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Bis(ethylene) Complexes of Molybdenum and Tungsten and Their Reactivity toward CO_2. New Examples of Acrylate Formation by Coupling of Ethylene and Carbon Dioxide

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The compounds *trans*-$M(C_2H_4)_2(P\text{-}P)(PMe_3)_2$ (M = Mo, P-P = $Me_2PCH_2CH_2PMe_2$ (dmpe; **1a**), $Et_2PCH_2CH_2PEt_2$ (depe; **2a**), $Me_2PCH_2PMe_2$ (dmpm; **3**); M = W, P-P = dmpe (**1b**), depe (**2b**)) have been prepared by straightforward substitution reactions employing the *trans*-$M(C_2H_4)_2(PMe_3)_4$ complexes and the corresponding phosphine. Further reaction with the chelating phosphine has been investigated for **1a** and **2a** and affords the fully substituted *trans*-$Mo(C_2H_4)_2(P\text{-}P)_2$ (P-P = dmpe (**6**), depe (**7**)), while reactions with CO lead to various substituted *trans*-$M(C_2H_4)_2(CO)(PMe_3)(P\text{-}P)$ products. Compounds **6** and **7** can also be synthesized by the direct reduction of $MoCl_4(THF)_2$ with Na–Hg under C_2H_4, in the presence of the appropriate diphosphine. The analogous reduction of $MoCl_3(THF)_3$ (Na–Hg, C_2H_4, PMe_2Ph) furnishes *trans*-$Mo(C_2H_4)_2(PMe_2Ph)_4$ (**8**). Application of Lever's additive ligand approach to complexes of this type shows an interdependence between the electron density at the metal center in this and other bis(ethylene) complexes of Mo and W and the ^{13}C chemical shift of the coordinated C_2H_4 ligand. The reaction of CO_2 with some of the above ethylene complexes has been investigated. The majority of the complexes studied have proved unreactive, but compounds **2b** and **8** provide isolable acrylate derivatives of composition $WH(OOCCH{=}CH_2)(C_2H_4)(PMe_3)(depe)$ (**13**) and $[MoH(OOCCH{=}CH_2)(C_2H_4)(PMe_2Ph)_2]_2$ (**14**), respectively.

Introduction

Research on olefin complexes of the transition metals has received great impetus in the last few decades due largely to the industrial importance of these compounds as intermediates and catalysts in a wide range of reactions.[1] Both theoretical and experimental facets of M–olefin compounds continue to attract the attention of many researchers. The well known Dewar, Chatt, and Duncanson model still constitutes the best pictorial description of the M–olefin bonding interaction.[2] A number of recent studies have been concerned with the structural and conformational preferences and rotational barriers found in these complexes,[3,4] especially in those having more than one olefin ligand. On the reactivity side, attack of the coordinated olefin by nucleophiles is a general feature of many transition-metal compounds containing olefin ligands.[5]

In recent years we have been attracted by the observation of a coupling reaction between ethylene and carbon dioxide in the coordination sphere of Mo and W complexes[6] (eq 1). This reaction constitutes an unusual example of C–C

$$\textit{trans}\text{-}M(C_2H_4)_2(PMe_3)_4 + CO_2 \rightarrow {}^1/_2[MH(OOCCH{=}CH_2)(C_2H_4)(PMe_3)_2]_2 + 2PMe_3 \quad (1)$$

$$M = Mo, W$$

bond formation, involving in addition C–H bond cleavage. C–C couplings involving CO_2 and unsaturated hydrocarbons have been extensively studied,[7,8] and activation reactions of other heterocumulenes by these *trans*-$M(C_2H_4)_2(PMe_3)_4$ complexes[9] have also been observed.[10]

In view of the potential usefulness of this transformation, we have attempted its extension to other related systems. A number of $M(C_2H_4)_2$ complexes of Mo and W containing

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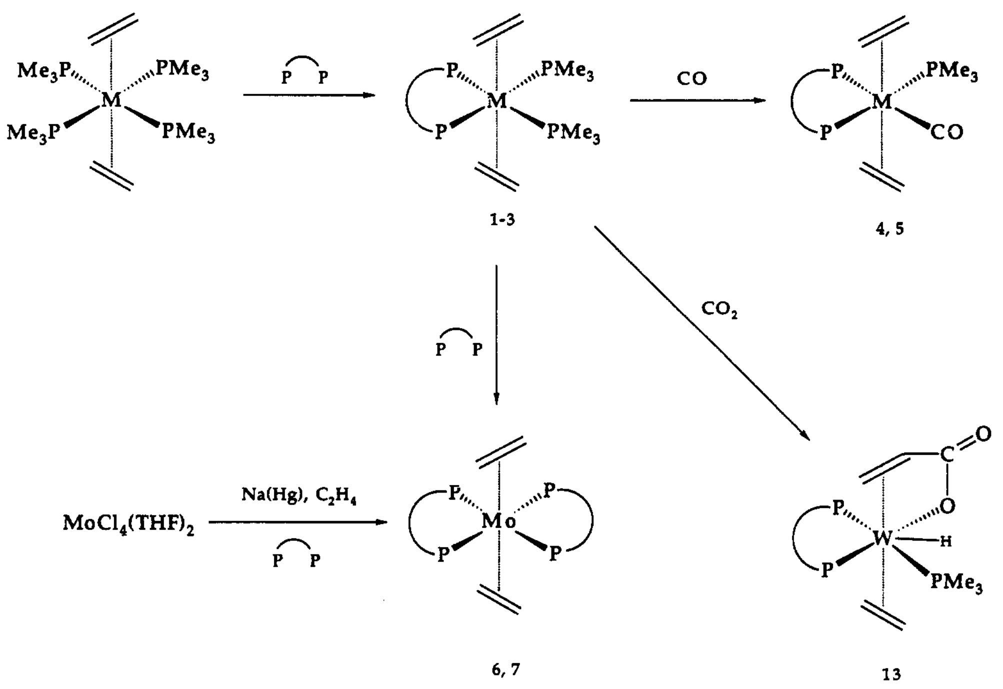
Scheme I



different phosphines, and in some cases CO and CNBu^t ligands, have been prepared and their spectroscopic properties examined. An interesting correlation between the electron density at the metal center, estimated with the aid of Lever's parameters,[11] and NMR data for the coordinated C_2H_4 groups has been found. The chemical reactivity of these species toward CO_2 has also been investigated, and as a consequence two new cases of CO_2–C_2H_4 coupling have been observed, leading respectively to the dimer $[MoH(OOCCH{=}CH_2)(C_2H_4)(PMe_2Ph)_2]_2$ (**14**) and to the monomeric $WH(OOCCH{=}CH_2)(C_2H_4)(PMe_3)(depe)$ (**13**). The reactions that afford the new complexes described in this work are summarized in Schemes I and II.

Results

***trans*-$M(C_2H_4)_2(P\text{-}P)(PMe_3)_2$ (M = Mo, W).** Addition of equimolar amounts of the bidentate phosphines dmpe, depe, and dmpm (dmpe = $Me_2PCH_2CH_2PMe_2$, depe = $Et_2PCH_2CH_2PEt_2$, dmpm = $Me_2PCH_2PMe_2$) to petroleum ether solutions of *trans*-$M(C_2H_4)_2(PMe_3)_4$ (M = Mo, W) effects, under very mild conditions, the substitution of two PMe_3 groups by the corresponding chelating phosphine (eq 2). Monitoring these reactions by $^{31}P\{^1H\}$ NMR

$$trans\text{-}M(C_2H_4)_2(PMe_3)_4 + P\text{-}P \rightarrow \underset{\mathbf{1\text{-}3}}{trans\text{-}M(C_2H_4)_2(P\text{-}P)(PMe_3)_2} + 2PMe_3 \quad (2)$$

M = Mo, P-P = dmpe (**1a**), depe (**2a**), dmpm (**3**);
M = W, P-P = dmpe (**1b**), depe (**2b**)

spectroscopy shows the disappearance of the single resonance characteristic of the starting materials and the emergence of an AA′XX′ spin system for complexes **1–3**. Yields are quantitative by NMR; isolated yields are also close to 100%. These complexes are obtained as pale yellow or off-white crystalline solids after crystallization from petroleum ether solutions. They are soluble in common organic solvents, and their solutions decompose rapidly in contact with air. In a crystalline form, they are stable enough to be handled in open air for a few minutes.

The IR spectra recorded for complexes **1–3** are not very informative, although they show characteristic absorptions due to the coordinated ethylene and phosphine ligands (see Experimental Section). However, NMR data lead to an unambiguous assignment of the structure of these complexes. As mentioned above, their $^{31}P\{^1H\}$ NMR spectra show an AA′XX′ spin system, indicating the existence of four phosphorus nuclei in the equatorial plane of the molecule. Moreover, both ethylene ligands appear to be equivalent in the $^{13}C\{^1H\}$ NMR spectra, as the result of the existence of a C_2 symmetry axis located on the equatorial plane. Two resonances in the range 24–29 ppm (Mo) or 16–18 ppm (W) (50 MHz, 20 °C, see Experimental Section) are observed for the two distinct carbon nuclei of each C_2H_4 ligand. These $^{13}C\{^1H\}$ chemical shift values are similar to those encountered in the parent complexes *trans*-$M(C_2H_4)_2(PMe_3)_4$ (M = Mo,[9a] W[9b]). From all these data, structure **I** can be proposed for these complexes.

The parent *trans*-$M(C_2H_4)_2(PMe_3)_4$ complexes readily undergo exchange of one of the PMe_3 groups by N_2 with

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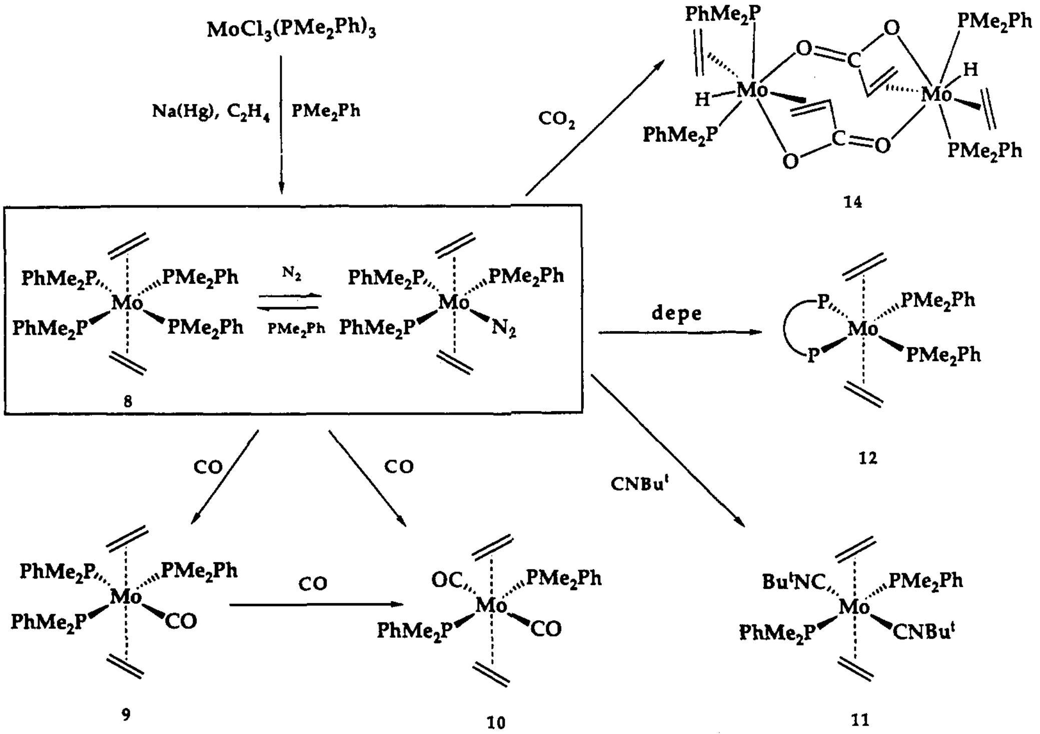
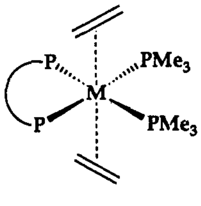
Scheme II





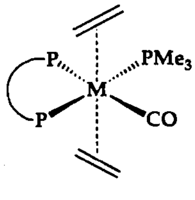
I

formation of the dinitrogen derivatives *trans,mer*-M(C_2H_4)$_2$(N_2)(PMe_3)$_3$. In contrast with this behavior, compounds 1–3 do not show any appreciable tendency to undergo such a ligand exchange and their solutions remain unaltered after prolonged exposures to an atmosphere of N_2. However, if these solutions are pressurized with carbon monoxide (2–3 atm, room temperature), substitution of one of the PMe_3 groups by CO is observed with formation of complexes **4** and **5**, as shown in eq 3. They are isolated

$$trans\text{-}M(C_2H_4)_2(P\text{-}P)(PMe_3)_2 + CO \rightarrow \underset{\mathbf{4,5}}{trans\text{-}M(C_2H_4)_2(P\text{-}P)(CO)(PMe_3)} + PMe_3 \quad (3)$$

$$M = Mo,\ P\text{-}P = depe\ (\mathbf{4a}),\ dmpe\ (\mathbf{5});\quad M = W,\ P\text{-}P = depe\ (\mathbf{4b})$$

as off-white crystalline materials whose spectroscopic data are in support of structure **II**.



II

A related reaction occurs upon addition of 1 equiv of dmpe or depe to a solution of **1a** or **2a** or of 2 equiv of these phosphines to solutions of *trans*-Mo(C_2H_4)$_2$(PMe_3)$_4$. New bis(ethylene) species of general formula *trans*-Mo(C_2H_4)$_2$(P-P)$_2$ (P-P = dmpe (**6**), depe (**7**)) (eqs 4 and 5) are obtained

$$trans\text{-}Mo(C_2H_4)_2(PMe_3)_4 + 2P\text{-}P \rightarrow \underset{\mathbf{6,7}}{trans\text{-}Mo(C_2H_4)_2(P\text{-}P)_2} + 4PMe_3 \quad (4)$$

$$trans\text{-}Mo(C_2H_4)_2(P\text{-}P)(PMe_3)_2 + P\text{-}P \rightarrow \underset{\mathbf{6,7}}{trans\text{-}Mo(C_2H_4)_2(P\text{-}P)_2} + 2PMe_3 \quad (5)$$

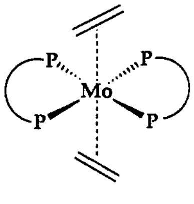
$$P\text{-}P = dmpe\ (\mathbf{6}),\ depe\ (\mathbf{7})$$

in this way. Complexes **6** and **7** can be prepared in one step by the direct reduction of $MoCl_4(THF)_2$ with sodium amalgam under an ethylene atmosphere and in the presence of the bidentate phosphine (eq 6). Crystallization from petroleum ether or acetone solutions affords complexes **6** and **7** as pale yellow crystals, soluble in the common organic solvents.

$$MoCl_4(THF)_2 + Na(Hg) + 2P\text{-}P + C_2H_4 \rightarrow trans\text{-}Mo(C_2H_4)_2(P\text{-}P)_2 \quad (6)$$

$$P\text{-}P = dmpe\ (\mathbf{6}),\ depe\ (\mathbf{7})$$

The existence of a high degree of symmetry in the molecules of these compounds is manifested by the observation of a unique resonance for all four phosphorus nuclei in the $^{31}P\{^1H\}$ NMR spectra as well as a unique resonance for all the ethylenic carbon nuclei. The latter appears as a pseudoquintet centered at 25.4 ppm for **6** (50 MHz, 20 °C, 2 C_2H_4, $^2J_{CP}$ = 5 Hz) and at 22.9 ppm for **7** (50 MHz, 20 °C, 2 C_2H_4, $^2J_{CP}$ = 8 Hz). These data are in support of structure III for these complexes, similar to that reported for *trans*-$Mo(C_2H_4)_2(dppe)_2$.[4f]



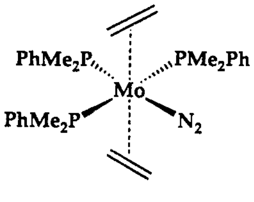
III

Synthesis and Chemical Properties of *trans*-$Mo(C_2H_4)_2(PMe_2Ph)_4$ (8). Following a procedure commonly used for the synthesis of M–N_2 complexes[12] and later applied to the preparation of the M–C_2H_4 analogs, we have obtained the complex *trans*-$Mo(C_2H_4)_2(PMe_2Ph)_4$ (8) by reduction of $MoCl_3(PMe_2Ph)_3$ with sodium amalgam under an ethylene atmosphere and in the presence of free PMe_2Ph (eq 7). Complex 8 separates from the THF solution during the reaction as an orange-brown microcrystalline solid, which redissolves upon admission of N_2 to give an orange solution that exhibits an IR absorption at *ca.* 2080 cm^{-1}. This band is absent in the IR spectrum of a solid sample of 8. By similarity with the behavior previously found for the analogous PMe_3 complexes,[9] the formation of the mono(dinitrogen) complex *trans,mer*-$Mo(C_2H_4)_2(N_2)(PMe_2Ph)_3$ can be proposed, as indicated in eq 8. This process is reversible, so that the replacement

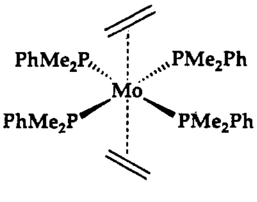
$$MoCl_3(PMe_2Ph)_3 + Na(Hg) + PMe_2Ph + C_2H_4 \rightarrow \underset{8}{trans\text{-}Mo(C_2H_4)_2(PMe_2Ph)_4} \quad (7)$$

$$trans\text{-}Mo(C_2H_4)_2(PMe_2Ph)_4 + N_2 \rightarrow trans,mer\text{-}Mo(C_2H_4)_2(N_2)(PMe_2Ph)_3 + PMe_2Ph \quad (8)$$

of the N_2 atmosphere by C_2H_4 regenerates complex 8. NMR studies are in accord with this proposal and confirm that solutions of 8 contain an equimolar mixture of *trans,mer*-$Mo(C_2H_4)_2(N_2)(PMe_2Ph)_3$ and PMe_2Ph. Thus, in addition to the resonance due to free PMe_2Ph, the $^{31}P\{^1H\}$ NMR spectrum of 8 contains signals corresponding to an AX_2 spin system (δ_A 23.8, δ_X 20.1 ppm; $^2J_{AX}$ = 18 Hz). From these and other data, structures IV and V can be proposed for these two complexes.

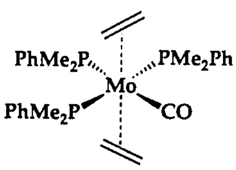


IV

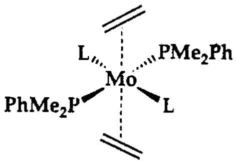


V

The chemical reactivity of 8 is governed by the facility with which PMe_2Ph substitution takes place. Several reactions with CO, $CNBu^t$, and depe have been carried out and shown to result in the formation of the new compounds *trans*-$Mo(C_2H_4)_2(CO)_2(PMe_2Ph)_2$ (10), *trans*-$Mo(C_2H_4)_2(CNBu^t)_2(PMe_2Ph)_2$ (11), and *trans*-$Mo(C_2H_4)_2(depe)(PMe_2Ph)_2$ (12). When the CO reaction is effected at −80 °C (1 atm), the monocarbonyl $Mo(C_2H_4)_2(CO)(PMe_2Ph)_3$ (9) is obtained. The spectroscopic properties of these complexes are similar to those found for the analogous PMe_3 derivatives[9] and need no further comment. They are in support of structures VI–VIII.

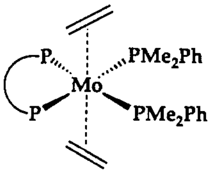


VI



L = CO, $CNBu^t$

VII



VIII

CO_2–C_2H_4 Coupling: Formation of the Acrylate Derivatives $WH(OOCCH{=}CH_2)(C_2H_4)(PMe_3)(depe)$ (13) and $[MoH(OOCCH{=}CH_2)(C_2H_4)(PMe_2Ph)_2]_2$ (14). As indicated in the Introduction, one of the main objectives of this work was the extension of the CO_2–C_2H_4 coupling reaction, already investigated for the complexes *trans*-$M(C_2H_4)_2(PMe_3)_4$,[6] to other related systems. Accordingly, the reactivity toward CO_2 of some of the above complexes, namely **1a,b**, **2a,b**, **3**, and **8**, has been investigated. Of these compounds only **2a,b** and **8** have been found to react with CO_2 under the experimental conditions used (see the Experimental Section). For the remaining compounds, as well as for the previously reported[9c] *trans*-$M(C_2H_4)_2(L)_n(PMe_3)_{4-n}$ (n = 1, 2; L = CO, $CNBu^t$), no reactivity toward CO_2 has been observed.

The molybdenum compound **2a** reacts with CO_2 (3 atm) at room temperature, but despite our efforts, no pure product has been isolated from the resulting reaction mixtures. A more favorable situation is found in the cases of complexes **2b** and **8**. Treatment of their solutions with CO_2 (20 °C; 3 atm for **2b**, 1 atm in the case of **8**) affords crystalline samples of the acrylate derivatives $WH(OOCCH{=}CH_2)(C_2H_4)(PMe_3)(depe)$ (**13**) and $[MoH(OOCCH{=}CH_2)(C_2H_4)(PMe_2Ph)_2]_2$ (**14**), respectively. As will become apparent from the following pieces of information, spectroscopic data for these species are similar to those already reported for the analogous PMe_3 derivatives[6] $[MH(OOCCH{=}CH_2)(C_2H_4)(PMe_3)_2]_2$. The observation of a medium-intensity absorption near 1800 cm^{-1} in the IR spectra of **13** and **14** suggests the existence of a hydride ligand which is confirmed by the presence of a characteristic high-field resonance in the ^1H NMR spectra of these derivatives (e.g. δ −5.2 ppm, br t, $^2J_{PH}$ = 98 Hz, data for **14**). On the other hand, evidence for the coupling of CO_2 and C_2H_4, with formation of a carboxylate group, can be inferred from the appearance of distinct IR bands and ^{13}C resonances. The IR spectrum of **14** presents a strong absorption at *ca.* 1540 cm^{-1}, which can be attributed[13] to a bridging carboxylate ligand (this band appears at *ca.*

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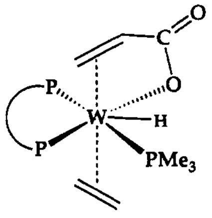
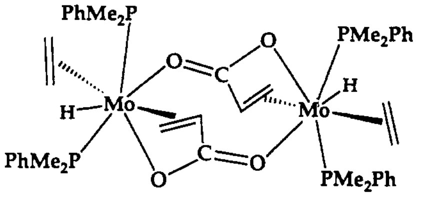
[12] Chatt, J.; Dilworth, J. R.; Richards, R. L. *Chem. Rev.* **1978**, *78*, 589.

1510 cm^{-1} in the IR spectra of [MH(OOCCH=CH$_2$)(C$_2$H$_4$)(PMe$_3$)$_2$]$_2$[6]). A somewhat different situation is found for the tungsten complex **13**, for which a monomeric formulation is proposed. Supporting evidence for this structure includes the following: (i) the presence of a strong IR band centered at *ca.* 1630 cm^{-1}, suggestive of monodentate carboxylate coordination,[13c] (ii) the observation of a broad ^{13}C singlet at 179.9 ppm corresponding to the carboxylate ^{13}C nuclei, and (iii) the existence of three phosphine functionalities in the molecules of this compound, a chelating depe and a PMe$_3$ ligand, clearly evidenced by ^{31}P{^{1}H} NMR studies (AMX spin system: δ_A −2.7, δ_M 12.9, δ_X 51 ppm; $^2J_{AM}$ = 51, $^2J_{AX}$ = 123, $^2J_{MX}$ = 14 Hz). This is in contrast with the binuclear species [MH(OOCCH=CH$_2$)(C$_2$H$_4$)(PR$_3$)$_2$]$_2$, which display AX spin systems. The similarity of these and other data collected in the Experimental Section (including 2D-NMR studies) with those previously found for the closely related [MH(OOCCH=CH$_2$)(C$_2$H$_4$)(PMe$_3$)$_2$]$_2$[6] is in accord with structures **IX** and **X** for compounds **13** and **14**, respectively.



IX



X

Discussion

The activation of CO$_2$ by transition-metal compounds arouses considerable interest because of the possibility of using this molecule as a useful C1 synthetic unit.[7,8,14] We have recently shown that the bis(ethylene) derivatives *trans*-M(C$_2$H$_4$)$_2$(PMe$_3$)$_4$ (M = Mo, W) induce the coupling of CO$_2$ and C$_2$H$_4$, under very mild conditions, with formation of an acrylate ligand.[6] The metal center in these complexes is highly basic,[11] this electron richness facilitating the activation of CO$_2$. Moreover, a vacant coordination site can be readily made available by facile dissociation of one of the PMe$_3$ ligands. These two features make the above compounds ideal candidates for simultaneous CO$_2$ and C$_2$H$_4$ activation.

In order to acquire a better understanding of the importance of the electronic and steric effects in this unusual transformation, we have studied the reactivity of CO$_2$ toward a number of M(C$_2$H$_4$)$_2$ complexes of Mo and W containing different phosphine ligands and in some cases CO and CNBu^t groups. Compounds of composition M(C$_2$H$_4$)$_2$(L)$_n$(PMe$_3$)$_{4-n}$[9] (n = 1, 2; L = CO, CNBu^t), M(C$_2$H$_4$)$_2$(P-P)(PMe$_3$)$_2$ (M = Mo, W; P-P = dmpe, depe), and Mo(C$_2$H$_4$)$_2$(PMe$_2$Ph)$_4$ have been chosen for this investigation. As already mentioned, and will now be discussed, only in two cases have the expected acrylate complexes been isolated.

Trimethylphosphine substitution in *trans*-M(C$_2$H$_4$)$_2$(PMe$_3$)$_4$ by CO or CNBu^t makes the resulting metal center more inert toward carbon dioxide; in fact, no reaction between CO$_2$ and M(C$_2$H$_4$)$_2$(L)(PMe$_3$)$_3$ or M(C$_2$H$_4$)$_2$(L)$_2$(PMe$_3$)$_2$ complexes (L = CO, CNBu^t) has been observed under a variety of experimental conditions. This could, in principle, be attributed to the decrease in metal basicity[15] expected upon substitution of one of the strongly basic PMe$_3$ groups by the π-acids CO and CNBu^t. It should be borne in mind, however, that both CO and CNBu^t have smaller cone angles[16] than PMe$_3$ (PMe$_3$, 118 °; CO, ~95°; CNBu^t,[17] 102°) and hence that the steric pressure in the substituted M(C$_2$H$_4$)$_2$(L)$_n$(PMe$_3$)$_{4-n}$ (n = 1, 2) species should be inferior to that in the parent M(C$_2$H$_4$)$_2$(PMe$_3$)$_4$. Indeed, the substituted complexes show no tendency toward PMe$_3$ (or other coligand) dissociation and this seems to determine their lack of reactivity toward CO$_2$.

The substitution of two PMe$_3$ ligands in *trans*-M(C$_2$H$_4$)$_2$(PMe$_3$)$_4$ by one molecule of the chelating phosphine dmpe is not expected to alter significantly the electronic properties of the metal center (see also Table I and discussion below). Nevertheless, since the cone angle for dmpe is only 107° (value corresponding to each of the halves of the diphosphine[16]), the complexes M(C$_2$H$_4$)$_2$(dmpe)(PMe$_3$)$_2$ can be surmised to be sterically relieved as compared to the parent M(C$_2$H$_4$)$_2$(PMe$_3$)$_4$ derivatives. Again, no evidence for PMe$_3$ dissociation, occurring either in the laboratory or on the NMR time scale, can be traced and, accordingly, these derivatives exhibit no detectable reactivity toward CO$_2$ under the conditions used. These qualitative arguments suggest that the tendency of M(C$_2$H$_4$)$_2$(PMe$_3$)$_4$ complexes to undergo PMe$_3$ dissociation has steric (rather than electronic) origin, and in good agreement with this line of reasoning, the analogous M(C$_2$H$_4$)$_2$(depe)(PMe$_3$)$_2$ species, containing the bulkier depe ligand (θ = 115°), do react with CO$_2$. No clean product has been isolated from mixtures of the Mo complex M(C$_2$H$_4$)$_2$(depe)(PMe$_3$)$_2$ and CO$_2$, but the tungsten analog provides the monomeric acrylate WH(O$_2$CCH=CH$_2$)(C$_2$H$_4$)(PMe$_3$)(depe) (**13**). Furthermore, the *trans*-Mo(C$_2$H$_4$)$_2$(PMe$_2$Ph)$_4$ complex (**8**), which accommodates the less basic (ν = 2065.3 cm^{-1}, as compared with 2064.1 cm^{-1} for PMe$_3$[16]) but more sterically demanding PMe$_2$Ph ligand (θ = 122°), readily dissociates PMe$_2$Ph in solution and reacts rapidly with CO$_2$ to produce the corresponding acrylate [MoH(OOCCH=CH$_2$)(C$_2$H$_4$)(PMe$_2$Ph)$_2$]$_2$ (**14**). All these pieces of information strongly suggest that, while a high electron density on the metal may be needed in order for the desired transformation to occur, the reaction indispensably requires the availability of a vacant coordination site. Once this requisite is fulfilled, CO$_2$ incorporation[18] may be followed by the oxidative coupling[8] of this molecule with C$_2$H$_4$, as depicted in Scheme III.

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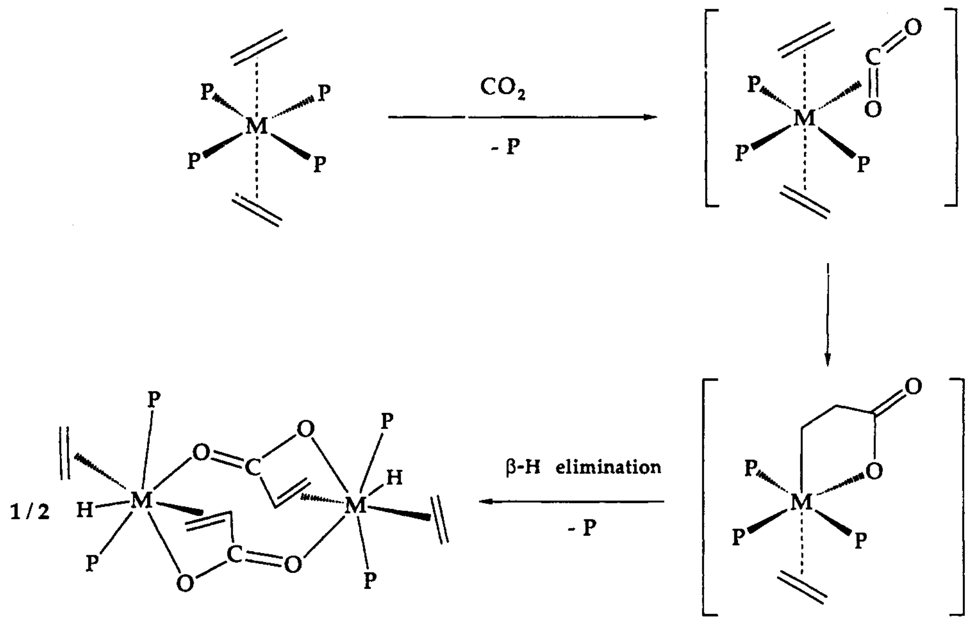
[17] de Lange, P. P. M.; Frühauf, H.-W.; Kraakman, M. J. A.; van Wijnkoop, M.; Kranenburg, M.; Groot, A. H. J. P.; Vrieze, K.; Fraanje, J.; Wang, Y.; Numan, M. *Organometallics* **1993**, *12*, 417.

Scheme III



Subsequent β-H elimination (and dimerization where appropriate) would afford the finally observed product.[6]

The spectroscopic characterization of the new *trans*-$M(C_2H_4)_2$ complex of Mo and W described in this work allows the accumulation of a sufficient body of information on ^{13}C NMR data for the coordinated C_2H_4 ligand and, hence, the study of the effect (if any) of the electron density at the metal on the value of $\delta(C_2H_4)$. This can be done by indirectly estimating the metal basicity by means of theoretically calculated electrochemical data,[19] specifically the oxidation potential $E_{1/2}(M(I)/M(0))$ determined with the aid of Lever's equation and parameters E_L.[11] Recently, Morris has shown the utility of this additive ligand approach for predicting the chemistry[20] of dihydrogen complexes of the transition metals of composition $M(\eta^2\text{-}H_2)L_5$. In the present case Lever's approximation will be applied to series of complexes of composition *trans*-$Mo(C_2H_4)_2(L)_4$ (and to the tungsten analogs), and therefore, all that is needed is a calculation of the sum of the E_L parameters corresponding to the four ligands, that is, $\sum^4 E_L$. The theoretical $E_{1/2}(Mo(0)/Mo(I))$ data ($E_{1/2} = 0.74\sum E_L - 2.25$[11]) or, in our case, $\sum E_L$ for the four ligands are expected to be related to the HOMO energy and, accordingly, to be a good measure of the electron richness of the compound under consideration. Table I shows the $^{13}C\{^1H\}$ NMR data for the C_2H_4 ligands of some bis(ethylene) complexes of Mo(0) and the values of $\sum^4 E_L$ for the coligands bonded to the $Mo(C_2H_4)_2$ core. Figure 1 displays the plot of $\delta(C_2H_4)$ (average values) versus $\sum^4 E_L$. As can be seen, two reasonably good correlations, one for complexes containing coordinated CO (△, $R = 0.97$) and the other for those having no carbonyl ligands (□, $R = 0.88$), can be discerned. An interdependence between the $M(d\pi) \rightarrow \text{olefin}(\pi^*)$ back-donation and the coordination shift ($\Delta\delta = \delta(\text{free olefin}) - \delta(\text{coordinated olefin})$) was previously foreseen by Grevels et al.,[3c,d] but no data were reported. The representation in Figure 1 corresponds to an analogous relationship, although expressed in terms of δ_C vs $\sum^4 E_L$ for *trans*-$M(C_2H_4)_2(L)_4$ complexes.

Table I. Ethylene ^{13}C Chemical Shift Data for $Mo(C_2H_4)_2$ Complexes as a Function of $\sum^4 E_L$

complex[a]	δ_C, ppm	$\sum^4 E_L$, V	ref
trans-$Mo(C_2H_4)_2(depe)_2$ (**7**)	22.9	1.08	
trans-$Mo(C_2H_4)_2(dmpe)_2$ (**6**)	25.4	1.12	
trans-$Mo(C_2H_4)_2(depe)(PMe_3)_2$ (**2a**)	25.6, 26.8	1.20	
trans-$Mo(C_2H_4)_2(dmpe)(PMe_3)_2$ (**1a**)	24.4, 25.3	1.22	
trans-$Mo(C_2H_4)_2(depe)(PMe_2Ph)_2$ (**12**)	26.4, 27.5	1.22	
trans-$Mo(C_2H_4)_2(CNCy)_2(PMe_3)_2$	30.2	1.30	9c
trans-$Mo(C_2H_4)_2(PMe_3)_4$	27.6	1.32	
trans-$Mo(C_2H_4)_2(CNCy)(CNBu^t)(PMe_3)_2$	30.2	1.34	9c
trans-$Mo(C_2H_4)_2(CNBu^t)(PMe_3)_3$	27.5, 30.1	1.35	9c
trans-$Mo(C_2H_4)_2(CNPr^i)(PMe_3)_3$	27.8, 30.9	1.35	9c
trans-$Mo(C_2H_4)_2(PMe_2Ph)_4$ (**8**)	31.7, 35.8	1.36	
trans-$Mo(C_2H_4)_2(CNBu^t)_2(PMe_3)_2$	30.3	1.38	9c
trans-$Mo(C_2H_4)_2(CNPr^i)_2(PMe_3)_2$	30.4	1.38	9c
trans-$Mo(C_2H_4)_2(CNBu^t)_2(PMe_2Ph)_2$ (**11**)	31.5	1.40	
trans-$Mo(C_2H_4)_2(depe)(CO)(PMe_3)$ (**4a**)	28.1, 30.5, 36.5	1.86	
trans-$Mo(C_2H_4)_2(dmpe)(CO)(PMe_3)$ (**5**)	27.0, 27.8, 30.4, 34.6	1.88	
trans-$Mo(C_2H_4)_2(CNCy)(CO)(PMe_3)_2$	31.5	1.97	9c
trans-$Mo(C_2H_4)_2(CO)(PMe_2Ph)_3$ (**9**)	30.0	2.01	
trans-$Mo(C_2H_4)_2(CNBu^t)(CO)(PMe_3)_2$	31.5	2.01	9c
trans-$Mo(C_2H_4)_2(CNPr^i)(CO)(PMe_3)_2$	32.0	2.01	9c
trans-$Mo(C_2H_4)_2(CNCH_2Ph)(CO)(PMe_3)_2$	31.8	2.21	9c
trans-$Mo(C_2H_4)_2(CO)_2(PMe_3)_2$	33.1	2.64	9b
trans-$Mo(C_2H_4)_2(CO)_2(PMe_2Ph)_2$ (**10**)	34.8	2.66	
trans-$Mo(C_2H_4)_2(CO)_4$[b]	41.9	3.96	3f

[a] Recorded in C_6D_6 at 293 K. [b] In toluene-d_8.

The trends in Figure 1 can be qualitatively explained in terms of the Dewar, Chatt, and Duncanson model.[2] Thus, an increase in the value of $\sum^4 E_L$, which would in fact indicate a decrease in the electronic density on the metal, is accompanied by a low-field shift of the $^{13}C\{^1H\}$ NMR resonances of the C_2H_4 ligands. Diminished $M(d\pi) \rightarrow C_2H_4(\pi^*)$ back-bonding would imply greater sp^2 character for the bound carbon atoms and consequently higher δ values. The presence of coordinated CO ligands in these $M(C_2H_4)_2(L)_4$ complexes should produce quite different electronic situations on the metal, back-bonding now being shared between CO and C_2H_4. For this reason the particular δ_C vs $\sum^4 E_L$ correlation shows a different slope. Similar trends are found for the $W(C_2H_4)_2(L)_4$ analogs (Table II, Figure 2), although the smaller number of

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(19) Preliminary results show a reversible electrochemical behavior for some *trans*-bis(ethylene) complexes of Mo and W(0) in accordance with the applicability conditions[11] for Lever's E_L parameters: Galindo, A.; Pickett, C. Unpublished results.

(20) Morris, R. H. *Inorg. Chem.* **1992**, *31*, 1471.

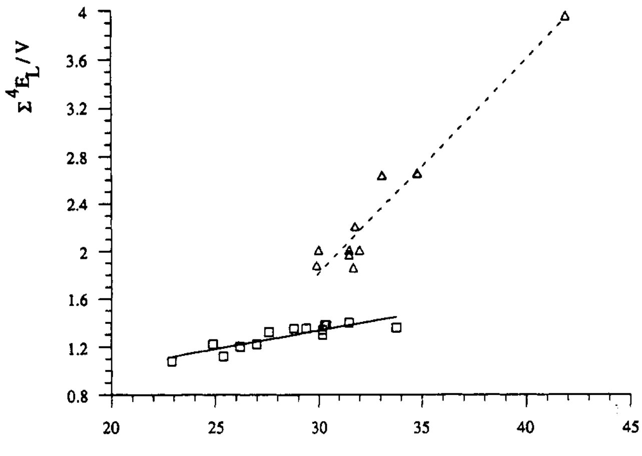

Figure 1. Plot of Σ^4E_L against ethylene ^{13}C chemical shift average for $Mo(C_2H_4)_2$ complexes: (bottom, squares) complexes without carbonyl coligand; (top, triangles) compounds containing some CO coligand.

Table II. Ethylene ^{13}C Chemical Shift Data for $W(C_2H_4)_2$ Complexes as a Function of Σ^4E_L

complex[a]	δ_C, ppm	Σ^4E_L, V	ref
trans-$W(C_2H_4)_2(depe)(PMe_3)_2$ (**2b**)	16.8, 18.1	1.20	
trans-$W(C_2H_4)_2(dmpe)(PMe_3)_2$ (**1b**)	16.8, 17.5	1.22	
trans-$W(C_2H_4)_2(CNCy)_2(PMe_3)_2$	20.8, 21.8	1.30	9c
trans-$W(C_2H_4)_2(PMe_3)_4$	19.3	1.32	
trans-$W(C_2H_4)_2(CNPr^i)_2(PMe_3)_2$	20.7, 22.0	1.38	9c
trans-$W(C_2H_4)_2(depe)(CO)(PMe_3)$ (**4b**)	18.8, 21.2, 26.2	1.86	
trans-$W(C_2H_4)_2(CNCy)(CO)(PMe_3)_2$	19.7, 27.2	1.97	9c
trans-$W(C_2H_4)_2(CO)(PMe_3)_3$	18.5, 22.0, 27.1	1.98	9b
trans-$W(C_2H_4)_2(CNPr^i)(CO)(PMe_3)_2$	22.0	2.01	9c
trans-$W(C_2H_4)_2(CO)_4$[b]	31.3	3.96	3f

[a] Recorded in C_6D_6 at 293 K. [b] In toluene-d_8.

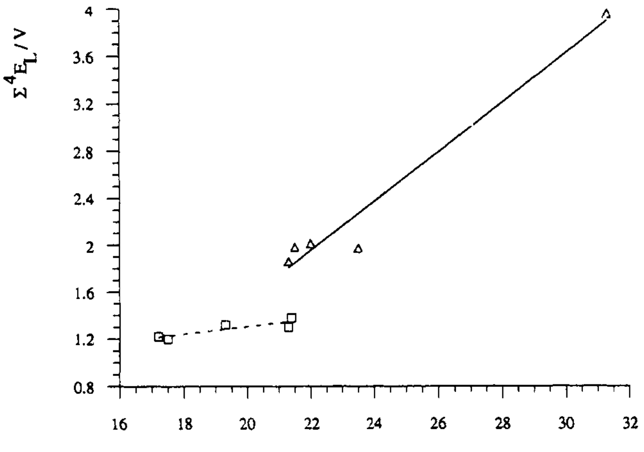

Figure 2. Plot of Σ^4E_L against ethylene ^{13}C chemical shift average for $W(C_2H_4)_2$ compounds: (bottom, squares) complexes without carbonyl coligand, correlation coefficient 0.88; (top, triangles) compounds containing some CO coligand, correlation coefficient 0.98.

compounds of this type available limits the validity of this relationship. Extension to other metals (for example, $Pt(C_2H_4)_2(L)$ cores[21]) is also possible. From all this, it seems evident that, despite its limitations, this additive ligand approach can be qualitatively employed as an approximate probe for the electron density at the metal center and even as a rough prediction of the ^{13}C chemical shifts of the coordinated C_2H_4 ligands in unknown complexes of this type.

Experimental Section

Microanalyses were performed by Pascher Microanalytical Laboratory, Remagen, Germany, and by the Microanalytical Service of the University of Sevilla. Infrared spectra were recorded on Perkin-Elmer Models 684 and 883 spectrophotometers. ^1H, ^{13}C, and ^{31}P NMR spectra were run on Varian XL-200, Bruker AMX-300, and Bruker AMX-500 spectrometers. ^{31}P shifts were measured with respect to external 85% H_3PO_4. ^{13}C NMR spectra were referenced using the ^{13}C resonance of the solvent as an internal standard but are reported with respect to $SiMe_4$. All preparations and other operations were carried out under oxygen-free nitrogen by following conventional Schlenk techniques. Solvents were dried and degassed before use. The petroleum ether used had bp 40–60 °C. The compounds $MoCl_4(THF)_2$, $MoCl_3(PMe_2Ph)_3$, and *trans*-$M(C_2H_4)_2(PMe_3)_4$ and the PMe_3, dmpm, dmpe, and depe ligands were prepared according to the literature procedures.

Synthesis of *trans*-$M(C_2H_4)_2$(P-P)$(PMe_3)_2$ (M = Mo, P-P = dmpe (1a), depe (2a), dmpm (3); M = W, P-P = dmpe (1b), depe (2b)) Complexes. To a solution of *trans*-$[Mo(C_2H_4)_2(PMe_3)_4]$ (0.49 g, 1.1 mmol) in petroleum ether (30 mL) was added dmpe (0.22 mL, 1.1 mmol) via syringe. The resulting mixture was stirred at room temperature for 1 h, and the volatiles were removed under vacuum. The residue was dissolved in petroleum ether and cooled at −30 °C to give complex **1a** as pale yellow crystals in 95% yield. By a similar procedure, complexes **1b**, **2a**,**b**, and **3** were obtained in 71%, 80%, 65%, and 88% yields, respectively. Compounds **1–3** all exhibit similar IR absorptions (cm^{-1}) for the coordinated ethylene and phosphine ligands: 3040–3020 w, 1150–1130 s (C_2H_4); 950–900 br (phosphine).

***trans*-$Mo(C_2H_4)_2(dmpe)(PMe_3)_2$ (1a).** ^1H NMR (200 MHz, C_6D_6): δ 0.7 (d, 2 $P(CH_3)(CH_3)$ of dmpe, $^2J_{HP}$ = 5 Hz), 1.1 (filled-in d, 2 $P(CH_3)_3$ *cis*, $J_{HP(app)}$ = 6 Hz), 1.2 (d, 2 $P(CH_3)(CH_3)$ of dmpe, $^2J_{HP}$ = 6 Hz). The C_2H_4 ligands and the $-CH_2CH_2-$ fragment of dmpe resonate between 2 and 0 ppm, the signals due to the C_2H_4 groups being obscured by the phosphine absorptions. $^{31}P\{^1H\}$ NMR (81 MHz, C_6D_6): AA′XX′ spin system, δ_A 41.4, δ_X 3.4 ($J_{AA'}$ = 21, $J_{XX'}$ = 3, $J_{AX(cis)}$ = 21, $J_{AX'(trans)}$ = 115 Hz, absolute values). $^{13}C\{^1H\}$ NMR (50 MHz, C_6D_6): δ 7.0 (br s, 2 $P(CH_3)(CH_3)$ of dmpe, 17.7 (d, 2 $P(CH_3)(CH_3)$ of dmpe, $^1J_{CP}$ = 21 Hz), 18.7 (filled-in d, 2 $P(CH_3)_3$ *cis*, $J_{CP(app)}$ = 15 Hz), 24.4 (br d, 2 $H_2C{=}CH_2$ *trans*, $J_{CP(app)}$ = 10 Hz), 25.3 (br d, 2 $H_2C{=}CH_2$ *trans*, $J_{CP(app)}$ = 10 Hz), 29.7 (m, 2 $-CH_2P$ of dmpe). Anal. Calcd for $C_{16}H_{42}P_4Mo$: C, 42.3; H, 9.3. Found: C, 42.5; H, 9.3.

***trans*-$W(C_2H_4)_2(dmpe)(PMe_3)_2$ (1b).** ^1H NMR (200 MHz, C_6D_6): δ 0.6 (d, 2 $P(CH_3)(CH_3)$ of dmpe, $^2J_{HP}$ = 5 Hz), 1.1 (d, 2 $P(CH_3)_3$ *cis*, $J_{HP(app)}$ = 6 Hz), 1.2 (d, 2 $P(CH_3)(CH_3)$ of dmpe, $^2J_{HP}$ = 6 Hz). The C_2H_4 ligands and the $-CH_2CH_2-$ fragment of dmpe resonate between 2 and 0 ppm, the signals due to the C_2H_4 groups being obscured by the phosphine absorptions. $^{31}P\{^1H\}$ NMR (81 MHz, C_6D_6): AA′XX′ spin system, δ_A 11.3 ($^1J_{PW}$ = 339 Hz), δ_X −33.9 ($^1J_{PW}$ = 357 Hz) ($J_{AA'}$ = 15, $J_{XX'}$ = 3, $J_{AX(cis)}$ = 18, $J_{AX'(trans)}$ = 118 Hz, absolute values). $^{13}C\{^1H\}$ NMR (50 MHz, C_6D_6): δ 6.0 (filled-in d, 2 $P(CH_3)(CH_3)$ of dmpe, $J_{CP(app)}$ = 9 Hz), 16.8 (m, 2 $H_2C{=}CH_2$ *trans*), 17.5 (m, 2 $H_2C{=}CH_2$ *trans*), 19.0 (d, 2 $P(CH_3)(CH_3)$ of dmpe, $^1J_{CP}$ = 27 Hz), 19.9 (filled-in d, 2 $P(CH_3)_3$ *cis*, $J_{CP(app)}$ = 20 Hz), 32.7 (m, 2 $-CH_2P$ of dmpe). Anal. Calcd for $C_{16}H_{42}P_4W$: C, 35.4; H, 7.8. Found: C, 35.3; H, 7.8.

***trans*-$Mo(C_2H_4)_2(depe)(PMe_3)_2$ (2a).** ^1H NMR (300 MHz, C_6D_6): δ 0.86 (t, 3 H, $P(CH_2CH_3)(CH_2CH_3)$ of depe, $^3J_{HH}$ = 7 Hz), 0.89 (t, 3 H, $P(CH_2CH_3)(CH_2CH_3)$, $^3J_{HH}$ = 7 Hz), 0.93 (t, 3 H, $P(CH_2CH_3)(CH_2CH_3)$, $^3J_{HH}$ = 7 Hz), 0.97 (t, 3 H, $P(CH_2CH_3)(CH_2CH_3)$, $^3J_{HH}$ = 7 Hz), 1.06 (d, 2 $P(CH_3)_3$ *cis*, $J_{HP(app)}$ = 5 Hz), 1.16 (q, 4 H, $P(CH_2CH_3)(CH_2CH_3)$ and $P(CH_2CH_3)(CH_2CH_3)$, $^3J_{HH}$ = 7 Hz), 1.54 (ddc, 2 H, $P(CHHCH_3)(CHHCH_3)$, $^2J_{HH}$ = 14, $^3J_{HH}$ = 7, $^2J_{HP}$ = 3 Hz), 1.79 (ddq, 2 H, $P(CHHCH_3)(CHHCH_3)$, $^2J_{HH}$ = 14, $^3J_{HH}$ = 7, $^2J_{HP}$ = 3 Hz). The C_2H_4 ligands and the $-CH_2CH_2-$ fragment of depe resonate between 1.5 and 0 ppm, the signals due to the C_2H_4 groups being obscured by the

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(21) Galindo, A. Unpublished results.

phosphine absorptions. $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (81 MHz, $\mathrm{C_6D_6}$): AA′XX′ spin system, δ_A 50.1, δ_X 4.6 ($J_{AA'} = 21$, $J_{XX'} = 7$, $J_{AX(cis)} = 18.5$, $J_{AX'(trans)} = 109$ Hz, absolute values). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (50 MHz, $\mathrm{C_6D_6}$): δ 9.2 (d, 2 $\mathrm{P(CH_2\mathit{C}H_3)(CH_2CH_3)}$ of depe, $^2J_{CP} = 4$ Hz), 9.5 (d, 2 $\mathrm{P(CH_2CH_3)(CH_2\mathit{C}H_3)}$, $^2J_{CP} = 5$ Hz), 11.2 (s, 2 $\mathrm{P(\mathit{C}H_2CH_3)(CH_2CH_3)}$), 20.6 (filled-in d, 2 $\mathrm{P(\mathit{C}H_3)_3}$ *cis*, $J_{CP(app)} =$ 14 Hz), 21.2 (d, 2 $\mathrm{P(CH_2CH_3)(\mathit{C}H_2CH_3)}$, $^1J_{CP} = 16$ Hz), 22.2 (pt, $\mathrm{P\mathit{C}H_2\mathit{C}H_2P}$, $J_{CP(app)} = 7$ Hz), 25.6 (br d, 2 $\mathrm{H_2\mathit{C}{=}CH_2}$ *trans*, $J_{CP(app)} = 12$ Hz), 26.8 (br d, 2 $\mathrm{H_2C{=}\mathit{C}H_2}$ *trans*, $J_{CP(app)} = 13$ Hz). Anal. Calcd for $\mathrm{C_{20}H_{50}P_4Mo}$: C, 47.1; H, 9.9. Found: C, 47.1; H, 9.8.

***trans*-W(C₂H₄)₂(depe)(PMe₃)₂ (2b).** ^{1}H NMR (200 MHz, $\mathrm{C_6D_6}$): δ 0.8–1.0 (m, 12 H, 2 $\mathrm{P(CH_2C\mathit{H}_3)_2}$ of depe), 1.19 (d, 2 $\mathrm{P(C\mathit{H}_3)_3}$ *cis*, $J_{HP(app)} = 5$ Hz), 1.2–1.3 (m, 4 H, $\mathrm{P(C\mathit{H}_2CH_3)(CH_2CH_3)}$ and $\mathrm{P(CH_2CH_3)(C\mathit{H}_2CH_3)}$), 1.61 (ddq, 2 H, $\mathrm{P(C\mathit{H}HCH_3)(CH\mathit{H}CH_3)}$, $^2J_{HH} = 14$, $^3J_{HH} = 7$, $^2J_{HP} = 3$ Hz), 1.89 (ddq, 2 H, $\mathrm{P(CH\mathit{H}CH_3)(C\mathit{H}HCH_3)}$, $^2J_{HH} = 14$, $^3J_{HH} = 7$, $^2J_{HP} = 3$ Hz). The $\mathrm{C_2H_4}$ ligands and the $\mathrm{–CH_2CH_2–}$ fragment of dmpe resonate between 1.5 and 0 ppm, the signals due to the $\mathrm{C_2H_4}$ groups being obscured by the phosphine absorptions. $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (81 MHz, $\mathrm{C_6D_6}$): AA′XX′ spin system, δ_A 19.3 ($^1J_{PW} = 320$ Hz), δ_X −34.6 ($^1J_{PW} = 356$ Hz) ($J_{AA'} = 0$, $J_{XX'} = 15.5$, $J_{AX(cis)} = 22$, $J_{AX'(trans)} =$ 118 Hz, absolute values). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (50 MHz, $\mathrm{C_6D_6}$): δ 9.2 (d, 2 $\mathrm{P(CH_2\mathit{C}H_3)(CH_2CH_3)}$ of depe, $^2J_{CP} = 4$ Hz), 9.3 (d, 2 $\mathrm{P(\mathit{C}H_2CH_3)(CH_2CH_3)}$ of depe, $^1J_{CP} = 6$ Hz), 9.9 (d, 2 $\mathrm{P(CH_2CH_3)(CH_2\mathit{C}H_3)}$ of depe, $^1J_{CP} = 5$ Hz), 16.8 (m, 2 $\mathrm{H_2\mathit{C}{=}CH_2}$ *trans*), 18.1 (m, $\mathrm{H_2C{=}\mathit{C}H_2}$ *trans*), 20.7 (filled-in d, 2 $\mathrm{P(\mathit{C}H_3)_3}$ *cis*, $J_{CP(app)} = 19$ Hz), 21.6 (d, 2 $\mathrm{P(CH_2CH_3)(\mathit{C}H_2CH_3)}$ of depe, $^1J_{CP}$ = 23 Hz), 24.1 (filled-in d, $\mathrm{P\mathit{C}H_2\mathit{C}H_2P}$, $J_{CP(app)} = 35$ Hz). Anal. Calcd for $\mathrm{C_{20}H_{50}P_4W}$: C, 40.1; H, 8.4. Found: C, 40.2; H, 8.5.

***trans*-Mo(C₂H₄)₂(dmpm)(PMe₃)₂ (3).** ^{1}H NMR (200 MHz, $\mathrm{C_6D_6}$): δ 0.69 (d, 2 $\mathrm{P(C\mathit{H}_3)(CH_3)}$ of dmpm, $^2J_{HP} = 4$ Hz), 0.94 (filled-in d, 2 $\mathrm{P(C\mathit{H}_3)_3}$ *cis*, $J_{HP(app)} = 5$ Hz), 1.12 (d, 2 $\mathrm{P(CH_3)(C\mathit{H}_3)}$ of dmpm, $^2J_{HP} = 6$ Hz), 3.26 (t, $\mathrm{PC\mathit{H}_2P}$, $^2J_{HP} = 8$ Hz). The $\mathrm{C_2H_4}$ ligands resonate between 2 and 0 ppm, but the signals are obscured by the phosphine absorptions. $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (81 MHz, $\mathrm{C_6D_6}$): AA′XX′ spin system, δ_A 12.2, δ_X −9.2 ($J_{AA'} = 16$, $J_{XX'} = 10$, $J_{AX(cis)}$ = 27, $J_{AX'(trans)} = 114$ Hz, absolute values). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (50 MHz, $\mathrm{C_6D_6}$): δ 8.6 (d, 2 $\mathrm{P(\mathit{C}H_3)(CH_3)}$ of dmpm, $^1J_{CP} = 6$ Hz), 18.7 (pt, 2 $\mathrm{P(CH_3)(\mathit{C}H_3)}$ of dmpm, $J_{CP(app)} = 10$ Hz), 19.5 (d, 2 $\mathrm{P(\mathit{C}H_3)_3}$ *cis*, $J_{CP(app)} = 15$ Hz), 25.6 (br d, 2 $\mathrm{H_2\mathit{C}{=}CH_2}$ *trans*, $J_{CP(app)} = 13$ Hz), 28.4 (br d, 2 $\mathrm{H_2C{=}\mathit{C}H_2}$ *trans*, $J_{CP(app)} = 12$ Hz), 59.1 (t, $\mathrm{P\mathit{C}H_2P}$, $^1J_{CP} = 15$ Hz). Anal. Calcd for $\mathrm{C_{15}H_{40}P_4Mo}$: C, 40.9; H, 9.2. Found: C, 40.7; H, 9.2.

Synthesis of *trans*-M(C₂H₄)₂(CO)(PMe₃)(P-P) (M = Mo, P-P = depe (4a), dmpe (5); M = W, P-P = depe (4b)) Complexes. Complex 1a was generated in situ by addition of 1 equiv of depe to a solution of *trans*-$\mathrm{Mo(C_2H_4)_2(PMe_3)_4}$ (0.33 g, 0.72 mmol) in petroleum ether (40 mL). After 1 h of stirring, the solvent was removed under reduced pressure. The resulting solid was dissolved in 30 mL of THF and pressurized with CO (2 atm) in a pressure bottle. The mixture was stirred for 2 h, the volatiles were removed under vacuum, and the residue was extracted with petroleum ether. White crystals of **4a** were obtained after cooling at −30 °C overnight. Yield: 0.23 g (69%). By similar procedures complexes **4b** and **5** were obtained in 54% and 65% yields, respectively.

***trans*-Mo(C₂H₄)₂(CO)(PMe₃)(depe) (4a).** All ^{1}H nuclei in complexes 4 and 5 resonate in a short range (3–1 ppm); their complete assignment has not been attempted. $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (81 MHz, $\mathrm{C_6D_6}$): AMX spin system, δ_A 48.5 (dd, $J_{AM} = 6$, $J_{AX} = 104$ Hz), δ_M 30.6 (dd, $J_{MX} = 23$ Hz), δ_X 7.1 (dd). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (75.5 MHz, $\mathrm{C_6D_6}$): δ 7.5 (br, $\mathrm{P(CH_2\mathit{C}H_3)}$ of depe), 8.2 (br, $\mathrm{P(CH_2\mathit{C}H_3)}$), 8.7 (br, $\mathrm{P(\mathit{C}H_2CH_3)}$), 9.5 (br, $\mathrm{P(\mathit{C}H_2CH_3)}$), 18.1 (d, 2 $\mathrm{P(\mathit{C}H_3)_3}$ *cis*, $J_{CP(app)} = 18$ Hz), 18.8 (br, $\mathrm{P(\mathit{C}H_2CH_3)}$), 21.8 (dd, $\mathrm{PCH_2\mathit{C}H_2P}$, $^1J_{CP} = 17$, $^2J_{CP} = 15$ Hz), 23.5 (ddd, $\mathrm{P\mathit{C}H_2CH_2P}$, $^1J_{CP} = 19$, $^2J_{CP}$ = 17, $^3J_{CP} = 4$ Hz), 28.1 (br $\mathrm{\mathit{C}_2H_4}$), 30.4 (br, $\mathrm{\mathit{C}_2H_4}$), 36.5 (br, $\mathrm{\mathit{C}_2H_4}$), 228.6 (dt, *C*O, $^2J_{CP(trans)} = 37$, $^2J_{CP(cis)} = 10$ Hz). Anal. Calcd for $\mathrm{C_{18}H_{41}P_3OMo}$: C, 46.8; H, 8.9. Found: C, 46.4; H, 9.5.

***trans*-W(C₂H₄)₂(CO)(PMe₃)(depe) (4b).** $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (81 MHz, $\mathrm{C_6D_6}$): AMX spin systems, δ_A 29.6 (d, $J_{AM} = 0$, $J_{AX} = 94$, $^1J_{PW} = 230$ Hz), $\delta_M = 14.3$ (d, $J_{MX} = 17.5$, $^1J_{PW} = 173$ Hz), δ_X 7.1 (dd, $^1J_{PW} = 246$ Hz). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (50 MHz, $\mathrm{C_6D_6}$): δ 6.4 (d, $\mathrm{P(CH_2\mathit{C}H_3)}$ of depe, $^2J_{CP} = 11$ Hz), 7.0 (d, $\mathrm{P(CH_2\mathit{C}H_3)}$, $^2J_{CP} =$ 6 Hz), 7.1 (d, $\mathrm{P(CH_2\mathit{C}H_3)}$, $^2J_{CP} = 6$ Hz), 7.5 (d, $\mathrm{P(CH_2\mathit{C}H_3)}$, $^2J_{CP}$ = 7 Hz), 8.3 (d, $\mathrm{P(\mathit{C}H_2CH_3)}$, $^1J_{CP} = 22$ Hz), 17.4 (d, 2 $\mathrm{P(\mathit{C}H_3)_3}$ *cis*, $J_{CP(app)} = 22$ Hz), 18.4 (d, $\mathrm{P(\mathit{C}H_2CH_3)}$, $^1J_{CP} = 21$ Hz), 18.8 (m, $\mathrm{\mathit{C}_2H_4}$), 21.2 (br m, $\mathrm{\mathit{C}_2H_4}$), 22.6 (dd, $\mathrm{PCH_2\mathit{C}H_2P}$, $^1J_{CP} = 20$, $^2J_{CP}$ = 13 Hz), 24.7 (ddd, $\mathrm{P\mathit{C}H_2CH_2P}$, $^1J_{CP} = 22$, $^2J_{CP} = 14$, $^3J_{CP} = 4$ Hz), 26.2 (br s, $\mathrm{\mathit{C}_2H_4}$), 219.3 (dt, *C*O, $^2J_{CP(trans)} = 36$, $^2J_{CP(cis)} = 6$ Hz). Anal. Calcd for $\mathrm{C_{18}H_{41}P_3OW}$: C, 39.3; H, 7.5. Found: C, 38.5; H, 7.4.

***trans*-Mo(C₂H₄)₂(CO)(PMe₃)(dmpe) (5).** $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (81 MHz, $\mathrm{C_6D_6}$): AMX spin system, δ_A 56.7 (dd, $J_{AM} = 6$, $J_{AX} = 99.5$ Hz), δ_M 37.0 (dd, $J_{MX} = 23.5$ Hz), δ_X 0.7 (dd). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (75.5 MHz, $\mathrm{C_6D_6}$): δ 6.1 (d, $\mathrm{P(\mathit{C}H_3)}$ of dmpe, $^1J_{CP} = 7$ Hz), 7.0 (d, $\mathrm{P(\mathit{C}H_3)}$ of dmpe, $^1J_{CP} = 7$ Hz), 16.6 (d, $\mathrm{P(\mathit{C}H_3)}$ of dmpe, $^1J_{CP} =$ 19 Hz), 16.9 (d, $\mathrm{P(\mathit{C}H_3)}$ of dmpe, $^1J_{CP} = 29$ Hz), 17.5 (d, 2 $\mathrm{P(\mathit{C}H_3)_3}$ *cis*, $J_{CP(app)} = 16$ Hz), 26.9 (m, $\mathrm{\mathit{C}_2H_4}$), 27.7 (m, $\mathrm{\mathit{C}_2H_4}$), 28.6 (dd, $\mathrm{PCH_2\mathit{C}H_2P}$, $^1J_{CP} = 20$, $^2J_{CP} = 15$ Hz), 29.3 (ddd, $\mathrm{P\mathit{C}H_2CH_2P}$, $^1J_{CP}$ = 21, $^2J_{CP} = 18$, $^3J_{CP} = 4$ Hz), 30.3 (m, br, $\mathrm{\mathit{C}_2H_4}$), 34.5 (br s, $\mathrm{\mathit{C}_2H_4}$), 227.7 (dt, *C*O, $^2J_{CP(trans)} = 39$, $^2J_{CP(cis)} = 9$ Hz). Anal. Calcd for $\mathrm{C_{14}H_{33}P_3OMo}$: C, 41.4; H, 8.2. Found: C, 41.4; H, 8.3.

Synthesis of *trans*-Mo(C₂H₄)₂(P-P)₂ (P-P = dmpe (6), depe (7)) Complexes. One equivalent of dmpe was added to a suspension of $\mathrm{MoCl_4(THF)_2}$ (1.8 g, 4.7 mmol) in THF (40 mL) and stirred for 1 h. The resulting solution was transferred into a flask containing a suspension of Na(Hg) (1%, ca. 0.7 g of Na) in THF (100 mL), under an ethylene atmosphere. The mixture was stirred for 20–30 min, and then a second equivalent of dmpe was added via syringe. The reaction mixture was stirred for a further 4–5 h, the resulting suspension centrifuged, and the solution evaporated to dryness. The residue was extracted with petroleum ether and concentrated. Addition of MeOH induced the precipitation of a yellow solid, which was filtered off, washed with cold MeOH, and dried under vacuum. Yield: 25%.

Compound 7 was synthesized using a similar procedure, but crystallization was achieved from acetone solutions cooled to −30 °C. Yield: 40%.

Two alternative routes to complex 7 have been developed. The reaction of *trans*-$\mathrm{Mo(C_2H_4)_2(depe)(PMe_3)_2}$ (**2a**) with 1 equivalent of depe carried out at 60 °C for 3 h allows the isolation of 7 in 58% yield. On the other hand, formation of complex 7 was also achieved by heating a THF solution of *trans*-$\mathrm{Mo(C_2H_4)_2(PMe_3)_4}$ with 2 equiv of the diphosphine for 3.5 h. Yield: 50%.

***trans*-Mo(C₂H₄)₂(dmpe)₂ (6).** $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (81 MHz, $\mathrm{C_6D_6}$): δ 44.7 (s). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (50 MHz, $\mathrm{C_6D_6}$): δ 8.1 (s, 4 $\mathrm{P(\mathit{C}H_3)(CH_3)}$ of dmpe), 19.7 (pt, 4 $\mathrm{P(CH_3)(\mathit{C}H_3)}$ of dmpe, $^1J_{CP(app)}$ = 6 Hz), 25.4 (pseudoquintet, 2 $\mathrm{\mathit{C}_2H_4}$, $^2J_{CP} = 5$ Hz), 30.3 (pt, 4 $\mathrm{–\mathit{C}H_2P}$ of dmpe, $J_{CP(app)} = 9$ Hz).

***trans*-Mo(C₂H₄)₂(depe)₂ (7).** $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (81 MHz, $\mathrm{C_6D_6}$): δ 55.9 (s). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (50 MHz, $\mathrm{C_6D_6}$): δ 8.8 (s, 4 $\mathrm{P(CH_2\mathit{C}H_3)(CH_2CH_3)}$ of depe), 9.3 (s, 4 $\mathrm{P(CH_2CH_3)(CH_2\mathit{C}H_3)}$ of depe), 9.8 (s, 4 $\mathrm{P(\mathit{C}H_2CH_3)(CH_2CH_3)}$ of depe), 21.7 (pt, 4 $\mathrm{P(CH_2CH_3)(\mathit{C}H_2CH_3)}$ of depe, $^1J_{CP(app)} = 5$ Hz), 22.9 (pseudoquintet, 2 $\mathrm{\mathit{C}_2H_4}$, $^2J_{CP} = 8$ Hz), 26.3 (pt, 4 $\mathrm{–\mathit{C}H_2P}$ of depe, $J_{CP(app)} = 6$ Hz). Anal. Calcd for $\mathrm{C_{24}H_{56}P_4Mo}$: C, 51.1; H, 10.0. Found: C, 49.8; H, 9.3.

***trans*-Bis(ethylene)tetrakis(dimethylphenylphosphine)molybdenum(0), *trans*-[Mo(C₂H₄)₂(PMe₂Ph)₄] (8).** $\mathrm{MoCl_3(PMe_2Ph)_3}$ (3.1 g, 5 mmol) and 1 equiv of $\mathrm{PMe_2Ph}$ were successively added to a suspension of Na(Hg) (1%, ca. 1 g of Na) in THF (225 mL) under an ethylene atmosphere. The mixture was stirred for 3–4 h, the resulting suspension centrifuged, and the solvent evaporated under vacuum. The orange solid obtained was washed with petroleum ether and dried in vacuo. Yield: 60%. Complex 8 exists in solution, under a $\mathrm{N_2}$ atmosphere, as a 1:1 mixture of *trans,mer*-$\mathrm{[Mo(C_2H_4)_2(N_2)(PMe_2Ph)_3]}$ and $\mathrm{PMe_2Ph}$ according to the following spectroscopic data. IR (THF): 2080 cm^{-1} (ν(N≡N)). $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (81 MHz, $\mathrm{C_6D_6}$): $\mathrm{AX_2}$ spin system for the complex, δ_A 23.8 (t, $^2J_{PP} = 18$ Hz), δ_X 20.1, and δ −45.8 (s) for the free $\mathrm{PMe_2Ph}$. Other selected data for *trans,mer*-$\mathrm{[Mo(C_2H_4)_2(N_2)(PMe_2Ph)_3]}$: ^{1}H NMR (200 MHz,

$\mathrm{C_6D_6}$) δ 7.2 (m, $\mathrm{PMe_2}\mathit{Ph}$), 2–1.5 (br m, $\mathrm{C_2}\mathit{H_4}$), 1.05 (m, $\mathrm{P}\mathit{Me_2}\mathrm{Ph}$); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (50 MHz, $\mathrm{C_6D_6}$) δ 35.8 (br s, $\mathit{C_2}\mathrm{H_4}$), 31.7 (br s, $\mathit{C_2}\mathrm{H_4}$), 14.5 (br s, 2 $\mathrm{P}\mathit{Me_2}\mathrm{Ph}$ *trans*), 11.2 (br s, 1 $\mathrm{P}\mathit{Me_2}\mathrm{Ph}$).

Reaction of 8 with CO: *trans,mer*-[Mo(C_2H_4)$_2$(CO)(PMe$_2$Ph)$_3$] (9) and *trans,trans,trans*-[Mo(C_2H_4)$_2$(CO)$_2$(PMe$_2$Ph)$_2$] (10). Carbon monoxide was bubbled at −80 °C for 5 min through a solution of 8 (0.3 g, 0.42 mmol) in THF (30 mL). The solvent was stripped off, the residue extracted with a 1:1 petroleum ether–$\mathrm{Et_2O}$ mixture (20 mL), and the extract then centrifuged. The resulting solution was concentrated and cooled to −30 °C to afford yellow crystals of **9** in 60% yield.

Complex **10** was obtained as white crystals by following the same procedure but carrying out the reaction at room temperature. The crystallization solvent was a 4:1 petroleum ether–$\mathrm{Et_2O}$ mixture, and a yield of 75% was obtained.

***trans,mer*-Mo(C_2H_4)$_2$(CO)(PMe$_2$Ph)$_3$ (9).** IR (Nujol): 1850 cm^{-1} (ν(CO)). ^{1}H NMR (200 MHz, $\mathrm{C_6D_6}$): δ 7.00 (m, $\mathrm{PMe_2}\mathit{Ph}$), 1.87 (br s, $\mathrm{C_2}\mathit{H_4}$), 1.20 (br s, 2 $\mathrm{P}\mathit{Me_2}\mathrm{Ph}$ *trans*), 0.96 (d, $\mathrm{P}\mathit{Me_2}\mathrm{Ph}$ *cis*). $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (81 MHz, $\mathrm{C_6D_6}$): $\mathrm{AX_2}$ spin system, δ_A −1.64 (t, $^2J_\mathrm{PP}$ = 22 Hz), δ_X 13.6 (d). Selected $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR data (50 MHz, $\mathrm{C_6D_6}$): δ 14.6 (d, $\mathrm{P}\mathit{Me_2}\mathrm{Ph}$, $^1J_\mathrm{CP}$ = 14 Hz), 15.8 (t, 2 $\mathrm{P}\mathit{Me_2}\mathrm{Ph}$, $J_\mathrm{CP(app)}$ = 20 Hz), 30.0 (br s, $\mathit{C_2}\mathrm{H_4}$). Anal. Calcd for $\mathrm{C_{29}H_{41}OP_3Mo}$: C, 58.6; H, 7.0. Found: C, 58.9; H, 7.0.

***trans,trans,trans*-Mo(C_2H_4)$_2$(CO)$_2$(PMe$_2$Ph)$_2$ (10).** IR (Nujol): 1850 cm^{-1} (ν(CO)). ^{1}H NMR (200 MHz, $\mathrm{C_6D_6}$): δ 1.2 (t, 2 $\mathrm{P}\mathit{Me_2}\mathrm{Ph}$, $J_\mathrm{HP(app)}$ = 3 Hz), 1.76 (t, 2 $\mathrm{C_2}\mathit{H_4}$, $^3J_\mathrm{HP}$ = 5 Hz), 7.0 (m, 2 $\mathrm{PMe_2}\mathit{Ph}$). $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (81 MHz, $\mathrm{C_6D_6}$): δ 16.9 (s). Selected $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR data (50 MHz, $\mathrm{C_6D_6}$): δ 15.8 (t, 2 $\mathrm{P}\mathit{Me_2}\mathrm{Ph}$, $J_\mathrm{CP(app)}$ = 11 Hz), 34.8 (br s, $\mathit{C_2}\mathrm{H_4}$). Anal. Calcd for $\mathrm{C_{22}H_{30}O_2P_2Mo}$: C, 54.6; H, 6.2. Found: C, 54.6; H, 6.2.

Reaction of 8 with CN^{t}Bu: *trans,trans,trans*-Mo(C_2H_4)$_2$(CN^{t}Bu)$_2$(PMe$_2$Ph)$_2$ (11). A solution of 8 (0.2 g, 0.28 mmol) in THF (40 mL) was reacted with a slight excess of CN^{t}Bu (0.7 mL of a 1 M solution in THF) and the mixture stirred for 2 h. The solvent was removed in vacuo and the residue extracted with petroleum ether (10 mL). Filtration and crystallization of the resulting solution at −30 °C afforded **11** as yellow crystals. Yield: 75%. IR (Nujol): 1965 cm^{-1} (br, ν(CN)). ^{1}H NMR (200 MHz, $\mathrm{C_6D_6}$): δ 1.0 (s, $\mathrm{CNC}\mathit{Me_3}$), 1.46 (t, 2 $\mathrm{P}\mathit{Me_2}\mathrm{Ph}$, $J_\mathrm{HP(app)}$ = 3 Hz), 1.62 (t, 2 $\mathrm{C_2}\mathit{H_4}$, $^3J_\mathrm{HP}$ = 5 Hz), 7.15 (m, 2 $\mathrm{PMe_2}\mathit{Ph}$). $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (81 MHz, $\mathrm{C_6D_6}$): δ 20.2 (s, 2 $\mathrm{PMe_3}$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (50 MHz, $\mathrm{C_6D_6}$): δ 15.6 (pt, 2 $\mathrm{P}\mathit{Me_2}\mathrm{Ph}$, $J_\mathrm{CP(app)}$ = 8 Hz), 31.3 (s, $\mathrm{CNC}\mathit{Me_3}$), 31.5 (br s, $\mathit{C_2}\mathrm{H_4}$), 54.0 (s, $\mathrm{CN}\mathit{C}\mathrm{Me_3}$), and signals due to Ph group of $\mathrm{PMe_2Ph}$. The $\mathit{C}\mathrm{NCMe_3}$ resonance was not observed.

Reaction of 8 with depe: *trans*-Mo(C_2H_4)$_2$(depe)(PMe$_2$Ph)$_2$ (12). To a stirred solution of 8 (0.35 g, 0.5 mmol) in THF (30 mL) was added 1 equiv of depe via syringe (0.5 mL of a 1 M solution in THF). After 30 min of stirring, the resulting mixture was taken to dryness and the residue crystallized from acetone at −30 °C. Orange-red crystals were obtained in 80% yield. ^{1}H NMR (200 MHz, $\mathrm{C_6D_6}$): δ 7.2–7.0 (m, $\mathrm{PMe_2}\mathit{Ph}$), 1.3 (dd, *Me* depe), 1.5–1.0 (m, $\mathrm{C_2}\mathit{H_4}$ and $\mathrm{C}\mathit{H_2}$ depe), 0.85 (m, $\mathrm{P}\mathit{Me_2}\mathrm{Ph}$). $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (81 MHz, $\mathrm{C_6D_6}$): AA′XX′ spin system, δ_A 15.4 ($\mathrm{PMe_3}$), δ_X 47.9 (depe) ($J_\mathrm{AA'}$ = 17, $J_\mathrm{XX'}$ = 8, $J_{\mathrm{AX}(cis)}$ = 17, $J_{\mathrm{AX'}(trans)}$ = 105 Hz, absolute values). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (50 MHz, $\mathrm{C_6D_6}$): δ 9.5 (m, 2 $\mathrm{P(CH_2CH_3)_2}$ of depe), 10.1 (s, 2 $\mathrm{P(}\mathit{C}\mathrm{H_2CH_3)(CH_2CH_3)}$ of depe), 18.4 (filled-in d, $\mathrm{P}\mathit{Me_2}\mathrm{Ph}$, $J_\mathrm{CP(app)}$ = 5 Hz), 17.0 (filled-in d, $\mathrm{P}\mathit{Me_2}\mathrm{Ph}$, $J_\mathrm{CP(app)}$ = 5 Hz), 20.2 (d, 2 $\mathrm{P(CH_2CH_3)(}\mathit{C}\mathrm{H_2CH_3)}$ of depe, $^1J_\mathrm{CP}$ = 17 Hz), 20.6 (pt, 4 $-\mathit{C}\mathrm{H_2P}$, $J_\mathrm{CP(app)}$ = 18 Hz), 26.4 (br d, 2 $\mathrm{H_2}\mathit{C}{=}\mathrm{CH_2}$ *trans*, $J_\mathrm{CP(app)}$ = 14 Hz), 27.5 (br d, 2 $\mathrm{H_2C{=}CH_2}$ *trans*, $J_\mathrm{CP(app)}$ = 9 Hz), and signals due to Ph group in $\mathrm{PMe_2Ph}$. Anal. Calcd for $\mathrm{C_{30}H_{54}P_4Mo}$: C, 56.8; H, 8.6. Found: C, 55.9; H, 8.5.

Reactions with Carbon Dioxide. The following reactions with carbon dioxide have been carried out under the stated experimental conditions. The starting material was recovered unaltered at the end of the experimental time. Complex **1a**: THF, 40 °C, 3 atm, 24 h. Complex **1b**: $\mathrm{Et_2O}$, 20 °C, 3 atm, 48 h. Complex **3**: THF, 20 °C, 3 atm, 8 h. Complex **2a** reacts with $\mathrm{CO_2}$ (THF, 20 °C, 3 atm), but no pure products could be isolated from the reaction mixture. The following bis(ethylene) complexes[9] do not react with 3 atm of $\mathrm{CO_2}$ at room temperature: *trans*-$\mathrm{M(C_2H_4)_2(CO)(PMe_3)_3}$, *trans*-$\mathrm{M(C_2H_4)_2(CO)_2(PMe_3)_2}$, *trans*-$\mathrm{M(C_2H_4)_2(CNR)(PMe_3)_3}$, and *trans*-$\mathrm{M(C_2H_4)_2(CNR)_2(PMe_3)_2}$ (M = Mo, W).

Reaction of 2b with Carbon Dioxide: Synthesis of WH(OOCCH=CH$_2$)(C$_2$H$_4$)(PMe$_3$)(depe) (13). A solution of complex **2b** (0.25 g, 0.4 mmol) in $\mathrm{Et_2O}$ (30 mL) was pressurized with 3 atm of $\mathrm{CO_2}$ and was stirred for 20 h. The resulting orange solution was centrifuged and concentrated. White crystals of compound **13** were obtained after cooling at −30 °C overnight. Yield: 62%. IR (Nujol): 1850 (ν(Mo—H)), 1630 (ν(COO)) cm^{-1}. ^{1}H NMR (500 MHz, $\mathrm{C_6D_6}$): δ −3.31 (dt, 1 H, W—*H*, $^2J_\mathrm{HP}$ = 91, $^2J_\mathrm{HP}$ = 20 Hz), 0.59 (m, 3 H, *Me* depe), 0.72 (m, 3 H, *Me* depe), 0.95 (m, 3 H, *Me* depe), 0.97 (d, 9 H, $\mathrm{P}\mathit{Me_3}$, $^2J_\mathrm{HP}$ = 8 Hz), 1.10 (m, 3 H, *Me* depe), 1.2 (br m, 2 H, $\mathit{H_2}\mathrm{C{=}CH{-}}$), 1.36 (m, 2 H, $\mathit{H_2}\mathrm{C{=}CH_2}$), 1.4 (br m, 2 H, $\mathrm{C}\mathit{H_2}$ depe), 1.6 (br m, 2 H, $\mathrm{C}\mathit{H_2}$ depe), 2.7 (br m, 2 H, $\mathrm{C}\mathit{H_2}$ depe), 3.21 (br s, $\mathrm{CH_2{=}C}\mathit{H}\mathrm{COO}$). The other ethylene resonance ($\mathrm{H_2C{=}C}\mathit{H_2}$) is obscured by the phosphine absorptions. $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (81 MHz, $\mathrm{C_6D_6}$): AMX spin system, δ_A −2.7 (dd, $^2J_\mathrm{AM}$ = 51, $^2J_\mathrm{AX}$ = 123, $^1J_\mathrm{PW}$ = 156 Hz), δ_M 12.9 (dd, $^2J_\mathrm{MX}$ = 14, $^1J_\mathrm{PW}$ = 159 Hz), δ_X 51 (dd, $^1J_\mathrm{PW}$ = 157 Hz). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (75.5 MHz, $\mathrm{C_6D_6}$): δ 4.0 (d, $\mathrm{P(}\mathit{C}\mathrm{H_2CH_3)}$ of depe, $^1J_\mathrm{CP}$ = 13 Hz), 5.8 (d, $\mathrm{P(CH_2CH_3)}$ of depe, $^1J_\mathrm{CP}$ = 5 Hz), 7.3 (d, $\mathrm{P(CH_2CH_3)}$ of depe, $^1J_\mathrm{CP}$ = 4 Hz), 7.6 (d, $\mathrm{P(CH_2}\mathit{C}\mathrm{H_3)}$ of depe, $^1J_\mathrm{CP}$ = 6 Hz), 7.9 (d, $\mathrm{P(CH_2}\mathit{C}\mathrm{H_3)}$ of depe, $^1J_\mathrm{CP}$ = 4 Hz), 12.1 (d, $\mathrm{P}\mathit{Me_3}$, $^1J_\mathrm{CP}$ = 30 Hz), 12.3 (d, $-\mathrm{CH_2}-$, $^1J_\mathrm{CP}$ = 23 Hz), 16.9 (d, $-\mathrm{CH_2}-$, $^1J_\mathrm{CP}$ = 28 Hz), 20.9 (m, 2 $-\mathrm{CH_2}-$), 21.4 (d, $\mathrm{H_2}\mathit{C}{=}\mathrm{CH_2}$, $^1J_\mathrm{CP}$ = 9 Hz), 23.0 (dd, $-\mathrm{CH_2}-$, J_CP = 16, J_CP = 11 Hz), 28.5 (m, $\mathrm{H_2C{=}}\mathit{C}\mathrm{H_2}$), 33.6 (d, $\mathrm{H_2}\mathit{C}{=}\mathrm{CH{-}}$, $^1J_\mathrm{CP}$ = 9 Hz), 46.8 (s, $\mathrm{H_2C{=}}\mathit{C}\mathrm{H{-}}$), 179.9 (br s, *C*OO).

Reaction of 8 with Carbon Dioxide: Synthesis of [MoH(OOCCH=CH$_2$)(C$_2$H$_4$)(PMe$_2$Ph)$_2$]$_2$ (14). Complex **8** (0.25 g, 0.35 mmol) was dissolved in THF (30 mL) and $\mathrm{CO_2}$ bubbled through the solution at room temperature for 15 min. The solvent was removed in vacuo and the residue extracted with acetone. Concentration and cooling at −30 °C afforded **14** as white crystals. Yield: 60%. IR (Nujol): 1790 (ν(Mo—H)), 1540 (ν(COO)) cm^{-1}. ^{1}H NMR (200 MHz, $\mathrm{C_6D_6}$): δ −5.2 (br t, 1 H, Mo—*H*, $^2J_\mathrm{HP}$ = 98 Hz), 1.4 (d, 3 H, $\mathrm{P}\mathit{Me}\mathrm{MePh}$, $^2J_\mathrm{HP}$ = 9 Hz), 1.5 (d, 3 H, $\mathrm{PMe}\mathit{Me}\mathrm{Ph}$, $^2J_\mathrm{HP}$ = 9 Hz), 1.6 (d, 3 H, $\mathrm{P}\mathit{Me}\mathrm{MePh}$, $^2J_\mathrm{HP}$ = 9 Hz), 1.7 (d, 3 H, $\mathrm{PMe}\mathit{Me}\mathrm{Ph}$, $^2J_\mathrm{HP}$ = 9 Hz), 2.4 (br s, 2 H, $\mathrm{C_2}\mathit{H_4}$), 3.3 (pseudoquartet, 1 H, $\mathrm{CH_2{=}C}\mathit{H}\mathrm{COO}$, $^3J_\mathrm{HP} \simeq {}^3J_\mathrm{HP}$ = 7 Hz), 7.3–7.4 (m, 10 H, $\mathrm{PMe_2(C_6}\mathit{H_5}\mathrm{)}$). The remaining olefinic resonances appear between 2 and 1 ppm and are obscured by $\mathrm{PMe_2Ph}$ absorptions, δ 7.3–7.4 (m, 10 H, $\mathrm{PMe_2(C_6}\mathit{H_5}\mathrm{)}$). $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR (81 MHz, $\mathrm{C_6D_6}$): AX spin system, δ_A 50.8 (d, $^2J_\mathrm{PP}$ = 51 Hz), δ_X 44.9 (d). Anal. Calcd for $\mathrm{C_{42}H_{60}P_4O_4Mo_2}$: C, 53.4; H, 6.4. Found: C, 52.6; H, 6.4.

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