7.4 (7)
C(24)	0.309 (2)	0.091 (2)	0.341 (2)	13 (1)
C(25)	0.233 (2)	0.103 (2)	0.344 (1)	11 (1)
C(26)	0.177 (1)	0.139 (1)	0.286 (1)	7.6 (7)
C(27)	0.201(1)	0.162 (1)	0.217 (1)	5.2 (6)
C(28)	0.3486 (9)	0.282 (1)	0.160 (1)	3.6 (5)
C(29)	0.321 (1)	0.326(1)	0.215 (1)	5.8 (6)
C(30)	0.346 (1)	0.402 (1)	0.235 (1)	7.7 (8)
C(31)	0.401 (2)	0.438 (2)	0.202 (2)	11 (1)
C(32)	0.429 (2)	0.398 (2)	0.150 (2)	9 (1)
C(33)	0.404 (1)	0.323 (1)	0.129 (1)	7.6 (7)
C(34)	0.072 (1)	0.303 (1)	0.046 (1)	3.6 (5)
C(35)	-0.003(1)	0.2656 (8)	0.039 (1)	4.3 (5)
C(36)	-0.039(1)	0.268 (1)	0.103 (1)	5.5 (6)
C(37)	-0.000(1)	0.304 (1)	0.172 (1)	6.1 (6)
C(38)	0.072 (1)	0.343 (1)	0.180 (1)	6.2 (7)
C(39)	0.108 (1)	0.342 (1)	0.116 (1)	3.8 (5)
C(40)	0.156 (1)	0.3955 (9)	-0.0429(8)	3.0 (5)
C(41)	0.233 (1)	0.417 (1)	-0.044(1)	5.2 (6)
C(42)	0.249 (1)	0.496 (1)	-0.058(1)	6.2 (6)
C(43)	0.192 (2)	0.550 (1)	-0.061(1)	6.1 (8)
C(44)	0.116 (1)	0.530 (1)	-0.056(1)	6.1 (7)
C(45)	0.098(1)	0.453 (1)	-0.047(1)	4.2 (5)
C(46)	0.1151 (8)	0.0560 (7)	-0.1847(9)	2.3 (4)
C(47)	0.071 (1)	0.0095 (9)	-0.1436(9)	4.1 (5)
C(48)	0.051 (1)	-0.065(1)	-0.166(1)	4.1 (5)
C(49)	0.072 (1)	-0.0966(9)	-0.230(1)	4.4 (5)
C(50)	0.118 (1)	-0.049(1)	-0.272(1)	4.7 (5)
C(51)	0.1359 (9)	0.026 (1)	-0.2490(9)	3.7 (5)
C(52)	0.169 (1)	0.1983 (8)	-0.2360(9)	2.6 (4)
C(53)	0.250 (1)	0.201 (1)	-0.2375(9)	4.1 (5)
C(54)	0.273 (1)	0.230 (1)	-0.302(1)	7.1 (7)
C(55)	0.218 (1)	0.256 (1)	-0.367(1)	5.7 (7)
C(56)	0.140 (1)	0.255 (1)	-0.365(1)	7.0 (7)
C(57)	0.116 (1)	0.228 (1)	-0.301(1)	5.8 (6)

Table 6. Atomic Coordinates and Equivalent Temperature Factors for Non-Hydrogen Atoms in **4b**

Atom	*x*	*y*	*z*	*B*(eq)
W	0.22234 (1)	0.18341 (1)	-0.00922(1)	2.659 (4)
P(1)	0.31417 (8)	0.06586 (8)	-0.00813(8)	3.64 (3)
P(2)	0.31262 (7)	0.18725 (9)	0.12543 (7)	3.47 (3)
P(3)	0.12759 (7)	0.29309 (7)	-0.03320(7)	2.89 (3)
P(4)	0.14206 (7)	0.15744 (7)	-0.14833(7)	2.61 (3)
O(1)	0.0823 (2)	0.0998 (2)	0.0472 (2)	5.4 (1)
O(2)	0.4924 (3)	0.2682 (3)	-0.1191(3)	8.9 (2)
O(3)	0.4755 (3)	0.3654(3)	-0.0380(3)	7.7 (1)
C(1)	0.1353 (3)	0.1302 (3)	0.0280 (3)	3.3 (1)
C(2)	0.3209 (3)	0.2418 (3)	-0.0478(3)	3.0 (1)
C(3)	0.3775 (3)	0.2683 (3)	-0.0646(3)	3.9 (1)
C(4)	0.4519 (4)	0.2977 (4)	-0.0766(4)	5.0 (2)
C(5)	0.5519 (4)	0.3971 (5)	-0.0434(4)	11.7 (3)
C(6)	0.4113 (3)	0.0901 (3)	0.0614 (4)	6.9 (2)
C(7)	0.4037 (3)	0.1267 (5)	0.1299 (3)	9.5 (2)
C(8)	0.0480 (3)	0.2824 (3)	-0.1268(3)	3.5 (1)
C(9)	0.0406 (2)	0.1984 (3)	-0.1540(2)	3.1 (1)
C(10)	0.2899 (3)	-0.0296(3)	0.0292 (3)	3.7 (1)
C(11)	0.2138 (4)	-0.0474(3)	0.0359 (4)	6.2 (2)
C(12)	0.1950 (4)	-0.1195(4)	0.0626 (5)	8.7 (3)
C(13)	0.2537 (5)	-0.1740(4)	0.0847 (4)	8.2 (2)
C(14)	0.3302 (4)	-0.1592(4)	0.0782 (4)	6.9 (2)
C(15)	0.3482 (3)	-0.0879(4)	0.0496 (3)	5.5 (2)
C(16)	0.3499 (3)	0.0360 (3)	-0.0957(3)	4.0 (1)
C(17)	0.3152 (3)	-0.0262(3)	-0.1410(3)	5.1 (2)
C(18)	0.3404 (4)	-0.0485(4)	-0.2081(4)	7.2 (2)
C(19)	0.4011 (5)	-0.0080(5)	-0.2286(4)	8.1 (3)
C(20)	0.4358 (5)	0.0542 (4)	-0.1869(5)	8.0 (3)
C(21)	0.4109 (4)	0.0771 (3)	-0.1192(4)	6.3 (2)
C(22)	0.2782 (3)	0.1508 (3)	0.2116 (3)	4.1 (1)
C(23)	0.3319 (4)	0.1166 (4)	0.2756 (4)	7.5 (2)
C(24)	0.3066 (5)	0.0923 (5)	0.3424 (4)	10.5 (3)
C(25)	0.2286 (6)	0.1052 (5)	0.3447 (4)	9.9 (3)
C(26)	0.1735 (4)	0.1407 (4)	0.2844 (4)	7.3 (2)
C(27)	0.1990 (4)	0.1625 (3)	0.2163 (3)	5.2 (2)
C(28)	0.3505 (3)	0.2834 (3)	0.1611 (3)	4.0 (1)
C(29)	0.3219 (3)	0.3246 (4)	0.2159 (3)	5.5 (2)
C(30)	0.3463 (4)	0.4009 (4)	0.2358 (5)	7.5 (2)
C(31)	0.4004 (5)	0.4369 (4)	0.2017 (5)	8.7 (3)
C(32)	0.4310 (5)	0.3960 (5)	0.1479 (4)	9.4 (3)
C(33)	0.4061 (4)	0.3212 (4)	0.1271 (3)	7.1 (2)
C(34)	0.0707 (3)	0.3027 (3)	0.0439 (3)	3.3 (1)
C(35)	-0.0021(3)	0.2646 (3)	0.0390 (3)	4.6 (2)
C(36)	-0.0379(4)	0.2659 (3)	0.1045 (4)	5.7 (2)
C(37)	-0.0003(4)	0.3030 (4)	0.1732 (4)	6.2 (2)
C(38)	0.0713 (4)	0.3423 (3)	0.1781 (3)	5.6 (2)
C(39)	0.1070 (3)	0.3417 (3)	0.1139 (3)	4.2 (1)
C(40)	0.1555 (3)	0.3952 (3)	-0.0418(3)	3.1 (1)
C(41)	0.2323 (3)	0.4161 (3)	-0.0470(3)	5.1 (2)
C(42)	0.2501 (4)	0.4962 (4)	-0.0568(4)	6.5 (2)
C(43)	0.1918 (5)	0.5514 (3)	-0.0622(3)	5.9 (2)
C(44)	0.1159 (4)	0.5306 (3)	-0.0572(3)	5.7 (2)
C(45)	0.0969 (3)	0.4534 (3)	-0.0472(3)	4.4 (1)
C(46)	0.1157 (3)	0.0571 (3)	-0.1822(3)	3.0 (1)
C(47)	0.0719 (3)	0.0107 (3)	-0.1417(3)	3.7 (1)
C(48)	0.0506 (3)	-0.0646(3)	-0.1662(3)	4.5 (1)
C(49)	0.0728 (3)	-0.0954(3)	-0.2306(3)	4.6 (2)
C(50)	0.1160 (3)	-0.0505(3)	-0.2710(3)	5.0 (2)
C(51)	0.1373 (3)	0.0254 (3)	-0.2475(3)	4.0 (1)
C(52)	0.1713 (3)	0.2003 (3)	-0.2344(3)	3.0 (1)
C(53)	0.2513 (3)	0.2014 (3)	-0.2367(3)	4.9 (2)
C(54)	0.2743 (3)	0.2305 (4)	-0.3024(3)	6.5 (2)
C(55)	0.2194 (4)	0.2573 (4)	-0.3666(3)	6.0 (2)
C(56)	0.1402 (4)	0.2566 (4)	-0.3659(3)	7.1 (2)
C(57)	0.1165 (3)	0.2289 (4)	-0.2996(3)	5.9 (2)

Table 7. Atomic Coordinates and Equivalent Temperature Factors for Non-Hydrogen Atoms in **9a**

Atom	x	y	z	B(eq)
Mo(1)	0.04376 (6)	0.08103 (3)	-0.25185(4)	2.57 (2)
P(1)	0.2185 (2)	0.1011 (1)	-0.1560(1)	3.28 (7)
P(2)	0.0231 (2)	0.1987 (1)	-0.2288(1)	3.30 (6)
P(3)	0.1268 (2)	0.1025 (1)	-0.3595 (1)	3.27 (6)
P(4)	-0.1237(2)	0.0568 (1)	-0.3516(1)	3.07 (6)
F(1)	0.9782 (5)	0.1304 (3)	0.4015 (3)	10.5 (2)
F(2)	0.9663 (6)	0.2227 (3)	0.3707 (5)	17.7 (4)
F(3)	0.8644 (6)	0.1925 (3)	0.4344 (3)	13.0 (3)
F(4)	0.8285 (5)	0.1679 (3)	0.3274 (3)	11.0 (2)
O(1)	-0.1032(5)	0.0673 (3)	-0.1427(3)	6.8 (2)
C(1)	0.0714 (6)	0.0050 (3)	-0.2431(4)	3.2 (2)
C(2)	0.0948 (8)	-0.0585(4)	-0.2324(5)	5.6 (3)
C(3)	0.0377 (8)	-0.0889(4)	-0.1821(5)	4.5 (3)
C(4)	-0.052(1)	-0.1285(5)	-0.2071(5)	6.3 (4)
C(5)	-0.100(1)	-0.1588(5)	-0.1586(7)	7.5 (4)
C(6)	-0.059(1)	-0.1495(5)	-0.0904(6)	6.0 (4)
C(7)	0.023 (1)	-0.1095(5)	-0.0666(5)	7.0 (4)
C(8)	0.0726 (8)	-0.0787(4)	-0.1122(5)	5.6 (3)
C(9)	-0.0490(7)	0.0728 (4)	-0.1803(4)	4.3 (3)
C(10)	0.2154 (7)	0.1742 (4)	-0.1177(4)	4.3 (3)
C(11)	0.1589 (7)	0.2199 (4)	-0.1697(4)	4.1 (3)
C(12)	0.2454 (7)	0.0543 (4)	-0.0783(4)	3.7 (3)
C(13)	0.1694 (8)	0.0583 (4)	-0.0354(5)	5.4 (3)
C(14)	0.186 (1)	0.0232 (5)	0.0238 (5)	7.3 (4)
C(15)	0.271 (1)	-0.0159(5)	0.0394 (5)	7.7 (4)
C(16)	0.3469 (8)	-0.0210(5)	-0.0014(5)	9.8 (4)
C(17)	0.3301 (8)	0.0161 (5)	-0.0603(5)	7.2 (4)
C(18)	0.3570 (7)	0.0960 (4)	-0.1721(5)	4.1 (3)
C(19)	0.3752 (8)	0.0505 (5)	-0.2135(5)	5.9 (3)
C(20)	0.480 (1)	0.0397 (6)	-0.2259(6)	8.8 (5)
C(21)	0.567 (1)	0.0766 (7)	-0.1995(7)	9.3 (5)
C(22)	0.553 (1)	0.1229 (6)	-0.1609(8)	9.0 (5)
C(23)	0.447 (1)	0.1335 (5)	-0.1474(6)	6.9 (4)
C(24)	-0.0051(7)	0.2562 (4)	-0.2959(5)	3.3 (3)
C(25)	0.0447 (9)	0.3116 (4)	-0.2833(5)	5.8 (3)
C(26)	0.011 (1)	0.3548 (4)	-0.3342(6)	7.1 (4)
C(27)	-0.067(1)	0.3435 (5)	-0.3955(6)	7.0 (4)
C(28)	-0.1126(9)	0.2893 (5)	-0.4082(5)	6.0 (3)
C(29)	-0.0808(8)	0.2465 (4)	-0.3580(5)	4.8 (3)
C(30)	-0.0828(7)	0.2182 (4)	-0.1800(5)	3.4 (3)
C(31)	-0.1887(9)	0.2331 (4)	-0.2143(5)	5.4 (3)
C(32)	-0.2720(8)	0.2480 (5)	-0.1803(7)	6.6 (4)
C(33)	-0.244(1)	0.2463 (5)	-0.1081(6)	5.9 (4)
C(34)	-0.141(1)	0.2306 (5)	-0.0736(5)	6.9 (4)
C(35)	-0.0583(8)	0.2175 (5)	-0.1082(5)	6.3 (3)
C(36)	0.0097 (6)	0.0940 (4)	-0.4365(4)	4.3 (2)
C(37)	-0.0693(6)	0.0422 (4)	-0.4285(4)	4.0 (2)
C(38)	0.1841 (8)	0.1733 (4)	-0.3717(5)	3.4 (3)
C(39)	0.2755 (8)	0.1946 (5)	-0.3197(5)	4.9 (3)
C(40)	0.3233 (9)	0.2492 (5)	-0.3235(6)	6.0 (4)
C(41)	0.278 (1)	0.2840 (5)	-0.3804(7)	6.7 (4)
C(42)	0.186 (1)	0.2656 (5)	-0.4330(6)	6.6 (4)
C(43)	0.1399 (8)	0.2094 (5)	-0.4297(5)	5.0 (3)
C(44)	0.2335 (7)	0.0519 (4)	-0.3790(4)	3.5 (2)
C(45)	0.2232 (8)	-0.0067(4)	-0.3719(4)	3.9 (3)
C(46)	0.300 (1)	-0.0444(4)	-0.3874(5)	5.6 (3)
C(47)	0.3928 (9)	-0.0235(5)	-0.4103(5)	5.8 (3)
C(48)	0.4046 (8)	0.0331 (5)	-0.4177(5)	6.0 (3)
C(49)	0.3255 (8)	0.0736 (4)	-0.4029(5)	5.3 (3)
C(50)	-0.2403(7)	0.1077 (4)	-0.3834(4)	3.4 (2)
C(51)	-0.2804(8)	0.1297 (4)	-0.4494(5)	4.6 (3)
C(52)	-0.3743(9)	0.1646 (4)	-0.4694(5)	5.9 (3)
C(53)	-0.4307(8)	0.1818 (4)	-0.4211(7)	6.3 (4)
C(54)	-0.3924(9)	0.1616 (4)	-0.3549(6)	6.1 (4)
C(55)	-0.2998(8)	0.1278 (4)	-0.3359(5)	5.1 (3)
C(56)	-0.2042(7)	-0.0092(4)	-0.3454(5)	3.4 (2)
C(57)	-0.2388(9)	-0.0457(5)	-0.3977(5)	7.0 (4)
C(58)	-0.304(1)	-0.0972(5)	-0.3947(6)	8.7 (5)
C(59)	-0.341(1)	-0.1072(5)	-0.3372(7)	7.4 (4)
C(60)	-0.3069(9)	-0.0692(5)	-0.2810(6)	7.3 (4)
C(61)	-0.2381(8)	-0.0209(4)	-0.2853(6)	5.9 (3)
B(1)	0.9112 (8)	0.1774 (4)	0.3847 (3)	5.1 (2)

C, 62.41; H, 4.95%. Calcd for $C_{57}H_{53}O_3P_4F_4BMo$: C, 62.66; H, 4.89%. IR(KBr) ν(C≡O), 1919; ν(C=O), 1736 cm^{-1}; ^{1}H NMR ($CDCl_3$), δ=3.20 (s, 3H, COOMe); 2.70 (s, 2H, $MoCCH_2$), 1.5—3.4 (br m, 8H, PCH_2); ^{13}C{^{1}H} NMR (CD_2Cl_2) δ=298 (M≡C), 230 (M–CO), 185 (COO); ^{31}P{^{1}H} NMR($CDCl_3$) δ=16.5 (ddd, J_{P-P}=4, 13, and 21 Hz, 1P), 42.5 (ddd, J_{P-P}=6, 14, and 23 Hz, 1P), 53.1 (ddd, J_{P-P}=6, 20, and 87 Hz, 1P), 56.3 (ddd, J_{P-P}=3, 25, and 87 Hz, 1P).

Preparation of *cis*-[W(≡CCH$_2$COOMe)(CO)(dppe)$_2$][BF$_4$] (10b). Complex **10b** was prepared from **4b** (198 mg, 0.182 mmol) and an equimolar amount of HBF_4·Et_2O (0.032 ml) in the similar manner to that for **10a**. Yield, 170 mg (85%). Found: C, 57.81; H, 4.72%. Calcd for $C_{57}H_{53}O_3P_4F_4BW$: C, 57.99; H, 4.52%. IR (KBr) ν(C≡O), 1902; ν(C=O), 1736 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=3.28 (s, 3H, COOMe), 2.60 (s, 2H, $WCCH_2$), 1.8—3.6 (br m, 8H, PCH_2); ^{13}C{^{1}H} NMR (CD_2Cl_2) δ=288 (M≡C), 225 (M–CO), 165 (COO); ^{31}P{^{1}H} NMR ($CDCl_3$) δ=10.3 (ddd, J_{P-P}=10, 12, and 22 Hz, 1P), 38.7 (ddd, J_{P-P}=5, 13, and 18 Hz, 1P), 42.2 (ddd, J_{P-P}=5, 16, and 81 Hz, 1P), 45.8 (ddd, J_{P-P}=10, 21, and 81 Hz, 1P).

Preparation of *cis*-[Mo(=C=CHCOOMe)(CO)(dppe)$_2$] (11a). A yellow suspension containing **10a** (139 mg, 0.137 mmol) and NaOMe (0.15 g, 2.8 mmol) in benzene (5 ml) was stirred at room temperature for 1 h. The red mixture obtained was filtered and the filtrate was concentrated. Addition of hexane afforded **11a**·$2C_6H_6$ as red crystals (130 mg, 82%). Found: C, 71.29; H, 5.64%. Calcd for $C_{57}H_{52}O_3P_4Mo$·$2C_6H_6$: C, 71.38; H, 5.56%. IR(KBr) ν(C≡O), 1825; ν(C=O), 1634; ν(C=C), 1501 cm^{-1}; ^{1}H NMR (C_6D_6) δ=5.03 (m, 1H, C=CH), 3.45 (s, 3H, OMe), 1.6—3.0 (br m, 8H, PCH_2).

Preparation of *cis*-[W(=C=CHCOOMe)(CO)(dppe)$_2$] (11b). This complex was prepared by a method analogous to that for obtaining **11a**, from **10b** (80.4 mg, 0.0681 mmol) and NaOMe (44 mg, 0.82 mmol) in benzene (10 ml). Complex **11b** was obtained as orange crystals containing two solvating C_6H_6 molecules (64.4 mg, 76%). Found: C, 66.14; H, 5.19%. Calcd for $C_{57}H_{52}O_3P_4W$·$2C_6H_6$: C, 66.35; H, 5.16%. IR (KBr) ν(C≡O), 1817; ν(C=O), 1630; ν(C=C), 1482 cm^{-1} (overlapped with the band arising from dppe); ^{1}H NMR (C_6D_6) δ=3.46 (s, 3H, OMe), 4.09 (m, 1H, WCCH), 1.7—3.2 (br m, 8H, PCH_2).

Preparation of *cis*-[W(≡CCH$_2$Ph)(CO)(dppe)$_2$][BF$_4$] (9b) form 8b. A solution of **8b** (72.3 mg, 0.0651 mmol) in THF (5 ml) was cooled to −78°C and an equimolar amount of HBF_4·Et_2O (0.011 ml) was added. The mixture was stirred at room temperature for 2 h, affording a yellow-brown suspension. A yellow solid was separated by filtration and recrystallized from CH_2Cl_2/hexane, giving yellow crystals (49.3 mg, 63%). Found: C, 60.22; H, 4.57%. Calcd for $C_{61}H_{55}OBF_4P_4W$: C, 61.12; H, 4.62%. IR (KBr) ν(C≡O), 1894 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.85 (s, 2H, $WCCH_2$), 1.8—3.5 (br m, 8H, PCH_2); ^{31}P{^{1}H} NMR ($CDCl_3$) δ= 10.5 (ddd, J_{P-P}=11, 11, and 22 Hz, 1P), 38.9 (ddd, J_{P-P}=6, 11, and 19 Hz, 1P), 41.1 (ddd, J_{P-P}=6, 22, and 81 Hz, 1P), 47.7 (ddd, J_{P-P}=11, 19, and 81 Hz, 1P).

Preparation of *cis*-[W(=C=CHPh)(CO)(dppe)$_2$] (6b) from 9b. To a yellow suspension of **9b** (119 mg, 0.996 mmol) in benzene (5 ml) was added NaOMe (0.12 g, 2.2 mmol) and the mixture was stirred at room temperature for 3 h. The resultant dark green suspension was filtered and the filtrate was concentrated. Addition of hexane gave a dark green solid, which was filtered off, washed with hexane and ether, and then drired in vacuo (70.3 mg, 64%). Found: C, 65.85; H, 4.93%. Calcd for $C_{61}H_{54}OP_4W$: C, 65.96; H, 4.90%. IR (KBr) ν(C≡O), 1798; ν(C=C), 1520 cm^{-1}; ^{1}H NMR (C_6D_6) δ=4.35 (m, 1H, WCCH), 1.7—3.1 (br m, 8H, PCH_2);

Table 8. Atomic Coordinates and Equivalent Temperature Factors for Non-Hydrogen Atoms in **11b**$\cdot 2C_6H_6$

Atom	*z*	*y*	*z*	*B*(eq)	Atom	*z*	*y*	*z*	*B*(eq)
W	0.21986 (4)	0.10131 (3)	0.19606 (2)	2.316 (8)	C(32)	-0.169(1)	0.2455 (7)	0.1702 (5)	5.0 (4)
P(1)	0.3881 (2)	0.1811 (2)	0.2355 (1)	2.87(7)	C(33)	-0.073(1)	0.2090 (6)	0.1893 (4)	4.1 (3)
P(2)	0.1316 (2)	0.1880 (2)	0.2483 (1)	2.75 (7)	C(34)	0.0148 (9)	0.1460 (6)	0.0766 (4)	3.0 (3)
P(3)	0.1557 (2)	0.1610 (2)	0.1093 (1)	2.85 (7)	C(35)	-0.060(1)	0.2035 (6)	0.0613 (4)	3.9 (3)
P(4)	0.3225 (2)	0.0236 (2)	0.1442 (1)	2.85 (8)	C(36)	-0.163(1)	0.1877 (7)	0.0333 (4)	5.1 (3)
O(1)	0.2907 (6)	0.0006 (4)	0.2903 (3)	4.0 (2)	C(37)	-0.195(1)	0.1175 (7)	0.0221 (4)	4.8 (4)
O(2)	-0.1011(6)	-0.1074(5)	0.1533 (3)	5.5 (2)	C(38)	-0.125(1)	0.0611 (7)	0.0378 (5)	4.7 (4)
O(3)	0.0412 (6)	-0.0744(4)	0.1157 (3)	4.7 (2)	C(39)	-0.0215(9)	0.0755 (6)	0.0639 (4)	3.2 (3)
C(1)	0.2666 (8)	0.0412 (6)	0.2534 (4)	2.9 (3)	C(40)	0.1696 (9)	0.2588 (6)	0.0944 (4)	3.2 (3)
C(2)	0.0920 (8)	0.0436 (6)	0.1830 (4)	2.7 (3)	C(41)	0.179 (1)	0.2827 (7)	0.0459 (5)	4.9 (4)
C(3)	0.0020 (8)	0.0001 (6)	0.1813 (4)	2.7 (3)	C(42)	0.186 (1)	0.3556 (8)	0.0363 (5)	5.7 (4)
C(4)	-0.025(1)	-0.0634(7)	0.1514 (5)	4.0 (4)	C(43)	0.186 (1)	0.4057 (8)	0.0752 (5)	6.0 (4)
C(5)	0.018 (1)	-0.1370(7)	0.0834 (5)	6.3 (4)	C(44)	0.175 (1)	0.3821 (8)	0.1232 (5)	5.6 (4)
C(6)	0.3451 (8)	0.2212 (6)	0.2911 (4)	3.4 (3)	C(45)	0.170 (1)	0.3103 (7)	0.1320 (5)	4.2 (3)
C(7)	0.2327 (8)	0.2569 (5)	0.2772 (4)	3.0 (3)	C(46)	0.4721 (8)	0.0319 (6)	0.1471 (4)	3.0 (3)
C(8)	0.2322 (8)	0.1181 (5)	0.0639 (4)	3.2 (3)	C(47)	0.543 (1)	-0.0107(6)	0.1796 (4)	4.0 (3)
C(9)	0.2657 (8)	0.0386 (5)	0.0769 (4)	3.1 (3)	C(48)	0.656 (1)	-0.0086(7)	0.1797 (5)	4.9 (4)
C(10)	0.5218 (9)	0.1397 (6)	0.2615 (4)	2.9 (3)	C(49)	0.697 (1)	0.0366 (7)	0.1472 (5)	5.5 (4)
C(11)	0.528 (1)	0.0903 (7)	0.3027 (5)	4.6 (4)	C(50)	0.629 (1)	0.0809 (7)	0.1154 (5)	5.3 (4)
C(12)	0.628 (1)	0.0596 (7)	0.3232 (5)	5.5 (4)	C(51)	0.515 (1)	0.0784 (6)	0.1142 (4)	3.9 (3)
C(13)	0.722 (1)	0.0759 (6)	0.3047 (5)	4.7 (3)	C(52)	0.3116 (8)	-0.0767(5)	0.1484 (4)	3.1 (3)
C(14)	0.716 (1)	0.1235 (6)	0.2665 (4)	4.6 (3)	C(53)	0.3633 (9)	-0.1191(6)	0.1160 (4)	3.9 (3)
C(15)	0.619 (1)	0.1563 (6)	0.2449 (4)	3.9 (3)	C(54)	0.357 (1)	-0.1944(7)	0.1171 (5)	4.3 (4)
C(16)	0.4349 (8)	0.2610 (6)	0.2032 (4)	2.5 (3)	C(55)	0.297 (1)	-0.2272(8)	0.1506 (5)	5.5 (4)
C(17)	0.476 (1)	0.3218 (7)	0.2287 (5)	4.9 (4)	C(56)	0.249 (1)	-0.1858(7)	0.1823 (5)	4.6 (4)
C(18)	0.513 (1)	0.3782 (8)	0.2025 (5)	5.8 (4)	C(57)	0.2552 (8)	-0.1119(7)	0.1816 (4)	3.8 (3)
C(19)	0.509 (1)	0.3754 (7)	0.1508 (5)	4.9 (4)	C(58)	0.749 (1)	0.1200 (6)	0.4621 (4)	8.9 (3)
C(20)	0.467 (1)	0.3137 (7)	0.1252 (5)	4.9 (4)	C(59)	0.661 (1)	0.0839 (6)	0.4721 (5)	10.0 (3)
C(21)	0.430 (1)	0.2576 (6)	0.1516 (5)	3.9 (3)	C(60)	0.644 (1)	0.0576 (6)	0.5150 (5)	10.9 (3)
C(22)	0.0796 (9)	0.1483 (6)	0.3041 (4)	2.8 (3)	C(61)	0.741 (1)	0.0485 (6)	0.5595 (5)	9.7 (3)
C(23)	0.057 (1)	0.1918 (7)	0.3445 (5)	4.9 (4)	C(62)	0.8311 (9)	0.0888 (7)	0.5478 (4)	8.8 (3)
C(24)	0.021 (1)	0.1626 (8)	0.3851 (6)	5.9 (5)	C(63)	0.847 (1)	0.1171 (6)	0.5006 (4)	9.3 (3)
C(25)	0.007 (1)	0.0884 (7)	0.3883 (5)	4.8 (4)	C(64)	0.335 (1)	0.2526 (6)	0.9359 (5)	8.4 (3)
C(26)	0.027 (1)	0.0444 (7)	0.3495 (5)	4.4 (4)	C(65)	0.314 (1)	0.1806 (7)	0.9262 (4)	7.1 (3)
C(27)	0.063 (1)	0.0736 (7)	0.3074 (5)	3.7 (4)	C(66)	0.377 (1)	0.1189 (6)	0.9478 (4)	7.8 (3)
C(28)	0.0114 (9)	0.2433 (6)	0.2214 (4)	2.8 (3)	C(67)	0.470 (1)	0.1383 (7)	0.9856 (5)	8.0 (3)
C(29)	-0.002(1)	0.3158 (6)	0.2336 (4)	3.9 (3)	C(68)	0.493 (1)	0.2074 (7)	0.9975 (5)	7.1 (3)
C(30)	-0.096(1)	0.3525 (7)	0.2128 (5)	4.5 (4)	C(69)	0.433 (1)	0.2609 (6)	0.9746 (5)	7.9 (3)
C(31)	-0.178(1)	0.3174 (7)	0.1816 (5)	5.0 (4)					

$^{31}P\{^1H\}$ NMR (C_6D_6) $\delta = 24.4$ (ddd, $J_{P-P}=3$, 6, and 21 Hz, 1P), 24.7 (ddd, $J_{P-P}=4$, 12, and 18 Hz, 1P), 43.4 (ddd, $J_{P-P}=12$, 23, and 80 Hz, 1P), 48.6 (ddd $J_{P-P}=6$, 20, and 81 Hz, 1P).

X-Ray Crystallographic Studies of 4a, 4b, 9a, and 11b$\cdot 2C_6H_6$. Single crystals of the complexes studied were mounted in glass capillaries under N_2 and transferred to a Rigaku AFC7R diffractometer. The orientation matrices and unit cell parameters were derived from the least-squares fit of 25 machine-centered reflections with $35° < 2\theta < 40°$. Three check reflections measured every 150 reflections showed no significant decay during data collections at room temperature. Intensity data were corrected for the Lorentz and polarization effects and for absorption (ψ-scans.). Crystallographic data are summarized in Table 4.

All calculations were performed by the use of the teXsan crystallographic software package.[32] The structures were solved by using the Patterson methods program DIRDIF92 PATTY[33] and the subsequent Fourier syntheses. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares techniques. Hydrogen atoms were included at their calculated position with fixed parameters at the final stages of refinements. Final coordinates of non-hydorgen atoms in **4a**, **4b**, **9a**, and **11b**$\cdot 2C_6H_6$ are collected in Tables 5, 6, 7, and 8, respectively.[34]

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