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Synthesis, Molecular Structures, and Fluxional Behavior of the Novel Ylide Complex $[\mathrm{Cp_2Mo_2(CO)_4}\{\mu\text{-}\eta^1{:}\eta^2\text{-}\mathrm{MeC{=}C{=}C(H)(PPh_3)}\}]$ Stabilized by a Bimetallic Frame

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Treatment of the propargyl alcohol complex $[\mathrm{Cp_2Mo_2(CO)_4}(\mu\text{-}\eta^2{:}\eta^2\text{-}\mathrm{MeC{\equiv}CCH_2OH})]$ (1) with $\mathrm{HBF_4{\cdot}Et_2O}$ in ether solution afforded the carbenium ion complex $[\mathrm{Cp_2Mo_2(CO)_4}(\mu\text{-}\eta^2{:}\eta^3\text{-}\mathrm{MeC{\equiv}CCH_2})][\mathrm{BF_4}]$ (2). Compound 2 undergoes a nucleophilic attack by several phosphine ligands ($\mathrm{PR'_3}$, R′ = Et, Ph) at the α-carbonium center ($-\mathrm{CH_2}^+$), thus forming the phosphonium derivatives $[\mathrm{Cp_2Mo_2(CO)_4}(\mu\text{-}\eta^2{:}\eta^2\text{-}\mathrm{MeC{\equiv}CHC_2PR'_3})][\mathrm{BF_4}]$ (3) and **4a**. In particular the phosphonium complex $[\mathrm{Cp_2Mo_2(CO)_4}(\mu\text{-}\eta^2{:}\eta^2\text{-}\mathrm{HC{\equiv}CCH_2PEt_3})][\mathrm{BF_4}]$ (**4b**) belonging to the previous family has been characterized by X-ray crystallography (space group *Pbca*, *a* = 8.932(2) Å, *b* = 15.820(6) Å, *c* = 37.432(4) Å, *V* = 5289 Å^3, *Z* = 8). The triphenyl phosphonium derivative $[\mathrm{Cp_2Mo_2(CO)_4}(\mu\text{-}\eta^2{:}\eta^2\text{-}\mathrm{MeC{\equiv}CCH_2PPh_3})][\mathrm{BF_4}]$ (3) can be deprotonated in cold $\mathrm{CH_3CN}$ by reaction with an excess of DBU (DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene) to yield the two stereoisomeric metal-stabilized ylides $[\mathrm{Cp_2Mo_2(CO)_4}\{\mu\text{-}\eta^1{:}\eta^2\text{-}\mathrm{MeC{=}C{=}C(H)(PPh_3)}\}]$ (**5a,b**) in a 2:1 ratio. The structure of the major isomer **5a** was identified by X-ray analysis (space group $P2_1$; *a* = 9.024(2) Å, *b* = 30.851(7) Å, *c* = 11.378(1) Å, *V* = 3123(9) Å^3, *Z* = 4). The fluxional behavior in solution of the complexes $[\mathrm{Cp_2Mo_2(CO)_4}\{\mu\text{-}\eta^1{:}\eta^2\text{-}\mathrm{MeC{=}C{=}C(H)(PPh_3)}\}]$ (**5a,b**) was investigated, and a mechanism of exchange is presented and compared to that of the parent cation complex $[\mathrm{Cp_2Mo_2(CO)_4}(\mu\text{-}\eta^2{:}\eta^3\text{-}\mathrm{MeC{\equiv}CCH_2})][\mathrm{BF_4}]$ (2).

Introduction

Carbenium ions of the type $[\mathrm{Cp_2Mo_2(CO)_4}(\mu\text{-}\eta^2{:}\eta^3\text{-}\mathrm{RC{\equiv}CCR1R2})][\mathrm{BF_4}]$ have attracted much interest from several authors due to their high stability, compared to their isolobal cobalt complexes $[\mathrm{Co_2(CO)_6}(\mu\text{-}\eta^2{:}\eta^3\text{-}\mathrm{RC{\equiv}CCR1R2})][\mathrm{BF_4}]$.[1] The latter are known as the Nicholas reagents and are useful reagents for organic syntheses where they act as alkylating agents.[2] Although the molybdenum analogues are less reactive, they can be used as models for alkyne coordination on metallic surfaces obtained in heterogeneous catalysis.[3] Indeed, several molecular structures have been reported for these carbenium ion complexes $[\mathrm{Cp_2Mo_2(CO)_4}(\mu\text{-}\eta^2{:}\eta^3\text{-}\mathrm{RC{\equiv}CCR1R2})][\mathrm{BF_4}]$ where the alkyne moiety $-\mathrm{C{\equiv}C}-$ bridges both molybdenum centers; furthermore a direct interaction between one molybdenum center and the carbonium ion ($-\mathrm{CR1R2}^+$) in the α-position is observed.[1a] This interaction is responsible for the high stability of these organometallic cations. Pursuing our research program in this area, we have prepared several phosphonium derivatives $[\mathrm{Cp_2Mo_2(CO)_4}(\mu\text{-}\eta^2{:}\eta^2\text{-}\mathrm{RC{\equiv}CCH_2PR'_3})][\mathrm{BF_4}]$ (R = Me, R′ = Ph (3); R = Me, H, R′ = Et (**4a**, **4b**), where the heteroatom is bearing the positive charge. Our major goal was to deprotonate these phosphonium derivatives in the hopes of obtaining the corresponding ylide complexes, which upon further treatment with aldehydes or ketones followed by oxidation would yield the organic enyne substrates, important species for organic syntheses[4] (see Scheme 1). Nevertheless, the deprotonation of 3 yielded the allene-like species $[\mathrm{Cp_2Mo_2(CO)_4}\{\mu\text{-}\eta^1{:}\eta^2\text{-}\mathrm{MeC{=}C{=}C(H)(PPh_3)}\}]$, which can be described as the zwitterion form of the expected ylide; the hydrocarbyl ligand exhibits an unprecedented coordination mode which is different from those reported for usual $[\mathrm{Cp_2Mo_2(CO)_4(allene)}]$ complexes. In this paper we describe the syntheses of these phosphonium derivatives 3 and **4a,b** and their corresponding metal-stabilized ylides **5a,b** as well as the X-ray molecular structures of **4b** and **5a**. Furthermore we report on the fluxional behavior of the metal-stabilized ylides $[\mathrm{Cp_2Mo_2(CO)_4}\{\mu\text{-}\eta^1{:}\eta^2\text{-}\mathrm{MeC{=}C{=}C(H)(PPh_3)}\}]$ (**5a,b**) obtained by deprotonation of $[\mathrm{Cp_2Mo_2(CO)_4}(\mu\text{-}\eta^2{:}\eta^2\text{-}\mathrm{MeC{\equiv}CCH_2PPh_3})][\mathrm{BF_4}]$ (3). The solution behavior of **5a,b** is also compared to that reported for the parent carbenium ions $[\mathrm{Cp_2Mo_2(CO)_4}(\mu\text{-}\eta^2{:}\eta^3\text{-}\mathrm{RC{\equiv}CCR1R2})][\mathrm{BF_4}]$.

Results and Discussion

Synthetic and NMR Studies. The preparation of the propargyl alcohol complex $[\mathrm{Cp_2Mo_2(CO)_4}(\mu\text{-}\eta^2{:}\eta^2\text{-}\mathrm{MeC{\equiv}CCH_2OH})]$ (1) has been performed similarly to that of $[\mathrm{Cp'_2Mo_2(CO)_4}(\mu\text{-}\eta^2{:}\eta^2\text{-}\mathrm{HC{\equiv}CCH_2OMe})]$ (Cp′ = $\mathrm{C_5H_4Me}$), reported by Curtis et al.[1a] (see Experimental Section).

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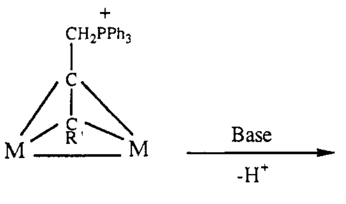
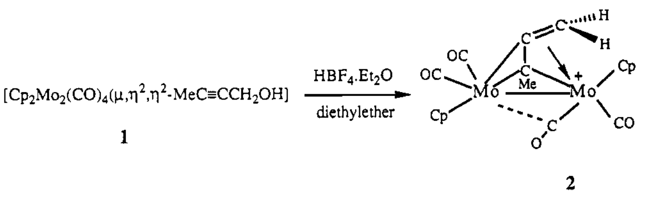
Scheme 1

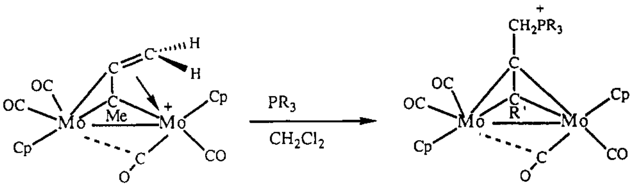


M = -CpMo(CO)$_2$

Scheme 2



Scheme 3



R' = Me, R = Ph; **3**

R' = Me, R = Et; **4a**

R' = H, R = Et; **4b**

The propargyl alcohol complex **1** reacts with HBF$_4$·Et$_2$O in diethyl ether to give an orange precipitate identified as [Cp$_2$Mo$_2$(CO)$_4$(μ-η^2:η^3-MeC≡CCH$_2$)][BF$_4$] (**2**) (Scheme 2). The spectroscopic data and its solution behavior are similar to those of carbenium ions of the type [Cp$_2$Mo$_2$(CO)$_4$(μ-η^2:η^3-RC≡CCR1R2)][BF$_4$] (R = H, R1 = R2 = H; R = H, R1 = R2 = Me) reported in the literature.[1b] Moreover the molecular structures of such carbenium ions were ascertained by X-ray analysis. The variable temperature NMR spectra of these carbenium ions in solution suggests that an intramolecular dynamic process is occurring whereby Mo(1) and Mo(2), Cp(1) and Cp(2), and the two pairs of the carbonyl groups are equilibrating by an interconversion process concomitant with a rotation around the C(1)—C(2) bond of the bridging propargyl moiety.[1,5]

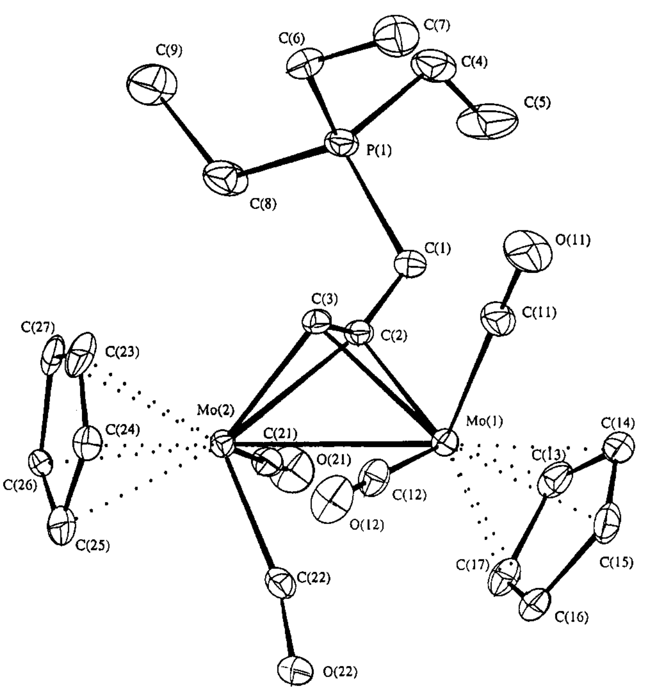


Figure 1. Molecular structure of [Cp$_2$Mo$_2$(CO)$_4$(μ-η^2:η^2-HC≡CCH$_2$PEt$_3$)]$^+$.

Table 1. Crystallographic Data for 4b

chemical formula	[(Mo(C$_5$H$_5$)(CO)$_2$)$_2$(C$_9$H$_{18}$P)]BF$_4$
fw	678.1
cryst syst	orthorhombic
space group	*Pbca*
Z	8
a, Å	8.932(2)
b, Å	15.820(6)
c, Å	37.432(4)
V, Å^3	5289
F(000)	2704
ρ(calcd), g cm^{-3}	1.70
μ(Mo Kα), cm^{-1}	10.39
cryst size, mm	0.15 × 0.20 × 0.60
diffractometer	Nonius CAD4
monochromator	graphite
radiation (λ, Å)	Mo Kα (0.710 70)
temp, °C	20
scan type	ω/2θ
scan range θ, deg	1.2 + 0.34 tan θ
2θ range, deg	3–50
no. of reflctn collected	4658
no. of reflctn used (criteria)	3405 ($I > 3\sigma(I)$)
R	0.044
R_w[a]	0.047
abs corr[b]	min 0.89, max 1.05
secondary ext × 10^6	12.5
weighting scheme	unit weights
rms (shift/esd) (last ref)	0.67
ls params	382

[a] $R_w = [\sum_i w_i (F_o - F_c)^2/\sum_i w_i F_o^2]^{1/2}$. [b] Difabs: Walter, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 159.

As expected, [Cp$_2$Mo$_2$(CO)$_4$(μ-η^2:η^3-MeC≡CCH$_2$)][BF$_4$] (**2**) reacts with nucleophiles such as phosphines PR$_3$ (R = Et, Ph) with nucleophilic attack at the methylene group -CH$_2$$^+$- at the α-position of the dimolybdenum cluster (Scheme 3). The novel phosphonium derivatives [Cp$_2$Mo$_2$(CO)$_4$(μ-η^2:η^2-MeC≡CCH$_2$PR$_3$)][BF$_4$] (R = Ph (**3**), R = Et (**4a**)) were completely characterized by spectroscopic methods; in addition the structure of the complex [Cp$_2$Mo$_2$(CO)$_4$(μ-η^2:η^2-HC≡CCH$_2$PEt$_3$)][BF$_4$] (**4b**) belonging to this family was ascertained by X-ray analysis (see Figure 1). Crystal data and selected bond distances and angles as well as fractional coordinates for **4b** are presented in Tables 1–3. The solid-state structure of the phosphonium cation in **4b** shows that the Mo$_2$C$_2$ core adopts a tetrahedral geometry where the -C≡C- unit bridges symmetrically both metal centers. The Mo—Mo bond length is 2.957(8) Å, and this compares well with the metal— metal single bond of neutral [(μ-η^2:η^2-alkyne) Cp$_2$Mo$_2$(CO)$_4$] complexes.[6] We note the absence of any direct stabilizing interaction the Mo center and the α-methylene group in contrast to that observed for the carbenium ion [Cp'$_2$Mo$_2$(CO)$_4$(μ-η^2:η^3-HC≡CCH$_2$)][BF$_4$] (Cp' = C$_5$H$_4$Me).[1a] Consistent with this observation, the carbonyl

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Table 2. Selected Bond Lengths (Å) and Angles (deg)

Mo(1)–Mo(2) = 2.9570(8)
Mo(1)–Cp_{av} = 2.329(8)
Mo(2)–Cp_{av} = 2.36(2)
C(1)–P(1) = 1.801(7)
Mo(1)–C(2) = 2.184(7)
Mo(2)–C(2) = 2.226(7)
C(1)–C(2) = 1.47(1)
C(3)–C(2)–C(1) = 137.7(7)
Mo(1)–C(3) = 2.207(7)
Mo(2)–C(3) = 2.127(7)
C(2)–C(3) = 1.35(1)
Mo(2)–C(22)–O(22) = 167.9(6)

Table 3. Fractional Coordinates for 4b

atom	x/a	y/b	z/c	U(eq), Å²
Mo(1)	0.15213(7)	0.36205(4)	0.17405(2)	0.0308
Mo(2)	–0.13790(7)	0.45197(4)	0.17138(2)	0.0297
C(11)	0.3072(9)	0.3863(6)	0.1376(2)	0.0503
O(11)	0.3990(7)	0.4019(5)	0.117892)	0.0676
C(12)	0.2217(8)	0.4715(5)	0.1938(2)	0.0421
O(12)	0.2616(8)	0.5350(4)	0.2057(2)	0.0606
C(21)	–0.2501(9)	0.3479(5)	0.1691(2)	0.0385
O(21)	–0.3213(8)	0.2861(4)	0.1663(2)	0.0654
C(22)	–0.0676(8)	0.4241(5)	0.2190(2)	0.0378
O(22)	–0.0408(7)	0.4195(4)	0.2495(2)	0.0515
C(1)	–0.0453(9)	0.3035(5)	0.1052(2)	0.0395
C(2)	–0.0196(8)	0.3687(4)	0.1326(2)	0.0308
C(3)	0.0435(8)	0.4459(5)	0.1347(2)	0.0335
P(1)	–0.1321(2)	0.3350(1)	0.06390(5)	0.0402
C(4)	–0.114(1)	0.2476(7)	0.0338(2)	0.0591
C(5)	–0.166(2)	0.1631(8)	0.0466(2)	0.0816
C(6)	–0.038(1)	0.4227(6)	0.0449(2)	0.0520
C(7)	0.128(1)	0.4099(7)	0.0393(3)	0.0716
C(8)	–0.322(1)	0.3621(8)	0.0718(2)	0.0627
C(9)	–0.410(1)	0.397(1)	0.0403(3)	0.0835
C(13)	0.098(1)	0.2160(5)	0.1773(2)	0.0500
C(14)	0.249(1)	0.2271(5)	0.1712(2)	0.0512
C(15)	0.312(1)	0.2686(6)	0.2006(3)	0.0512
C(16)	0.1979(9)	0.2855(6)	0.2258(2)	0.0455
C(17)	0.064(1)	0.2509(5)	0.2113(2)	0.0468
C(23)	–0.168(3)	0.588(1)	0.1478(8)	0.0544
C(24)	–0.126(2)	0.5998(9)	0.1794(7)	0.0333
C(25)	–0.243(4)	0.568(1)	0.2025(5)	0.0573
C(26)	–0.355(2)	0.534(1)	0.1763(7)	0.0352
C(27)	–0.301(3)	0.550(1)	0.1423(6)	0.0458
C(123)	–0.113(3)	0.599(1)	0.1600(8)	0.0501
C(124)	–0.174(3)	0.589(1)	0.1943(8)	0.0513
C(125)	–0.313(2)	0.545(1)	0.1950(6)	0.0375
C(126)	–0.343(2)	0.531(1)	0.1562(8)	0.0430
C(127)	–0.216(3)	0.570(1)	0.1374(6)	0.0522
B(1)	0.322(1)	0.1536(6)	0.0661(2)	0.0631
F(1)	0.293(2)	0.2300(6)	0.0664(4)	0.1897
F(2)	0.287(2)	0.1247(8)	0.0369(2)	0.2029
F(3)	0.265(2)	0.1144(8)	0.0915(3)	0.2112
F(4)	0.459(1)	0.137(1)	0.0687(7)	0.2702

absorptions of **4a** in CH_2Cl_2 are shifted to a lower wavenumber compared to those of the parent carbenium ion $[Cp_2Mo_2(CO)_4(\mu\text{-}\eta^2{:}\eta^3\text{-}MeC{\equiv}CCH_2)][BF_4]$ (**2**). This low shift is an indication of positive charge localization on the phosphorus atom rather than at the molybdenum centers of the phosphonium cluster **4a**; this situation contrasts with that of the parent species $[Cp_2Mo_2(CO)_4(\mu\text{-}\eta^2{:}\eta^3\text{-}MeC{\equiv}CCH_2)][BF_4]$, where the metal center stabilizes the carbonium moiety ($-CH_2^+$).[1,2,5]

Aiming at the preparation of the corresponding ylide complex of the above phosphonium derivative, we treated $[Cp_2Mo_2(CO)_4(\mu\text{-}\eta^2{:}\eta^2\text{-}MeC{\equiv}CCH_2PPh_3)][BF_4]$ (**3**) with an excess of the base DBU (DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene) in cold CH_3CN to obtain an orange brown precipitate. The ^1H NMR spectrum of this orange brown compound recorded in CD_3CN, at T = 233 K, shows the presence of two isomers **5a**/**5b** in a 2:1 ratio by integration. These species are fluxional and exchanging at room temperature (see Mechanistic Consideration). At T = 233 K two pairs of Cp environments are observed centered at 4.80 and 5.10 ppm, and two distinct doublets at 5.40 and 5.75 ppm are attributed to a CH—P– fragment with J_{H-P} = 27 and 32 Hz, respectively (see Figure 2); these coupling constants are an indication of a phosphorane unit. Similar results were reported for the bimetallic complex $[(i\text{-}Pr_2NP)_2HCOCHPR_3]Fe_2(CO)_6$ possessing a non-metal bonded phosphorane moiety.[7] Furthermore, two singlets appearing at 2.80 and 3.35 ppm are attributed to the CH_3– group of the bridging alkyne. We note the presence of multiplet

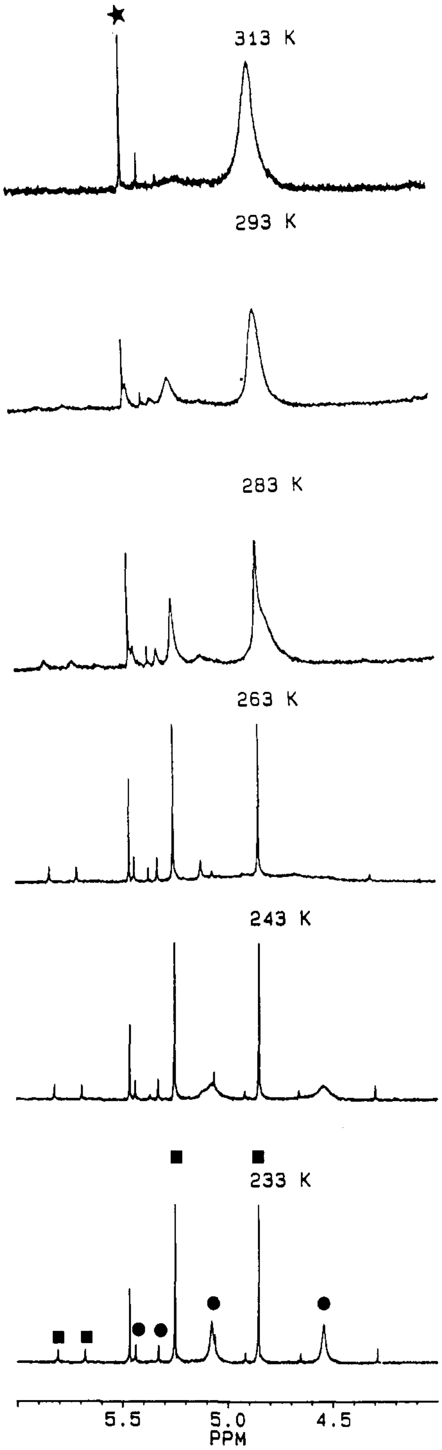
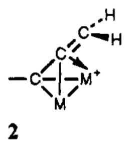
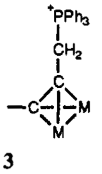
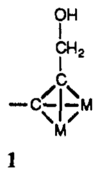
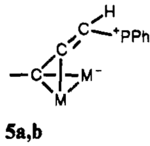
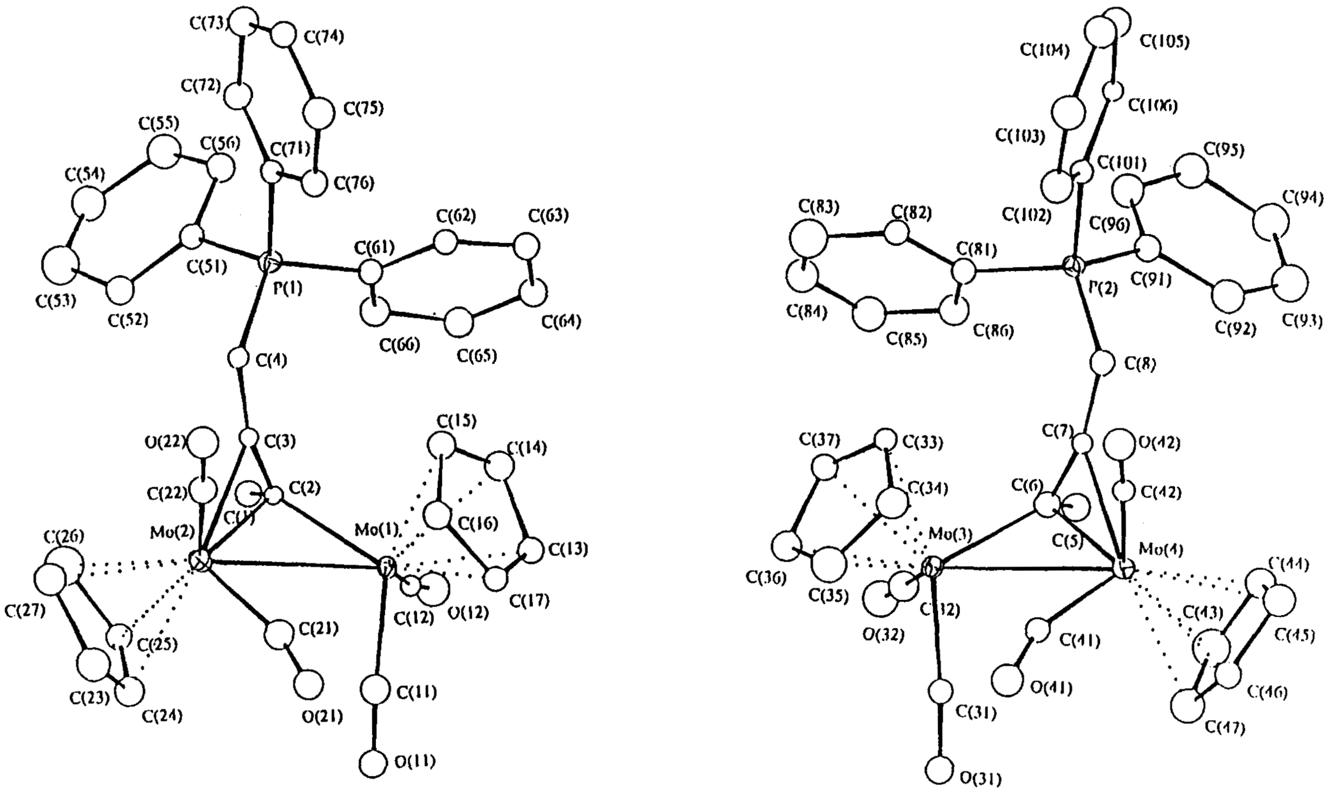


Figure 2. Excerpt of the variable temperature ^1H NMR spectra of the two isomers $[Cp_2Mo_2(CO)_4\{\mu\text{-}\eta^1{:}\eta^2\text{-}MeC{=}C{=}C(H)(PPh_3)\}]$ (**5a**,**b**) recorded in CD_3CN on a 250-MHz instrument. The signals are related to the cyclopentadienyl protons as well as to the phosphorane moieties –CH=P. Key: (★) CH_2Cl_2; (●) **5a**; (■) **5b**.

Table 4. Detailed Comparison of $\nu(CO)/CH_2Cl_2$ of 1 through 3 as Well as 5a,b[a]

formula[b]				
compd	2	3	1	5a,b
$\nu(CO/CH_2Cl_2)$, cm^{-1}	2046, 2015, 2000, 1908	1990, 1911, 1865	1983, 1912, 1853	1970, 1914, 1876, 1809, 1770

[a] The overall low wavenumber shift in this series is well correlated with the increase of the negative charge on the $-CpMo(CO)_2$ moieties. [b] M = $-CpMo(CO)_2$.



5a

Figure 3. Molecular structures of $[Cp_2Mo_2(CO)_4\{\mu\text{-}\eta^1\text{:}\eta^2\text{-}MeC{=}C{=}C(H)(PPh_3)\}]$ (**5a**). Two independent molecules (approximate enantiomers) are shown.

patterns in the aromatic region attributed to the phenyl group of the bonded triphenylphosphine.

The infrared spectra of the compounds **5a,b** recorded on KBr disks indicate the absence of the BF_4^- absorption while the carbonyl absorptions appear at 1977, 1900, 1883, 1801, and 1772 cm^{-1}, indicating a low wavenumber shift relative to the phosphonium derivative **3**; this result suggets the presence of a negative charge on the molybdenum cluster, hence an increase in the $d\pi \rightarrow p\pi^*$ CO back-donation, as observed.[8] Table 4 shows a detailed comparison of the carbonyl absorptions for the different $[Cp_2Mo_2(CO)_4(alkyne)]$ adducts **1–3** as well as the novel orange brown compound $[Cp_2Mo_2(CO)_4\{\mu\text{-}\eta^1\text{:}\eta^2\text{-}MeC{=}C{=}C(H)(PPh_3)\}]$ (**5a,b**). To ascertain the molecular structures of the above species without ambiguity, an X-ray study was carried out on isomer **5a**, which presumably is the major one (see Figure 3). Crystal data and selected bond distances and angles as well as fractional coordinates for **5a** are presented in Tables 5–7; the unit cell contains two independent molecules. Compound **5a** can be described as an allene-like complex where the "$MeC{=}C{=}CHPPh_3$" moiety bridges asymmetrically the two Mo centers, whereby C(2) interacts with two metal centers while the central carbon C(3) interacts exclusively with Mo(2). To our knowledge there are no examples of an $[Cp_2Mo_2(CO)_4(allene)]$ complex exhibiting such a coordination mode for the hydrocarbyl ligand; however, we note the existence of the σ,π-acetylide complexes $[Cp_2Mo_2(CO)_4(\mu\text{-}\eta^1\text{:}\eta^2\text{-}C{\equiv}CR]$[9] as well as the recently identified σ,π-allenylidene $[Cp_2Mo_2(CO)_4(\mu\text{-}\eta^2\text{:}\eta^2{=}C{=}C{=}CMe_2)]$ species.[9a] The C(2)—C(3)—C(4) bond angles are 145.6(35)° (**a**) and 147.5(34)° (**b**); they compare well with that reported for the allene $[Cp_2Mo_2(CO)_4(\mu\text{-}\eta^2\text{:}\eta^2\text{-}CH_2{=}C{=}CH_2)]$ (**6**) derivative.[10] The Mo(1)—Mo(2) metal distance

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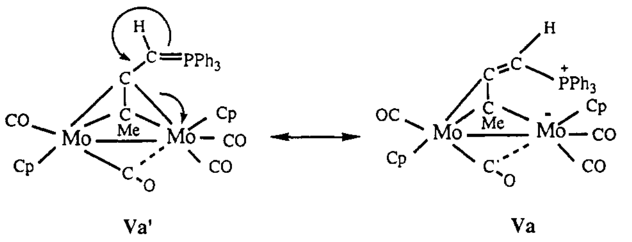


Va' Va

Figure 4.

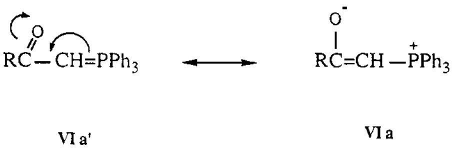
Table 5. Crystallographic Data for 5a

chemical formula	$Mo_2C_{36}H_{30}O_4P$
fw	749.5
cryst syst	monoclinic
space group	$P2_1$
Z	4
a, Å	9.024(2)
b, Å	30.851(7)
c, Å	11.378(1)
β, deg	99.65(2)
V, Å^3	3123(9)
$F(000)$	1508
ρ(calcd), g cm^{-3}	1.53
μ(Mo Kα), cm^{-1}	8.69
diffractometer	CAD4
monochromator	graphite
radiation (λ, Å)	Mo Kα (0.710 70)
temp, °C	20
scan type	$\omega/2\theta$
scan range θ, deg	$1.0 + 0.34 \tan \theta$
2θ range, deg	2–42
no. of reflctn collected	3420
no. of reflctn used (criteria)	1977 [$I > 3\sigma(I)$]
R	0.056
R_w[a]	0.064
abs corr[b]	min 0.85, max 1.19
secondary ext	no
weighting scheme	unit weights
rms (shift/esd) (last ref)	0.33
ls params	376

[a] $R_w = [\sum_i w_i (F_o - F_c)^2 / \sum_i w_i F_o^2]^{1/2}$. [b] Difabs: Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 159.

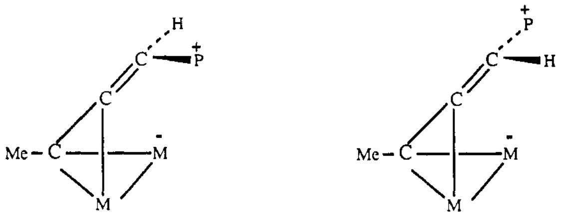
is 3.012(3) Å and slightly longer than that of the phosphonium derivative **3** but similar to that reported for **6**. The molecular structure also shows the presence of four carbonyl ligands, of which one strongly semibridging carbonyl is observed and consistent with the infrared data (vide supra).

We also note that the C(4)—P(1) bond distances 1.80 Å in form **a** and 1.75 Å (**b**) are typical for a single bond; hence complex **5a** can be considered to acquire the more hybrid character of Va (zwitterion) rather than the expected form Va′ (see Figure 4). This implies that the molecular formula should be presented as $[Cp_2Mo_2(CO)_4\{\mu\text{-}\eta^1{:}\eta^2\text{-}MeC{=}C{=}C(H)(PPh_3)\}]$ (**5a,b**). This is an unprecedented example of the molybdenum centers stabilizing the canonical form Va of a coordinated ylide. The $-CpMo(CO)_2$ moieties in complex **5a** behave as electron acceptors; this situation should be compared to that of the well-known organic carbonyl-stabilized phosphorus ylides "$Ph_3P{=}CHC(O)R$". In the latter example the oxygen atom bears the negative charge (see Figure 5). As an aside it should be mentioned that some mononuclear complexes possessing carbonyl-stabilized phosphorus ylides as a coordinating ligand have been reported.[11] The authors describe two different bonding modes for these coordinating ligand ylides as a C bonding via the methine carbon atom or O bonding via the carbonyl oxygen.[12]



VI a' VI a

Figure 5.



5a 5b

M = -CpMo(CO)$_2$

Figure 6.

The effect of a negative charge on the $-CpMo(CO)_2$ moieties in $[Cp_2Mo_2(CO)_4\{\mu\text{-}\eta^1{:}\eta^2\text{-}MeC{=}C{=}C(H)(PPh_3)\}]$ (**5a**) is manifested by the low wavenumber shift for the carbonyl absorptions as well as the presence of a strongly semibridging carbonyl in the molecular structure of **5a** with Mo(1)—C(21) and Mo(3)—C(41) distances of 2.64 Å (**a**) and 2.65 Å (**b**) and with bond angles Mo(2)—C(21)—O(21) and Mo(4)—C(41)—O(41) of 163.1(29)° (**a**) and 160.1(12)° (**b**). The spectroscopic and structural data obtained for $[Cp_2Mo_2(CO)_4\{\mu\text{-}\eta^1{:}\eta^2\text{-}MeC{=}C{=}C(H)(PPh_3)\}]$ (**5a,b**) allow us to consider that each molybdenum center is of formal oxidation state +1 where one molybdenum center interacts with two carbon centers while the other metal is only bonded to the central carbon of the allene moiety. To satisfy the 18e count rule this molybdenum center should bear a negative charge. The carbon in the α-position possesses two different groups ($-H$ and $-PPh_3$) with a positive charge on the phosphorus atom. This zwitterion form is also manifested by the low solubility of **5a,b** in the usual organic solvents including CH_3CN. The major isomer **5a** is better described as the species where $-PPh_3$ is pointed upward distal from the Mo—Mo metal bond with less steric hindrance while the minor isomer **5b** adopts the opposite orientation (see Figure 6). On the other hand these complexes $[Cp_2Mo_2(CO)_4\{\mu\text{-}\eta^1{:}\eta^2\text{-}MeC{=}C{=}C(H)(PPh_3)\}]$ were found to be stable indefinitely in the solid state under an inert atmosphere; however they decompose in solution (acetone, THF, even diethyl ether) upon standing for several hours. This constituted a major obstacle for obtaining crystals for an X-ray analysis; hence rapid crystallization from a cold acetonitrile solution of **5a,b** prepared in situ was performed several times in order to obtain crystals suitable for an X-ray study.

Mechanistic Consideration. Unlike usual allenes of $[Cp_2Mo_2(CO)_4\{\mu\text{-}\eta^2{:}\eta^2\text{-}R1R2C{=}C{=}CR3R4\}]$, our compounds $[Cp_2Mo_2(CO)_4\{\mu\text{-}\eta^1{:}\eta^2\text{-}MeC{=}C{=}C(H)(PPh_3)\}]$

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Table 6. Selected Bond Lengths (Å) and Angles (deg)

Mo(1)–Mo(2) = 3.012(3)
Mo(1)–C(2) = 2.21(3)
Mo(1)–Cp_{av} = 2.37(4)
Mo(2)–C(2) = 2.15(3)
Mo(2)–C(3) = 2.15(3)
Mo(2)–Cp_{av} = 2.39(4)
C(1)–C(2) = 1.62(5)
C(2)–C(3) = 1.34(4)
C(3)–C(4) = 1.30
C(4)–P(1) = 1.80(3)
C(2)–C(3)–C(4) = 145.6(35)
Mo(2)–C(21)–O(21) = 163.1(29)
Mo(3)–Mo(4) = 3.027(4)
Mo(3)–C(6) = 2.21(3)
Mo(3)–Cp_{av} = 2.34(4)
Mo(4)–C(6) = 2.27(3)
Mo(4)–C(7) = 2.18(3)
Mo(4)–Cp_{av} = 2.37(4)
C(5)–C(6) = 1.47(5)
C(6)–C(7) = 1.43
C(7)–C(8) = 1.29
C(8)–P(2) = 1.75(3)
C(6)–C(7)–C(8) = 147.4(33)
Mo(4)–C(41)–O(41) = 160.1(27)
Mo(1)–(3) = 2.97
Mo(3)–C(7) = 3.01

Table 7. Fractional Coordinates for 5a

atom	x/a	y/b	z/c	U(eq), Å^2	U(iso), Å^2	atom	x/a	y/b	z/c	U(eq), Å^2	U(iso), Å^2
Mo(1)	0.9184(3)	0.1281(1)	0.4998(2)	0.0259		Mo(3)	0.2503(3)	0.8592(1)	0.3174(2)	0.0267	
Mo(2)	0.6172(3)	0.1274(1)	0.5805(2)	0.0329		Mo(4)	0.5524(3)	0.8647(1)	0.2361(2)	0.0323	
P(1)	0.4951(9)	0.1215(3)	0.1423(7)	0.0303		P(2)	0.6847(8)	0.8668(3)	0.6704(7)	0.0284	
C(11)	1.011(4)	0.106(1)	0.653(3)		0.05(1)	C(31)	0.163(3)	0.881(1)	0.166(3)		0.037(9)
O(11)	1.071(3)	0.958(8)	0.747(2)		0.053(7)	O(31)	0.095(2)	0.8963(8)	0.072(2)		0.050(6)
C(12)	1.003(4)	0.072(1)	0.473(3)		0.037(8)	C(32)	0.157(4)	0.913(1)	0.355(3)		0.05(1)
O(12)	1.062(3)	0.041(1)	0.446(2)		0.077(9)	O(32)	0.091(3)	0.944(1)	0.375(2)		0.074(8)
C(21)	0.778(4)	0.161(1)	0.665(3)		0.05(1)	C(41)	0.398(4)	0.825(1)	0.157(3)		0.039(9)
O(21)	0.852(3)	0.1856(8)	0.734(2)		0.055(7)	O(41)	0.328(3)	0.8041(8)	0.082(2)		0.060(7)
C(22)	0.533(4)	0.181(1)	0.520(3)		0.05(1)	C(42)	0.643(3)	0.812(1)	0.298(3)		0.034(8)
O(22)	0.478(3)	0.2128(9)	0.477(2)		0.066(7)	O(42)	0.692(3)	0.7792(9)	0.334(2)		0.060(7)
C(1)	0.690(4)	0.045(1)	0.407(3)		0.05(1)	C(5)	0.470(4)	0.943(1)	0.412(3)		0.05(1)
C(2)	0.700(3)	0.097(1)	0.434(3)		0.024(9)	C(6)	0.456(4)	0.896(1)	0.387(3)		0.04(1)
C(3)	0.596(3)	0.126(1)	0.389(3)		0.025(8)	C(7)	0.575(3)	0.867(1)	0.430(3)		0.028(8)
C(4)	0.506(3)	0.139(1)	0.294(3)		0.027(9)	C(8)	0.673(4)	0.854(1)	0.519(3)		0.039(9)
C(13)	1.111(3)	0.164(1)	0.432(2)		0.039(9)	C(33)	0.302(3)	0.8047(9)	0.466(2)		0.032(8)
C(14)	1.003(3)	0.157(1)	0.329(3)		0.06(1)	C(34)	0.282(3)	0.783(1)	0.355(3)		0.06(1)
C(15)	0.877(3)	0.182(1)	0.346(3)		0.05(1)	C(35)	0.130(4)	0.791(1)	0.307(3)		0.08(1)
C(16)	0.911(3)	0.205(1)	0.455(2)		0.05(1)	C(36)	0.058(4)	0.819(1)	0.377(3)		0.05(1)
C(17)	1.060(3)	0.1942(9)	0.508(2)		0.036(8)	C(37)	0.169(3)	0.828(1)	0.476(3)		0.044(9)
C(23)	0.530(4)	0.119(1)	0.760(3)		0.07(1)	C(43)	0.592(4)	0.935(1)	0.153(3)		0.08(1)
C(24)	0.635(4)	0.085(1)	0.762(3)		0.06(1)	C(44)	0.728(4)	0.915(1)	0.203(3)		0.06(1)
C(25)	0.589(3)	0.056(1)	0.669(3)		0.045(9)	C(45)	0.769(4)	0.879(1)	0.138(3)		0.06(1)
C(26)	0.444(4)	0.070(1)	0.614(4)		0.09(1)	C(46)	0.639(3)	0.874(1)	0.054(3)		0.045(9)
C(27)	0.410(4)	0.109(1)	0.668(3)		0.07(1)	C(47)	0.532(4)	0.907(1)	0.060(3)		0.07(1)
C(51)	0.383(3)	0.071(1)	0.109(2)		0.035(8)	C(81)	0.502(3)	0.8711(8)	0.719(3)		0.038(9)
C(52)	0.316(4)	0.055(1)	0.205(3)		0.05(1)	C(82)	0.445(3)	0.8338(9)	0.767(3)		0.036(9)
C(53)	0.231(5)	0.016(1)	0.178(3)		0.09(1)	C(83)	0.300(4)	0.836(1)	0.800(4)		0.09(2)
C(54)	0.235(4)	−0.002(1)	0.065(3)		0.07(1)	C(84)	0.236(4)	0.878(1)	0.791(3)		0.06(1)
C(55)	0.309(4)	0.013(1)	−0.028(3)		0.07(1)	C(85)	0.292(4)	0.917(1)	0.745(3)		0.07(1)
C(56)	0.384(4)	0.054(1)	−0.007(2)		0.05(1)	C(86)	0.434(3)	0.913(1)	0.708(3)		0.06(1)
C(61)	0.668(3)	0.1107(8)	0.099(3)		0.035(9)	C(91)	0.784(4)	0.917(1)	0.709(2)		0.04(1)
C(62)	0.747(3)	0.1418(8)	0.043(3)		0.034(9)	C(92)	0.866(4)	0.935(1)	0.626(3)		0.06(1)
C(63)	0.885(3)	0.132(1)	0.004(3)		0.042(8)	C(93)	0.948(5)	0.974(1)	0.651(3)		0.08(1)
C(64)	0.958(4)	0.0918(9)	0.032(3)		0.05(1)	C(94)	0.946(5)	0.995(1)	0.759(3)		0.08(1)
C(65)	0.877(3)	0.061(1)	0.089(3)		0.06(1)	C(95)	0.867(4)	0.977(1)	0.846(3)		0.07(1)
C(66)	0.733(3)	0.069(1)	0.120(3)		0.06(1)	C(96)	0.776(4)	0.940(1)	0.815(3)		0.06(1)
C(71)	0.405(3)	0.1641(8)	0.053(2)		0.018(7)	C(101)	0.788(3)	0.8260(9)	0.757(2)		0.032(8)
C(72)	0.289(3)	0.155(1)	−0.042(2)		0.045(9)	C(102)	0.766(4)	0.7834(9)	0.710(3)		0.06(1)
C(73)	0.225(4)	0.1901(8)	−0.114(3)		0.06(1)	C(103)	0.857(14)	0.751(1)	0.775(3)		0.07(1)
C(74)	0.269(3)	0.2335(9)	−0.089(3)		0.043(9)	C(104)	0.961(4)	0.759(1)	0.879(3)		0.06(1)
C(75)	0.388(4)	0.241(1)	0.006(3)		0.07(1)	C(105)	0.966(4)	0.8018(9)	0.924(3)		0.06(1)
C(76)	0.456(3)	0.2071(8)	0.078(3)		0.042(9)	C(106)	0.887(3)	0.8375(9)	0.864(2)		0.025(8)

(**5a,b**) were found to be fluxional in solution. Thus the ^{1}H NMR spectrum of **5a,b** recorded in CD_3CN at T = 233 K shows two singlets for the cyclopentadienyl resonances for each isomer and two sets of doublets for the phosphorane moieties –CH=P. When the sample solution of **5a,b** is warmed, the signals attributed to the cyclopentadienyls of the major isomer **5a** broaden and then coalesce at ca. T = 263 K with $\Delta G^{\ddagger}$ = 12.5 ± 0.5 kcal/mol. Note that the signals corresponding to the CH=P– fragment of both isomers remain unchanged (Figure 2). If the sample is further heated, we note that the two singlets corresponding to the Cp environments of the minor isomer **5b** broaden and then coalesce at ca. T = 315 K with $\Delta G^{\ddagger}$ = 14.8 ± 0.5 kcal/mol; concomitant with this modification the signals corresponding to the phosphorane moieties of both isomers start to broaden at 283 K and flatten at higher temperatures (see Figure 2). An intramolecular process (see Figure 7) consistent with the above observations would be that at low temperature the major isomer **5a** interconverts into **5a′** via intermediate **5a″** where "MeC=C=C(H)(PPh_3)" is perpendicular to the Mo—Mo bond, with the –PPh_3 pointing upward distal from the Mo—Mo bond. During this process the Cp environments in **5a** are equilibrating with respect to the NMR time scale with $\Delta G^{\ddagger}_{int}$(**5a**) = 12.5 ± 0.5 kcal/mol (int = interconversion). At higher temperatures, a similar dynamic process occurs for the minor isomer **5b** but in this case the unit "MeC=C=C(H)(PPh_3)" of the intermediate **5b″** adopts an opposite geometry compared to that in **5a″** whereby the –PPh_3 leans toward the Mo—Mo metal bond. Due to steric hindrance such an interconversion process would possess a higher energy barrier and, as observed from the experimental data, $\Delta G^{\ddagger}_{int}$(**5b**) = 14.8 ± 0.5 kcal/mol. Note that these processes do not convert **5a** into **5b**. Upon warming to higher temperatures, another process starts to operate in which a rotation around the C(3)—C(4) bond takes place; this would exchange **5a** into **5b** and vice versa. These observations were also confirmed by recording the ^{31}P{^{1}H} NMR spectra at variable temperatures. For instance at T = 243 K two sharp signals occurring at 6.1

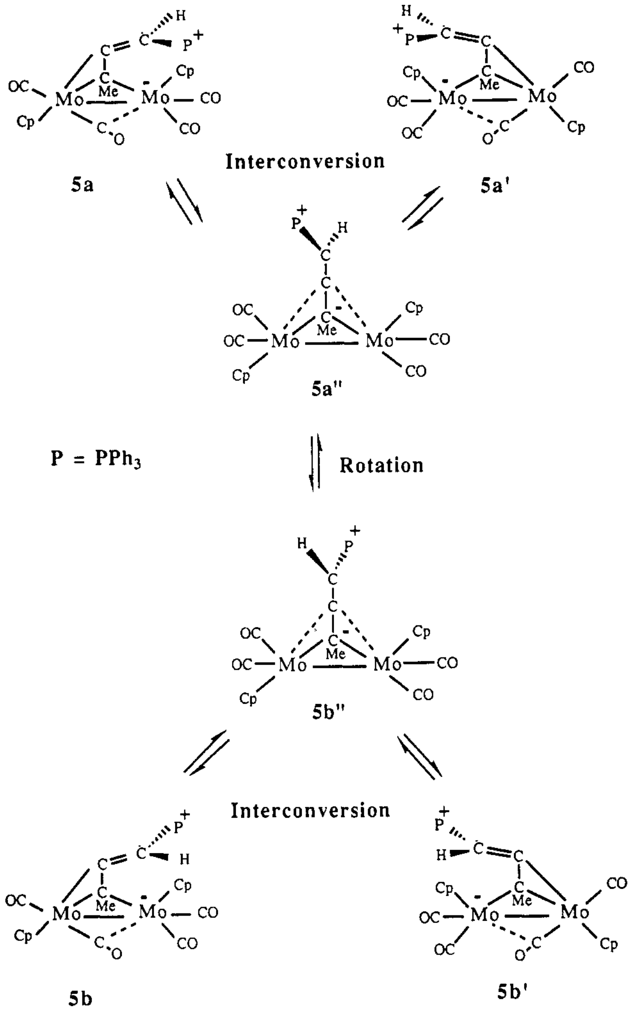

Figure 7. Proposed mechanism for the exchange process in **5a,b**.

and 9.8 ppm were observed with a 2:1 ratio (Figure 8). Upon warming, these signals start to broaden at T = 298 K, and the peak corresponding to the minor isomer flattened at T = 305 K; however upon further warming at T = 315 K for a long period and during acquisition, the sample started to decompose and a new singlet appeared at −6 ppm, which corresponds to the free phosphine PPh$_3$.

Summarizing the above spectroscopic data, we note that the mechanism of exchange for the stabilized ylides **5a,b** resembles that of the primary carbenium ions $\Delta G^{\ddagger}_{\rm int}$ where two main processes are taking place: an interconversion and a rotation process. It is worth comparing the values of the $\Delta G^{\ddagger}_{\rm int}$ of **5a,b** (12.5 and 15 kcal/mol), which are smaller than that of the primary carbenium ion $\Delta G^{\ddagger}_{\rm int}$ = 18 kcal/mol.[1a,5a] In fact if we examine the structure of **5a** in the solid state, we notice that the two independent molecules in the unit cell describe the interconversion process observed in solution to some extent (see Figure 3). In this process only one metal—carbon bond is broken, Mo(2)—C(3), in favor of the formation of the new metal—carbon bond Mo(4)–C(7); concomitant with this, we also notice changes in the Cp orientations as well as the semibridging carbonyl. The previous exchange scenario also takes place for the cationic carbenium ions, [Cp$_2$Mo$_2$(CO)$_4$(μ-η^2:η^3-RC≡CCH$_2$)][BF$_4$]; however, two Mo—C bonds and not one should be altered during the interconversion process, and this may explain the difference in the energy of activation. We note also the $\Delta G^{\ddagger}_{\rm rot}$ (rot = rotation) for **5a** should be higher than $\Delta G^{\ddagger}_{\rm int}$, as observed for the primary carbenium ions.[5]

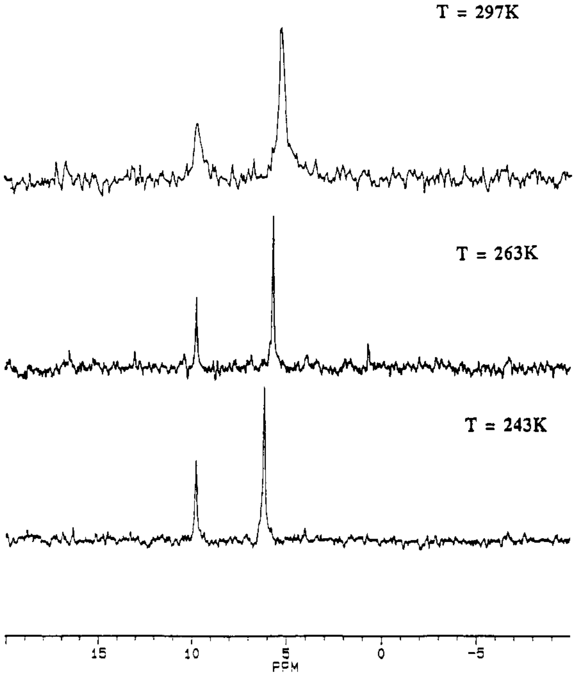

Figure 8. Variable temperature ^{31}P{^{1}H} NMR spectra of the two isomers [Cp$_2$Mo$_2$(CO)$_4${μ-η^1:η^2-MeC=C=C(H)(PPh$_3$)}] (**5a,b**) recorded in CD$_3$CN on 250-MHz instrument.

Recently, an organotransition-metal substituted ylide [(Ph$_3$PCH-η^5-C$_6$H$_6$)Mn(CO)$_3$] has been reported but not isolated.[13] This manganese substituted ylide has shown Wittig reaction[14] to occur with aldehydes, affording the cis and trans substituted olefins. We are currently studying the reactivity of **5a,b** with aldehydes; the results of these investigations will be the subject of future reports.

Experimental Section

General Procedures. All manipulations were carried out under an argon atmosphere using Shlenck techniques. Solvents were purified and dried prior to use by conventional distillation techniques. All reagents obtained from commercial sources were used without further purification. ^{1}H and ^{13}C NMR were recorded on a Bruker AM 250-MHz instrument. ^{1}H NMR chemical shifts are reported in parts per million referenced to the residual solvent proton resonance. Infrared spectra were obtained on a FT Bomem Michelson 100 spectrometer from samples prepared either on KBr disks or in CH$_2$Cl$_2$ solutions. All absorptions are expressed in wavenumbers (cm^{-1}). Elemental analyses were performed by the Microanalytical Laboratory of the CNRS ICSN, Gif/Yvette.

Synthesis of [Cp$_2$Mo$_2$(CO)$_4$(μ-η^2:η^2-MeC≡CCH$_2$OH)] (1). A solution of 2-butyn-1-ol (200 mL, 2.67 mmol) was added dropwise to a solution of Cp$_2$Mo$_2$(CO)$_4$ (670 mg, 1.37 mmol) in 15 mL of diglyme, and the mixture was refluxed for 3 h. Later the solution was eluted through silica gel using ether/pentane (1/4) as eluent, and the solvents were removed under vacuum to give a burgundy microcrystalline substance. Yield: 410 mg, 59%. ^{1}H NMR (250 MHz, CD$_3$Cl): δ 5.30 (s, 10H, Cp), 4.74 (d, 2H, -CH$_2$), 1.40 (t, 1H, -OH), 2.65 (s, 3H, -CH$_3$). IR/CH$_2$Cl$_2$, ν(CO)/cm^{-1}: 1983, 1912, 1853. Anal. Calcd for C$_{18}$H$_{16}$O$_5$Mo$_2$: C, 42.88; H, 3.19. Found: C, 43.47; H, 3.37.

Synthesis of [Cp$_2$Mo$_2$(CO)$_4$(μ-η^2:η^3-MeC≡CCH$_2$)][BF$_4$] (2). An excess of HBF$_4$·Et$_2$O (85%) in ether solution was added to

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(13) Lee, Si-G.; Chung, Y. K.; Yoon, Tae-S.; Shin, W. *Organometallics* **1993**, *12*, 2873.

(14) Wittig, G. *J. Organomet. Chem.* **1975**, *100*, 279.

a purple solution of [$Cp_2Mo_2(CO)_4(\mu$-η^2:η^2-MeC≡CCH_2OH)] (1) (460 mg, 0.91 mmol) in 20 mL of ether to afford an orange precipitate. The compound was separated and washed with ether and then recrystallized from CH_2Cl_2/ether to give orange crystals. Yield: 220 mg, 44%. ^{1}H NMR (250 MHz, $(CD_3)_2CO$): δ 5.87 (s, 10H, Cp), 5.68 (s, 1H), 4.92 (s, 1H), 2.89 (s, 3H, CH_3). $^{13}C\{^1H\}$ (62 MHz, CD_2Cl_2): δ 225.20, 223.10, 220.41, 217.93, 123.97, 97.24, 93.06, 72.46, 24.14. IR/CH_2Cl_2, ν(CO)/cm^{-1}: 2046, 2015, 2000, 1908. Anal. Calcd for $C_{18}H_{15}O_4Mo_2BF_4$: C, 37.67; H, 2.63. Found: C, 37.33; H, 2.96.

Synthesis of [$Cp_2Mo_2(CO)_4(\mu$-η^2:η^2-MeC≡CCH_2PPh_3)][BF_4] (3). A solution of PPh_3 (30 mg, 0.1 mmol) in 5 mL of CH_2Cl_2 was added dropwise to an orange solution of [$Cp_2Mo_2(CO)_4(\mu$-η^2:η^3-MeC≡CCH_2)][BF_4] (2) (50 mg, 0.087 mmol) in 5 mL of CH_2Cl_2, and the reaction mixture turned red. The reaction was stirred for 2 h, and then 20 mL of diethyl ether was added, affording an orange-red precipitate. This product was separated, washed several times with ether, and recrystallized from CH_2Cl_2/ether. Yield: 50 mg, 66%. ^{1}H NMR (250 MHz, $(CD_3)_2CO$): δ 8.09–7.81 (m, 15H, C—H phenyl group), 5.35 (d, 2H, –CH_2–, J_{P-H} = 12 Hz), 5.28 (s, 10H, Cp), 2.39 (s, 3H, –CH_3–). $^{13}C\{^1H\}$ (62.89 MHz, CD_2Cl_2): δ 248.40, 232.90, 135.80, 133.95, 130.90, 119.10 (d, J_{P-C} = 83 Hz), 118.50, 97.80, 93.75, 26.00. $^{31}P\{^1H\}$ (101.25 MHz, $(CD_3)_2CO$): δ 18.53 (s). IR/KBr disk: ν(CO) 1987, 1911, 1835 cm^{-1}; $\nu(BF_4^-)$ 1084, 650 cm^{-1}. Anal. Calcd for $C_{36}H_{30}O_4PMo_2BF_4$: C, 51.70; H, 3.62. Found: C, 51.34; H, 3.77.

Synthesis of [$Cp_2Mo_2(CO)_4(\mu$-η^2:η^2-MeC≡CCH_2PEt_3)][BF_4] (4a). The preparation of **4a** was performed similarly to that of **3** (vide supra). The starting materials and quantities used are as follows: 70 mg (0.1 mmol) of **2** in 5 mL of CH_2Cl_2 and 40 μL of PEt_3 in 2 mL of CH_2Cl_2. Thus compound [$Cp_2Mo_2(CO)_4(\mu$-η^2:η^2-MeC≡CCH_2PEt_3)][BF_4] (**4a**) was obtained as an orange microcrystalline solid. Yield: 50 mg, 64%. ^{1}H NMR (250 MHz, $(CD_3)_2CO$): δ 5.49 (s, 10H, Cp), 4.02 (d, 2H, J_{P-H} = 12 Hz, –CH_2–), 3.03 (s, 3H, –CH_3–), 2.36 (dq, 6H, J_{P-H} = 13 Hz, –P—CH_2–), 1.37 (dt, 9H, $^3J_{P-H}$ = 8 Hz, P—C—CH_3). $^{13}C\{^1H\}$ (62.89 MHz, CD_3CN): δ 238.87, 222.50, 101.50, 94.21, 66.20, 25.90, 12.30, 5.90. $^{31}P\{^1H\}$ (101.25 MHz, $(CD_3)_2CO$): δ 39.60 (s). IR (KBr disk): ν(CO) 1990, 1930, 1910, 1811 cm^{-1}; $\nu(BF_4^-)$ = 1084, 650 cm^{-1}. Anal. Calcd for $C_{24}H_{30}O_4PMo_2BF_4$: C, 41.65; H, 4.37. Found: C, 40.77; H, 4.40.

Synthesis of [$Cp_2Mo_2(CO)_4(\mu$-η^2:η^2-HC≡CCH_2PEt_3)][BF_4] (4b). The synthetic procedure of **4b** is similar to that described for the preparation of **4a**. Yield: 60%. ^{1}H NMR (250 MHz, $(CD_3)_2CO$): δ 6.60 (s, H, HC≡), 5.33 (s, 10H, Cp), 3.88 (d, 2H, J_{P-H} = 12.5 Hz, –CH_2–), 2.35 (d, P—CH_2—C, 6H, J_{P-H} = 14 Hz), 1.34 (d, P—C—CH_3, 9H, $^3J_{P-H}$ = 6 Hz). $^{13}C\{^1H\}$ (62.89 MHz, CD_3CN): δ 240.30, 233.49, 93.00, 83.70, 43.74, 25.01, 12.60, 6.00. $^{31}P\{^1H\}$: δ 38.02 (s). IR/CH_2Cl_2, ν(CO)/cm^{-1}: 1999.12 (s), 1919.30 (vs), 1841.21 (s).

Synthesis of [$Cp_2Mo_2(CO)_4\{\mu$-η^1:η^2-MeC=C=C(H)(PPh_3)\}] (5a,b). To a solution of **3** (50 mg, 0.06 mmol) in 2 mL of CH_3CN at –40 °C was added 21 μL (0.14 mmol) of DBU (1,8-diazabicyclo[5.4.0]undec-7-ene), and the reaction mixture was stirred for 10 min to afford an orange brown precipitate. After filtration the precipitate was washed with cold CH_3CN and then dried under vacuum. Yield: 20 mg, 45%. ^{1}H NMR (250 MHz, CD_3CN, T = –40 °C): (major isomer **5a**) δ 7.90–7.45 (m, 15H, C—H phenyl), 5.40 (d, J_{P-H} = 28 Hz, 1H, HC—P), 4.80 (d, 10H, Cp), 3.35 (s, 3H, CH_3–); (minor isomer **5b**) δ 7.9–7.45 (m, 15H, C—H phenyl), 5.80 (d, J_{P-H} = 32 Hz, 1H, HC—P), 5.10 (d, 10H, Cp), 2.8 (s, 3H, CH_3–). $^{13}C\{^1H\}$ (62.89 MHz, $(CD_3)_2CO$, T = –40 °C): (major isomer **5a**) δ 251.5, 246.4, 224.8, 212.2 (CO), 191.2 (=C=), 181.5 (Me—C=), 134.68, 130.54, 124.60 (J_{P-C} = 6.9, 13.1, 86.2 Hz, Ph), 93.80 (=C, d, J_{P-C} = 17 Hz), 93.40 (Cp), 35.07 (CH_3–); (minor isomer **5b**) δ 252.9, 247.20, 228.40, 219.30 (CO), 187.2 (=C=), 170.4 (Me—C=), 133.76, 129.75, 125.30 (J_{P-C} = 6.9, 13.1, 86.2 Hz, Ph), 93.60 (Cp), 92.5 (=C, d, J_{P-C} = 17 Hz), 37.20 (CH_3–). $^{31}P\{^1H\}$ (101.25 MHz, CD_3CN, T = –40 °C); (major isomer **5a**) δ 6.1 (s); (minor isomer **5b**) δ 9.8 (s). IR/CH_2Cl_2, ν(CO)/cm^{-1}: 1970 (w), 1914 (s), 1876 (s), 1809 (s), 1770 (m). Anal. Calcd for $C_{36}H_{29}O_4PMo_2$: C, 57.77; H, 3.91. Found: C, 57.64; H, 3.97.

Structure Determination of [$Cp_2Mo_2(CO)_4(\mu$-η^2:η^2-HC≡CCH_2PEt_3)][BF_4] (4b). Suitable crystals of [$Cp_2Mo_2(CO)_4(\mu$-η^2:η^2-HC≡CCH_2PEt_3)][BF_4] (**4b**) were obtained by recrystallization from dichloromethane/diethyl ether solution. Crystallographic data are collected in Table 1. Accurate cell dimensions and orientation matrices were obtained by least-squares refinement of 25 accurately centered reflections on a Nonius CAD4 diffractometer equipped with graphite-monochromated Mo Kα radiation. No significant variations were observed in the two check reflections during data collection. Computations were performed by using CRYSTALS[15] modified locally for a Microvax II computer. Scattering factors and corrections for anomalous absorption were taken from ref 16. The structure was solved by standard Patterson–Fourier techniques. Two sites of disorder were identified and modeled. The first one concerns the Mo(2) bonded cyclopentadienyl ring. A satisfactory solution was found consisting of two shifted cycles with 0.5 occupancies. The second problem arose from rotational motion displayed by the BF_4 anion. The best solution was in using restraints on the B—F bond lengths and the F—B—F angles; however it led to large thermal parameters for the F atoms. Some hydrogen atoms on C(3) and the C(13)–C(17) ring were located on a difference Fourier map and refined with an overall isotropic thermal parameter; others (on C(1) and ethyl groups) were included in calculated positions as fixed contributors; while those on disordered rings were omitted. The structure was refined to R = 0.044 and R_w = 0.047 with the use of 3405 reflections for 382 least-squares parameters. Final atomic coordinates and selected bond distances are listed in Tables 2 and 3.

Structure Determination of [$Cp_2Mo_2(CO)_4\{\mu$-η^1:η^2-MeC=C=C(H)(PPh_3)\}] (5a). Single crystals were grown from cooling a CD_3CN solution of an NMR sample tube of **5a,b**. [$Cp_2Mo_2(CO)_4\{\mu$-η^1:η^2-MeC=C=C(H)(PPh_3)\}] (**5a**) crystallizes in the $P2_1$ space group with Z = 4, and the asymmetric unit contains two independent molecules; despite the presence of a pseudoplane of symmetry, the structure could not be resolved in the higher symmetry space group $P2_1/m$. The structure was resolved by direct methods (SHELXS)[17] and refined by least squares. Due to the very small size of the crystal, there were only 1977 reflections ($I > 3\sigma(I)$) available to refine the coordinates of 86 non-hydrogen atoms. Thus only the molybdenum and phosphorus atoms were anisotropically refined; all other atoms were left isotropic, and hydrogen atoms were not localized. Furthermore, restraints were applied on phenyl –C—C– bond lengths (1.42, 0.02 Å). The structure was refined to R = 0.056 and R_w = 0.064 with the use of 1977 reflections for 376 least squares parameters.

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Supplementary Material Available: For the structural analysis of both **4b** and **5a**, tables of anisotropic displacement parameters (Tables S1 and S2) and bond distances and angles (Tables S3 and S4) (11 pages). Ordering information is given on any current masthead page.

OM940070C

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