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Reactions of *mer*-$Mo(H)(CO)(NO)(PMePh_2)_3$ with Ethylene, Propylene, and Styrene That Bear on Alternating CO/Olefin Coupling Chemistry

Tan-Yun Cheng, Joel S. Southern, and Gregory L. Hillhouse*

Searle Chemistry Laboratory, Department of Chemistry, The University of Chicago, Chicago, Illinois 60637

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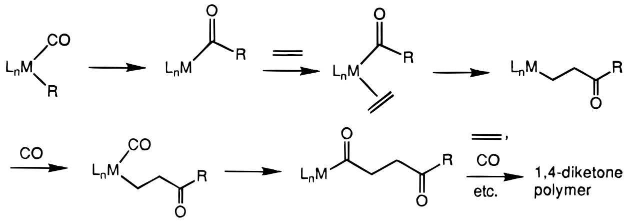
The tris(diphenylmethyl)phosphine molybdenum complex *mer*-$Mo(Cl)(CO)(NO)(PMePh_2)_3$ (**2**), prepared by the reaction of 4 equiv of $PMePh_2$ with *trans*-$Mo(ClAlCl_3)(NO)(CO)_4$ (**1**), undergoes a metathesis reaction with $LiBH_4$ to afford the hydrido nitrosyl complex *mer*-$Mo(H)(CO)(NO)(PMePh_2)_3$ (**3**). The reactions of several olefins (ethylene, propylene, styrene) with **3** have been examined, and these studies have uncovered interesting stoichiometric coupling reactions involving hydride, CO, olefin, acyl, and alkyl ligands which bear on alternating CO/olefin oligomerization chemistry. Reaction of **3** with C_2H_4 (50 °C, 50 psi, 48 h) results in the loss of a $PMePh_2$ ligand and incorporation of 3 equiv of C_2H_4 to give *trans*-$Mo\{CH_2CH_2C(O)CH_2CH_3\}(C_2H_4)(NO)(PMePh_2)_2$ (**4**) in good isolated yield. A slower reaction is observed between **3** and propylene with incorporation of only one olefin in the metal coordination sphere, giving isomeric *mer*-$Mo\{\eta^2\text{-}C(O)CH_2CH_2CH_3\}(NO)(PMePh_2)_3$ (**5**) and *mer*-$Mo\{\eta^2\text{-}C(O)CH(CH_3)_2\}(NO)(PMePh_2)_3$ (**6**). Treatment of solutions of **5** and **6** with HCl results in their conversion to two new aldehyde complexes, *mer*-$MoCl(\eta^1\text{-}O{=}CHCH_2CH_2CH_3)(NO)(PMePh_2)_3$ (**7**) and *mer*-$MoCl\{\eta^1\text{-}O{=}CHCH(CH_3)_2\}(NO)(PMePh_2)_3$ (**8**), respectively. Treatment of **7** and **8** with CO results in their ultimate conversion to $Mo(Cl)(CO)_2(NO)(PMePh_2)_2$ (**11**), butyraldehyde, and isobutyraldehyde via the bis(phosphine) aldehyde intermediates *trans*-$MoCl(\eta^1\text{-}O{=}CHCH_2CH_2CH_3)(CO)(NO)(PMePh_2)_2$ (**9**) and *trans*-$MoCl\{\eta^1\text{-}O{=}CHCH(CH_3)_2\}(CO)(NO)(PMePh_2)_2$ (**10**). Styrene reacts slowly (5 d, 50 °C) with benzene solutions of **3** to give 1 equiv of ethylbenzene and emerald-green *trans*-$Mo[PMePh\{C_6H_4C(O)CH_2CH_2C_6H_4\}](NO)(PMePh_2)_2$ (**12**) in high yield.

Introduction

Transition-metal-catalyzed alternating copolymerizations of carbon monoxide with olefins that give polyketones is an area under intense study.[1,2] The polymers produced in such systems (usually with Rh(I), Ni(II), or Pd(II) catalysts) are interesting ones because they (i) exhibit novel properties, (ii) possess a high degree of functionality, and (iii) are prepared from cheap, abundant feedstocks. The polymerization reactions (Scheme 1) are themselves interesting in that two distinct C−C bond-forming reactions are required for chain growth (i.e., alkyl/CO migratory insertion to give an acyl complex and olefin/acyl migratory insertion to give an alkyl complex), and these must occur sequentially to produce perfectly alternating copolymers—no olefin/alkyl or acyl/CO insertions occur even though both are precedented organometallic transformations in similar systems. Detailed studies describing mechanistic and energetic aspects of CO/olefin alternating copolymerizations catalyzed by late-transition-metal complexes have appeared.[1,3]

Scheme 1



During the course of our studies of the chemistry of d^6 hydrido phosphine complexes of the group 6 metals with unsaturated substrates,[4] we have examined the reactions of several olefins (ethylene, propylene, styrene) with *mer*-$Mo(H)(CO)(NO)(PMePh_2)_3$, and we report here the results of these studies, including interesting stoichiometric coupling reactions involving hydride, CO, olefin, acyl, and alkyl ligands which bear on alternating CO/olefin oligomerization chemistry.[5]

Results and Discussion

Synthesis of *mer*-$Mo(H)(CO)(NO)(PMePh_2)_3$ and Its Reaction with Ethylene. The six-coordinate

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[⊗] Abstract published in *Advance ACS Abstracts,* May 1, 1997.

[1] Sen, A. *Acc. Chem. Res.* **1993**, *26*, 303 and references therein.

[2] Sen, A. *Adv. Polym. Sci.* **1986**, *73/74*, 125.

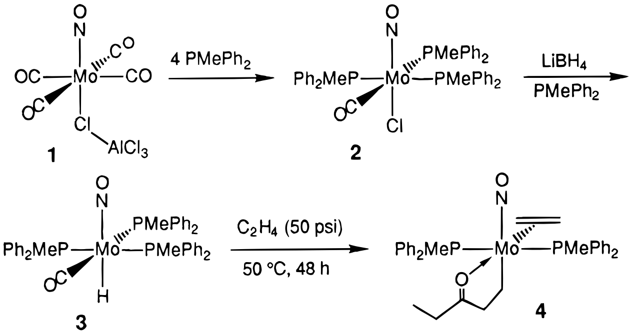
[3] Rix, F. C.; Brookhart, M.; White, P. S. *J. Am. Chem. Soc.* **1996**, *118*, 4746 and references therein.

[4] (a) Hillhouse, G. L. *J. Am. Chem. Soc.* **1985**, *107*, 7772. (b) Hillhouse, G. L.; Haymore, B. L. *Inorg. Chem.* **1987**, *26*, 1876. (c) Smith, M. R., III; Hillhouse, G. L. *J. Am. Chem. Soc.* **1988**, *110*, 4066. (d) Smith, M. R., III; Cheng, T.-Y.; Hillhouse, G. L. *Inorg. Chem.* **1992**, *31*, 1535.

[5] Some aspects of this work have been presented: Cheng, T.-Y.; Hillhouse, G. L. *Abstracts of Papers,* 206th National Meeting of the American Chemical Society, Chicago, IL, August 1993; American Chemical Society: Washington, DC, 1993; Abstract INOR 244.

S0276-7333(97)00160-X CCC: $14.00

Scheme 2



molybdenum nitrosyl complex *mer*-Mo(Cl)(CO)(NO)(PMePh$_2$)$_3$ (**2**), prepared by the reaction of 4 equiv of PMePh$_2$ with *trans*-Mo(ClAlCl$_3$)(NO)(CO)$_4$ (**1**),[6] undergoes a metathesis reaction with lithium borohydride in the presence of excess phosphine to afford the new molybdenum hydrido complex *mer*-Mo(H)(CO)(NO)(PMePh$_2$)$_3$ (**3**), isolated in 84% yield as analytically pure yellow crystals (Scheme 2). The resonance for the hydride ligand of **3** is observed in the ^{1}H NMR spectrum at δ −0.44 (C$_6$D$_6$) as a pseudoquartet ($^2J_{PH}$ = 28 Hz), characteristic of cis coupling to three meridionally disposed phosphine ligands. Strong coupling between the ν(NO) and ν(MoH) vibrations (1593, 1582 cm^{-1}) in the IR spectrum of **3** indicates that the hydrido ligand is trans to the nitrosyl ligand,[7] and this structure is confirmed by the ^{13}C NMR spectrum, which shows a carbonyl resonance at δ 236 (dt, $^2J_{CPcis}$ = 11, $^2J_{CPtrans}$ = 35 Hz).

Treatment of a benzene solution of **3** with C$_2$H$_4$ (50 °C, 50 psi, 48 h) results in the loss of a PMePh$_2$ ligand and incorporation of 3 equiv of ethylene to give *trans*-Mo{CH$_2$CH$_2$C(O)CH$_2$CH$_3$}(C$_2$H$_4$)(NO)(PMePh$_2$)$_2$ (**4**) in ~60% isolated yield (Scheme 2). The IR spectrum of **4** reveals a strong band for the ν(NO) at 1520 cm^{-1} and a medium-intensity band for ν(CO) at 1640 cm^{-1}; the weaker intensity and lower energy of ν(CO) (compared with a strong ν(CO) at 1910 cm^{-1} in **3**) is consistent with an organic ketone moiety. These IR assignments were confirmed by preparing the ^{13}C-labeled isotopomer *trans*-Mo{CH$_2$CH$_2$^{13}C(O)CH$_2$CH$_3$}(C$_2$H$_4$)(NO)(PMePh$_2$)$_2$ ([^{13}C]-**4**) according to Scheme 2 using isotopically enriched Mo(ClAlCl$_3$)(NO)(^{13}CO)$_4$. The IR spectrum of [^{13}C]-**4** shows ν(NO) at 1520 cm^{-1} (unshifted by the ^{13}C label) and ν(CO) at 1620 cm^{-1} (Δ = 20 cm^{-1}).

The ^{1}H NMR spectrum of **4** (C$_6$D$_6$, 500 MHz) is shown in Figure 1 (aryl protons are omitted). The C$_2$H$_4$ ligand in **4** shows resonances for two sets of inequivalent protons (g and g′) in the ^{1}H NMR spectrum, but only one ethylene carbon resonance is observed in the ^{13}C{^{1}H} NMR spectrum (δ 39.2), indicating that the ethylene carbon atoms are coplanar with Mo and the two P atoms. Attempts to measure the rotational barrier for the C$_2$H$_4$ ligand in **4** by variable-temperature NMR were unsuccessful owing to thermal decomposition of the complex before coalescence of the g and g′ resonances (see below), but the experiments allow for the estimation of a lower limit of $\Delta G^{\ddagger} \gg$ 16.5 kcal/mol for the rotation.[8,9] The phosphine methyl groups (f) appear as a virtual triplet at δ 1.99 in the ^{1}H NMR spectrum as expected for two equivalent phosphines in a trans orientation, and this geometry was confirmed by the observation of one unique resonance in the ^{31}P{^{1}H} NMR spectrum. The ethyl fragment of the ketonyl ligand can be recognized in the upfield region of the ^{1}H NMR spectrum by a quartet resonance (δ 1.02) for the methylene protons (b) and a triplet resonance (δ 0.11) for the methyl protons (a). The methylene protons (d) on the carbon adjacent to the carbonyl group appear as a triplet at δ 1.95 and the methylene protons (e) on the carbon attached to the metal appear as a multiplet at δ 1.54 with an apparent coupling constant of 7.3 Hz. This multiplet is a formal triplet of triplets arising from coupling to two phosphorus nuclei and two protons. When the proton resonance at δ 1.95 (d) is irradiated, the multiplet at δ 1.54 (e) collapses to a triplet with a coupling constant of 14.6 Hz which is assigned to three-bond P−H coupling.

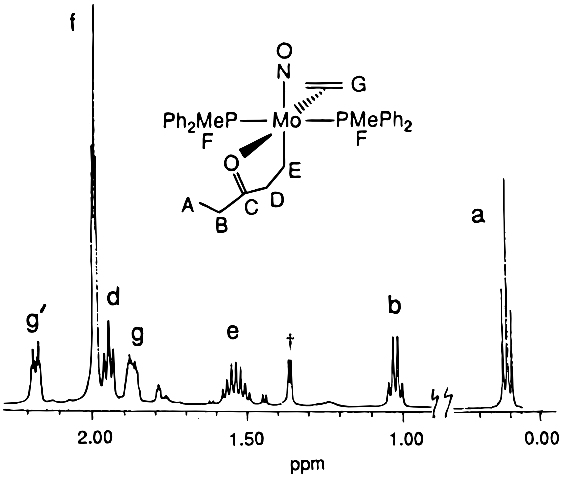


Figure 1. The ^{1}H NMR spectrum of *trans*-Mo{CH$_2$CH$_2$C(O)CH$_2$CH$_3$}(C$_2$H$_4$)(NO)(PMePh$_2$)$_2$ (**4**) (C$_6$D$_6$ solution, 20 °C, 500 MHz; aryl protons are not shown; † = free PMePh$_2$).

When *mer*-Mo(D)(CO)(NO)(PMePh$_2$)$_3$ (**3**-*d*) reacts with ethylene, the deuterium is statistically scrambled into the five ethyl proton positions of the ketonyl ligand to give two isomers of *trans*-Mo{CH$_2$CH$_2$C(O)C$_2$H$_4$D}(C$_2$H$_4$)(NO)(PMePh$_2$)$_2$ (**4**-*d*) as evidenced by ^{1}H NMR spectroscopy (Scheme 3). This result indicates that the insertion of ethylene into the Mo−H bond is reversible and that this reversible process is rapid with respect to subsequent ethyl migratory insertion to CO to give an acyl intermediate that undergoes a final ethylene insertion to give **4** (e.g., the sequence outlined in Scheme 1). The observed scrambling also has mechanistic implications regarding the initial insertion of the olefin into the Mo−H bond. Activated alkynes RC≡CCO$_2$Me (R = H, Me, Ph, CO$_2$Me), aldehydes, and ketones have been shown by Berke and co-workers to insert directly into

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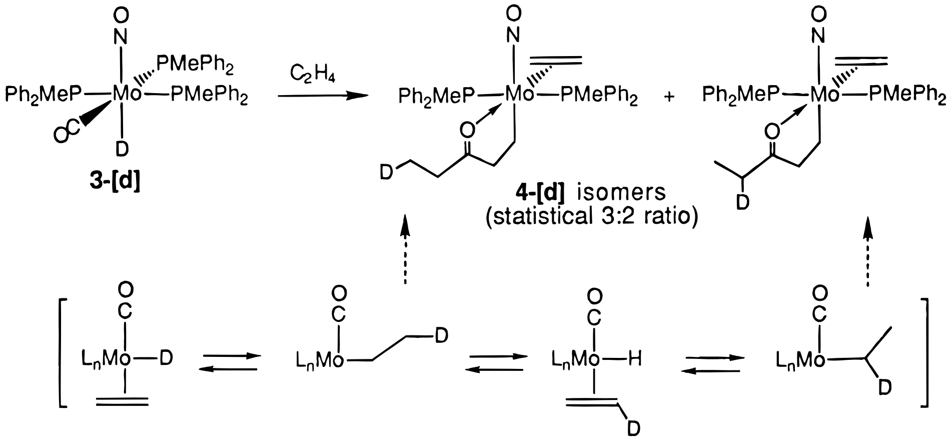
[6] Seyferth, K.; Taube, R. *J. Organomet. Chem.* **1982**, *229*, 275.

[7] Strongly coupled ν(NO) and ν(MH) vibrations are also observed in *trans,trans*-M(H)(CO)$_2$(NO)(PPh$_3$)$_2$ (M = Mo, W).[4b,d]

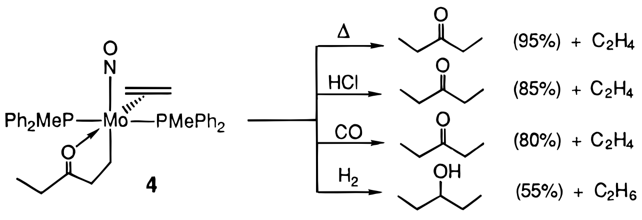
[8] This lower limit for the activation barrier was calculated using the Gutowsky−Holm approximation (T = 343 K; $\Delta\nu$ = 0.32 ppm at 300 MHz = 96 Hz). (a) Gutowsky, H. S.; Holm, J. *J. Chem. Phys.* **1956**, *25*, 1228. (b) Kurland, R. J.; Rubin, M. B.; Wise, W. B. *J. Chem. Phys.* **1964**, *40*, 2426. (c) Kost, D.; Zeichner, A. *Tetrahedron Lett.* **1974**, *4533*.

[9] This high barrier contrasts with the low activation barrier ($\Delta G^{\ddagger}$ ~ 9 kcal/mol) for ethylene rotation measured in the CO/C$_2$H$_4$ copolymerization catalyst [(phen)Pd(CH$_3$)(C$_2$H$_4$)$^+$].[3]

Scheme 3



Scheme 4



the W−H bond of *trans,trans*-W(H)(CO)$_2$(NO)(PMe$_3$)$_2$ without prior coordination of the substrate to the metal, via a mechanism involving direct nucleophilic attack of the hydride ligand at the electrophilic carbon of the alkyne, aldehyde, or ketone.[10] The results outlined in Scheme 3 suggest that the nonpolar ethylene molecule must first coordinate to the Mo center before hydride insertion to form a Mo−C$_2$H$_5$ intermediate, and predissociation of a labile PMePh$_2$ ligand is viewed as the key to activation of **3** in this chemistry.[11]

Neither **3** nor **4** is a catalyst for the coupling of CO and C$_2$H$_4$ to give alternating copolymers or oligomers using a CO/C$_2$H$_4$ (1:1) mixture. The reaction of **4** with CO at ambient temperature was monitored in a sealed NMR tube experiment over a period of several days. As shown in Scheme 4, **4** slowly decomposes in solution to give 3-pentanone (80%) and ethylene but no metal-containing products could be characterized. Solutions of **4** decompose over a period of 2 h at 70 °C to give 3-pentanone (95%) and ethylene as organic products. The likely source of protons in these reactions is the phosphine's *o*-aryl hydrogens (we have observed other ortho activation processes in this system, as exemplified below for the reaction of **3** with styrene). Treatment of solutions of **4** with aqueous HCl also effects cleavage of the ketonyl fragment to give 3-pentanone (85%). Finally, the reaction of **4** with H$_2$ was also monitored by NMR spectroscopy. Over a period of 19 days at ambient temperature, **4** is consumed to yield 3-pentanol (55%) and ethane as the major organic products. Many metal-containing products are observed under these conditions (^{31}P spectroscopy), so speculation regarding the species responsible for the hydrogenation of the ketone to the alcohol and ethylene to ethane is unwarranted.

Reaction of 3 with Propylene. The reaction of **3** with propylene has also been examined. Excess propylene was sealed with a C$_6$D$_6$ solution of **3** in a 5-mm NMR tube, and the solution was maintained at 50 °C. The slow reaction was monitored by ^{1}H and ^{31}P{^{1}H} NMR spectroscopies. Over a period of two days, the resonances for **3** decreased and two new sets of AB$_2$ resonances appeared in the ^{31}P{^{1}H} NMR spectrum, indicating three phosphine ligands in *mer* arrangements for the new compounds **5** and **6** (Scheme 5). Combined with the analysis of the ^{1}H and ^{13}C{^{1}H} NMR spectra (see below), these two new species are assigned as *mer*-Mo{η^2-C(O)CH$_2$CH$_2$CH$_3$}(NO)(PMePh$_2$)$_3$ (**5**) and *mer*-Mo{η^2-C(O)CH(CH$_3$)$_2$}(NO)(PMePh$_2$)$_3$ (**6**). Repeated experiments in which **3** was reacted with varied amounts of propylene show (determined by NMR spectroscopy) that the optimum yield of the mixture of **5** and **6** is ~60% after two days when ~1 equiv of propylene is used. Extended reaction times, higher temperatures, or higher propylene concentrations, while consuming **3**, also lead to an increase in decomposition products, and we were unable to isolate (or separate) samples of **5** and **6** that did not contain starting material (**3**) contaminant.[12] Although the ratio of **5** to **6** varies under the different conditions, **5**, the sterically less encumbered acyl isomer, is always found as the dominant product with the partition ranging from 60:40 to 85:15. As in the case of the insertion reaction of ethylene with **3**, insertion of propylene into the Mo−H bond to give isomeric Mo−propyl moieties is a reversible reaction.[13]

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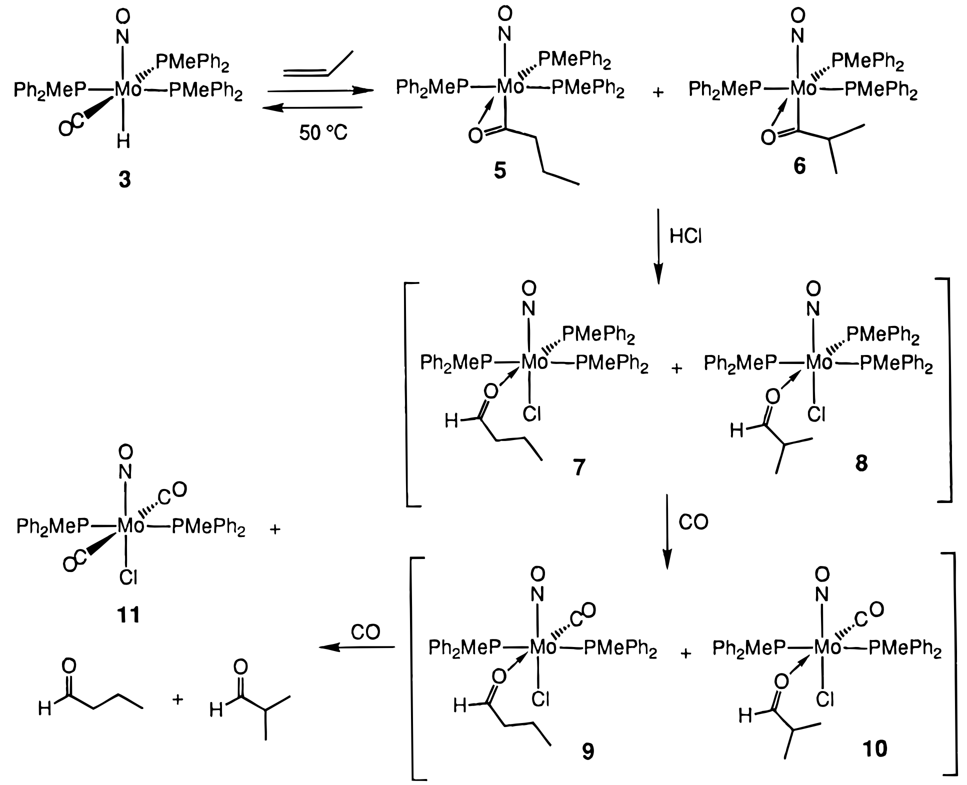
[10] (a) van der Zeijden, A. A. H.; Sontag, C.; Bosch, H. W.; Shklover, V.; Berke, H.; Nanz, D.; von, Philipsborn, W. *Helv. Chim. Acta* **1991**, *74*, 1194. (b) van der Zeijden, A. A. H.; Bosch, H. W.; Berke, H. *Organometallics* **1992**, *11*, 563. (c) van der Zeijden, A. A. H.; Bosch, H. W.; Berke, H. *Organometallics* **1992**, *11*, 2051. (d) van der Zeijden, A. A. H.; Veghini, D.; Berke, H. *Inorg. Chem.* **1992**, *31*, 5106.

[11] Because of the relatively high pressure of ethylene (~3 atm) required to effect the coupling reaction, and because the reaction between **3** and C$_2$H$_4$ is not a particularly clean one (giving ~60% of **4** along with many uncharacterized minor products including free PMePh$_2$), we cannot easily test for the predicted phosphine inhibition of this reaction. As pointed out by a reviewer, an alternative mechanism involving *reversible* H$^\bullet$ transfer to give a MoCH$_2$CH$_3$ intermediate (which would not require phosphine dissociation) cannot therefore be excluded, but we have shown that the reaction between **3** and styrene is inhibited by added PMePh$_2$ (vide infra) as expected for a dissociative preequilibrium.

[12] The equilibrium $\mathbf{5} + \mathbf{6} \rightleftharpoons \mathbf{3} + C_3H_6$ can be demonstrated by dissolving an isolated sample containing **3**, **5**, and **6** in C$_6$D$_6$ and monitoring the solution by ^{1}H NMR spectroscopy. Moreover, storing samples **5** and **6** for prolonged time in the glovebox results in their slow conversion to **3**, even in the solid state.

[13] In its reaction with C$_3$H$_6$, the ^{2}H label of **3**-*d* is diluted by scrambling into the seven proton positions of the acyl ligand, as well as into the reagent propylene. However, upon "quenching" as shown in Scheme 5 to give the free aldehydes, some deuterium incorporation into both methylene groups of butyraldehyde was indicated by ^{2}H NMR spectroscopy.

Scheme 5



Propylene reacts with [^{13}C]-**3** to give [^{13}C]-**5** and [^{13}C]-**6** in which the acyl carbons are isotopically enriched. These labeled carbons appear as pseudoquartets in the ^{13}C{^{1}H} NMR spectrum at δ 307 ($^{2}J_{CP}$ = 13.4 Hz) and 309 ($^{2}J_{CP}$ = 13.4 Hz) for complexes [^{13}C]-**5** and [^{13}C]-**6**, respectively, indicating that the acyl carbon is cis to three phosphorus atoms and trans to the nitrosyl ligand in each complex. The ^{31}P{^{1}H} NMR data are also consistent with this geometry. Since the geometry of the kinetic intermediate of propyl migratory insertion to the coordinated CO (which lies in the meridional plane containing the three PMePh$_2$ ligands) would still have the acyl carbon in the meridional plane (and cis to the NO ligand), the observed geometries of **5** and **6** must be the result of rearrangement subsequent to the migratory insertion step and are therefore thermodynamically favored ones.

The major difference in the observed reactivities of ethylene and propylene with **3** is that PMePh$_2$ successfully competes with propylene for the vacant coordination site of the initial acyl intermediate formed by CO insertion, whereas ethylene (perhaps for steric reasons) competes effectively with PMePh$_2$ and subsequently inserts into the corresponding acyl to give the C-5 ketonyl ligand of **4** (shown in Scheme 6).[14]

Complexes **5** and **6** are converted to two new aldehyde complexes, *mer*-MoCl(η^1-O=CHCH$_2$CH$_2$CH$_3$)(NO)(PMePh$_2$)$_3$ (**7**) and *mer*-MoCl{η^1-O=CHCH(CH$_3$)$_2$}(NO)(PMePh$_2$)$_3$ (**8**), respectively, by the treatment of the reaction mixture with anhydrous HCl (Scheme 5). The aldehyde proton resonances for **7** (δ 12.8) and **8** (δ 12.6) appear at lower field than those in organic aldehydes or related cationic aldehyde complexes of [W(CO)$_3$(NO)(PMe$_3$)(L)$^+$] (L = acrolein, crotonaldehyde) (usually from δ 9 to 10).[15] A *mer*-phosphine arrangement is indicated by the ^{31}P{^{1}H} NMR data.

Treatment of the mixture of **7** and **8** with CO (~2.5 atm) results in their ultimate conversion to Mo(Cl)(CO)$_2$(NO)(PMePh$_2$)$_2$ (**11**), butyraldehyde, and isobutyraldehyde (Scheme 5), which were characterized by spectroscopic comparison with authentic samples. When the reaction with CO was monitored by ^{31}P{^{1}H} and ^{1}H NMR spectroscopies, the bis(phosphine) aldehyde intermediates *trans*-MoCl(η^1-O=CHCH$_2$CH$_2$CH$_3$)(CO)(NO)(PMePh$_2$)$_2$ (**9**) and *trans*-MoCl{η^1-O=CHCH(CH$_3$)$_2$}(CO)(NO)(PMePh$_2$)$_2$ (**10**), formed by the substitution of a phosphine ligand by CO, were observed (for **9**, C*H*O = δ 14.45; for **10**, C*H*O = δ 14.35) along with free PMePh$_2$.

Reaction of 3 with Styrene. An intriguing reaction was discovered while the interaction of **3** with styrene was being studied. As shown in Scheme 7, styrene reacts slowly (5 d, 50 °C) with benzene solutions of **3** to give **1** equiv of ethylbenzene and an emerald-green Mo complex (**12**, 83% yield) that has incorporated 1 equiv of the olefin. The unexpected product, *trans*-Mo[PMePh{C$_6$H$_4$C(O)CH$_2$CH$_2$C$_6$H$_4$}](NO)(PMePh$_2$)$_2$ (**12**), was isolated and characterized by elemental analysis, by IR, ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopic techniques, and by spectroscopic comparison with the

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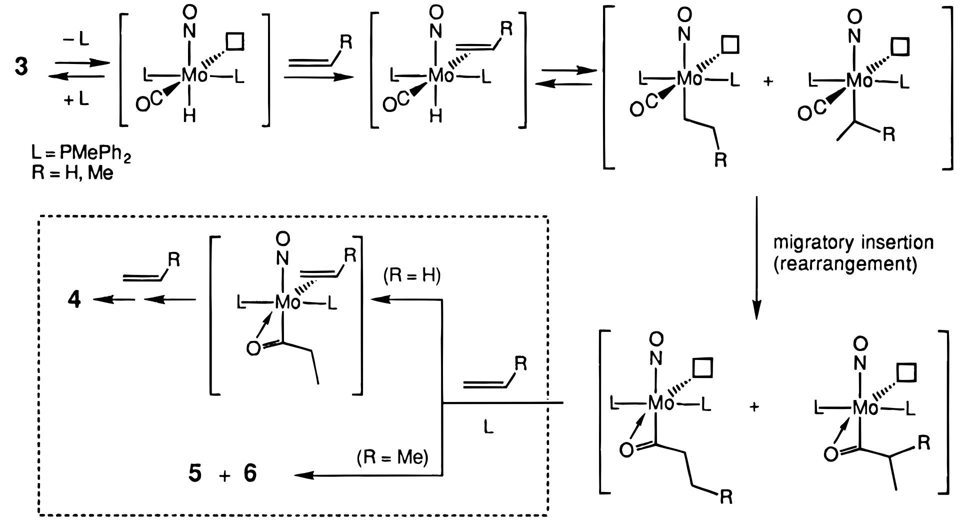
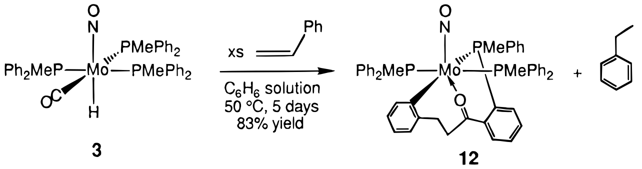
[14] It is well appreciated that, in CO/olefin alternating oligomerization reactions, the barriers to alkyl/CO migratory insertions are much lower than that for olefin insertions into a M−acyl bonds (with the barrier to acyl/CO migratory insertion higher still). These relative activation barriers are crucial for formation of perfectly alternating oligomers and polymers.[1,3] For steric reasons, the barrier for propylene insertion into a metal−acyl bond will be greater than for the corresponding insertion of ethylene, contributing to the observed reactivity differences.

[15] (a) Bonnesen, P. V.; Puckett, C. L.; Honeychuck, R. V.; Hersh, W. H. *J. Am. Chem. Soc.* **1989**, *111*, 6070. (b) Honeychuck, R. V.; Bonnesen, P. V.; Farahi, J.; Hersh, W. H. *J. Org. Chem.* **1987**, *52*, 5293.

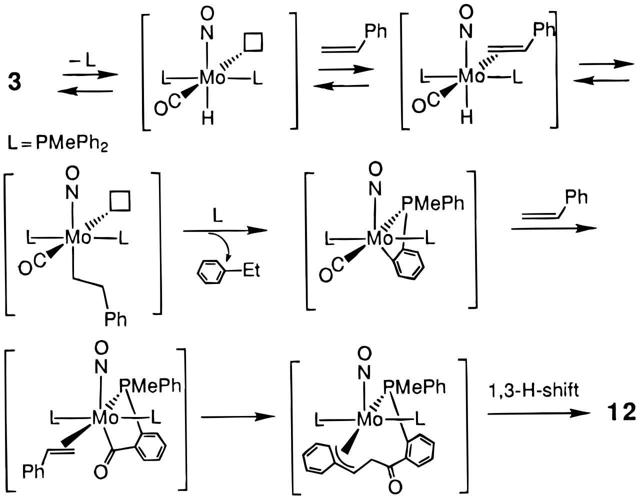
Scheme 6



Scheme 7



Scheme 8



^{13}C-labeled complex *trans*-Mo[PMePh{C$_6$H$_4$^{13}C(O)CH$_2$CH$_2$C$_6$H$_4$}](NO)(PMePh$_2$)$_2$ ([^{13}C]-**12**), which was prepared from [^{13}C]-**3** and styrene.

The IR spectrum of **12** exhibits a strong nitrosyl stretching vibration at 1514 cm^{-1} and a medium-intensity carbonyl stretch at 1464 cm^{-1} (for [^{13}C]-**12**, ν(NO) = 1514 and ν(CO) = 1447 cm^{-1}). The unusually low ν(CO) is probably a consequence of coordination of the ketone to the metal and its conjugation with the aryl group.

The ^{1}H NMR spectrum of **12**, in addition to the typical resonances for the aryl and phosphine methyl protons, exhibits resonances at δ 3.09 and 2.77 for the CH$_2$CH$_2$ protons. Because of the conformational rigidity imposed by the chelating ligand, these protons are diastereotopic and the resonances appear as the expected (symmetrical) multiplets. The ^{13}C{^{1}H} NMR spectrum of [^{13}C]-**12** reveals that the carbonyl carbon is coupled to only one phosphorus atom (δ 190, d, $^3J_{CP}$ = 10 Hz), and a typical $^1J_{CC}$ (42 Hz) is observed for the methylene carbon attached to the labeled carbonyl.[16] The ^{31}P{^{1}H} NMR spectrum reveals an AB$_2$ spin system (δ 10.7 (t); δ 18.6 (d); $^2J_{PP}$ = 24 Hz) indicating that three phosphorus atoms are in a meridional orientation; in [^{13}C]-**12**, only the resonance at δ 10.7 is split by the labeled carbon atom, producing a triplet of doublets with an observed $^3J_{PC}$ = 10 Hz.

A reasonable mechanism accounting for the high-yield formation of **12** is illustrated in Scheme 8. In experiments monitored by ^{1}H NMR spectroscopy, it was found that addition of PMePh$_2$ (0.35 M) to solutions (C$_6$D$_6$, 50 °C, 5 d) of **3** (0.04 M) and styrene (0.22 M) results in effective inhibition of the formation of **12**, evidence that, as in the cases of the other olefins studied, the initial reaction sequence probably involves PMePh$_2$ dissociation, olefin (styrene) coordination, and hydride insertion to give an alkyl ligand.[17] When the reaction is carried out using styrene-*d*$_8$, deuterium scrambles into the hydrido position of **3** during the course of the reaction to give **3**-*d*, demonstrating that the steps in the reaction sequence that give rise to the alkyl intermediate are all reversible, as indicated in Scheme 8. Orthometalation of a phenyl group of a phosphine ligand followed by reductive elimination accounts for the quantitative formation of ethylbenzene, and migratory insertion of the metalated aryl group to the carbonyl ligand gives rise to a benzoyl moiety. Strong precedent for the orthometalation, reductive elimination, “CO insertion” sequence is provided by the work of Kaesz, where it was found that thermolysis of (CH$_3$)Re(CO)$_4$ in the presence of PPh$_3$ and CO gives methane and the metallaacylphosphine (CO)$_4$Re(PPh$_2$C$_6$H$_4$C=O), formed from CO insertion into an intermediate orthometalated complex.[18] In the final C−C bond-forming step, styrene

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[16] Mann, B. E.; Taylor, B. F. *^{13}C NMR Data for Organometallic Compounds*; Academic Press: New York, 1981.

[17] For mechanistic studies regarding styrene insertions into early- and late-transition-metal M−H bonds, see: (a) Halpern, J.; Okamoto, T. *Inorg. Chim. Acta* **1984**, *89*, L53. (b) Doherty, N. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1984**, *107*, 2670. (c) Burger, B. J.; Santarsiero, B. D.; Trimmer, M. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 3134.

insertion gives the complete functionalized backbone of the new phosphine ligand. Such a complex could be stabilized by ligand coordination in a π-benzylic (η^3) fashion as shown,[19] from which a 1,3-hydride shift gives the ultimate product, **12**.

Conclusions

While developing and studying the chemistry of the d^6 molybdenum nitrosyl system Mo(NO)(X)(L_4), we observed that the reaction of diphenylmethylphosphine (instead of triphenylphosphine or tricyclohexylphosphine) with *trans*-Mo($ClAlCl_3$)(NO)$(CO)_4$ (**1**) results in the formation of a tris(diphenylmethyl)phosphine molybdenum complex *mer*-Mo(Cl)(CO)(NO)$(PMePh_2)_3$ (**2**) instead of the anticipated bis(phosphine) dicarbonyl derivative (*cf.*, *trans*,*trans*-Mo(Cl)$(CO)_2$(NO)$(PPh_3)_2$ and *trans*,*trans*-Mo(Cl)$(CO)_2$(NO)$(PCy_3)_2$).[4d] Subsequent reduction of **2** with $LiBH_4$ gives the molybdenum hydride *mer*-Mo(H)(CO)(NO)$(PMePh_2)_3$ (**3**), the reactivity of which differs substantially from related bis(phosphine) derivatives by virtue of its labile (third) phosphine ligand. In the current study, we have shown that the olefins ethylene, propylene, and styrene react with **3** to give interesting stoichiometric coupling products involving hydride, CO, olefin, and phosphine ligands. Whereas the reactions of activated alkynes, aldehydes, and ketones with *trans*-*trans*-W(H)$(CO)_2$(NO)$(PMe_3)_2$ apparently proceed by direct insertion into the W−H bond without prior coordination of the substrate to the metal,[10] our results indicate that simple olefins must first coordinate to the Mo center before (reversible) hydride insertion occurs, with predissociation of a labile $PMePh_2$ ligand of **3** providing the requisite site of coordinative unsaturation.

Experimental Section

General Considerations. Reactions were carried out using standard high-vacuum and Schlenk techniques using dry, air-free solvents. NMR spectra were recorded in C_6D_6 or $CDCl_3$ solutions at ambient temperature. ^1H NMR spectra were recorded at 500 MHz using a General Electric Ω-500 spectrometer; $^{13}C\{^1H\}$ NMR spectra were recorded using a GE Ω-500 or Ω-300 spectrometer operating at 125.00 or 75.5 MHz, respectively. $^{31}P\{^1H\}$ NMR spectra were recorded using a GE Ω-500 operating at 202.5 MHz. Infrared spectra were recorded on a Nicolet 20SXB spectrometer in a Fluorolube mull with CaF_2 plates. Elemental analyses were performed by Desert Analytics (Tucson, AZ). *trans*-Mo($ClAlCl_3$)(NO)$(CO)_4$ (**1**) was prepared according to the literature procedure from $Mo(CO)_6$ and [NO][$AlCl_4$].[6]

Preparation of *mer*-Mo(Cl)(CO)(NO)$(PMePh_2)_3$ (2). A 250 mL three-necked flask charged with 5.0 g (12.29 mmol) of **1** was connected to a needle-valve adapter. The flask was evacuated and placed under an argon atmosphere, and then 80 mL of THF was transferred via cannula. $PMePh_2$ (9.4 mL, 50.4 mmol) was added via syringe to the stirred solution. The mixture was warmed to near reflux for 1 h, then the flask was opened to the atmosphere, and the solution was filtered. The orange-brown filtrate was reduced to 30 mL, during which time the yellow precipitate began to form. Addition of 100 mL of absolute EtOH completed the precipitation, and the complex was collected on a frit. The product was washed with EtOH and then petroleum ether to give 6.80 g (70%) of **2**. Anal. Calcd for $C_{40}H_{39}NO_2P_3ClMo$: C, 60.81; H, 4.98; N, 1.77. Found: C, 60.37; H, 5.13; N, 1.71. ^1H NMR ($CDCl_3$): δ 7.57−7.45 (m, 3 H, P*Ph*), 7.40−7.37 (m, 3 H, P*Ph*), 7.35−7.28 (m, 8 H, P*Ph*), 7.22−7.18 (m, 12 H, P*Ph*), 7.13−6.99 (m, 4 H, P*Ph*), 1.81 (t, 6 H, PCH_3, $^2J_{PH} = 3.0$ Hz), 1.58 (d, 3 H, PCH_3, $^2J_{PH} = 6.0$ Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 13.2 (d, *P*$MePh_2$(trans), $^2J_{PP} = 24.4$ Hz), 2.4 (t, *P*$MePh_2$(cis), $^2J_{PP} = 24.4$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 227.2 (dt, *C*O, $^2J_{CPcis} = 9.8$ Hz, $^2J_{CPtrans} = 51.3$ Hz). IR: ν(CO) = 1941 (vs); ν(NO) = 1577 (s) cm^{-1}.

Preparation of *mer*-Mo(Cl)(^{13}CO)(NO)$(PMePh_2)_3$ ([^{13}C]-2). To a 0.79 g sample of **1** in a 100 mL Schlenk flask fitted with rubber septum was added 40 mL of THF via cannula, resulting in observable gas evolution. The yellow-orange solution was then cannula transferred into a Fisher-Porter pressure bottle. The solution was degassed, charged with 35 psi of ^{13}CO (99% isotopic enrichment), stirred at room temperature for 1 h, and then heated at 60 °C for 30 min. Upon cooling to ambient temperature, the pressure was vented, the resulting solution was transferred into a 100 mL two-necked flask via cannula, and 1.48 mL of $PMePh_2$ was added via syringe. [^{13}C]-**2** was isolated by the procedure described above for the unlabeled derivative to give 0.99 g. ^{13}C enrichment (75%) was determined from the $^{31}P\{^1H\}$ NMR spectrum, and this sample was used in subsequent (vide infra) labeling experiments. IR: ν(^{13}CO) = 1899 (vs); ν(NO) = 1577 (s) cm^{-1}.

Preparation of *mer*-Mo(H)(CO)(NO)$(PMePh_2)_3$ (3). A 100 mL two-necked flask was charged with 3.0 g (3.80 mmol) of **2** and 0.33 g (15.19 mmol) of $LiBH_4$, and then THF (50 mL) was vacuum transferred onto the solids at −78 °C. Under an argon counterflow, 4.66 mL (25.06 mmol) of $PMePh_2$ was added via syringe to this mixture. The cold bath was removed and the reaction mixture was warmed to 60 °C, during which time the yellow suspension changed to a deep red, homogeneous solution. After heating for 2 h, the flask was removed from the argon manifold, the solution was filtered through a Celite pad in the air, and the volume of the filtrate was reduced to 10 mL. Hot absolute ethanol (40 mL) was added to precipitate the orange solids. The mixture was filtered, and the precipitate was washed with hot EtOH (2 × 30 mL) followed by petroleum ether (15 mL) to give 2.41 g (84.1%) of analytically pure **3**. Anal. Calcd for $C_{40}H_{40}NO_2P_3Mo$: C, 63.58; H, 5.34; N, 1.85. Found: C, 63.71; H, 5.38; N, 1.87. ^1H NMR (C_6D_6): δ 7.72−7.56 (m, 4 H, P*Ph*), 7.70−7.58 (m, 4 H, P*Ph*), 7.40−7.32 (m, 4 H, P*Ph*), 7.01−6.98 (m, 10 H, P*Ph*), 6.95−6.90 (m, 4 H, P*Ph*), 6.88−6.80 (m, 4 H, P*Ph*), 1.79 (t, 6 H, PCH_3, $^2J_{PH} = 2.6$ Hz), 1.44 (d, 3 H, PCH_3, $^2J_{PH} = 5.9$ Hz), −0.44 (qt, 1 H, Mo*H*, $^2J_{PH} = 28.3$ Hz). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 30.7 (d, *P*$MePh_2$(trans), $^2J_{PP} = 24.4$ Hz), 22.0 (t, *P*$MePh_2$(cis), $^2J_{PP} = 24.4$ Hz). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 236.4 (dt, *C*O, $^2J_{CPcis} = 11.0$ Hz, $^2J_{CPtrans} = 34.5$ Hz). IR: ν(CO) = 1911 (vs); ν(MoH) = 1593 (s); ν(NO) = 1582 (s) cm^{-1} (the ν(MoH) and ν(NO) modes are strongly coupled). ***mer*-Mo(H)(^{13}CO)(NO)$(PMePh_2)_3$ (^{13}C]-3)** was analogously prepared from [^{13}C]-**2**. ^1H NMR (C_6D_6): δ −0.44 (dqt, 1 H, Mo*H*, $^2J_{PH} = 28.3$, $^2J_{CH} = 9.8$ Hz). IR: ν(CO) = 1869 (vs); ν(MoH) = 1593 (s); ν(NO) = 1581 (s) cm^{-1}. ***mer*-Mo(^2H)(CO)(NO)$(PMePh_2)_3$ (3-*d*)** was analogously prepared from **2** except that $NaBD_4$ and EtOD were used in the reduction and workup. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 30.8 (dt, *P*$MePh_2$(trans), $^2J_{PP} = 24.4$ Hz, $^2J_{PD} = 4.07$ Hz), 22.1 (tt, *P*$MePh_2$(cis), $^2J_{PP} = 24.4$ Hz, $^2J_{PD} = 4.07$ Hz). IR: ν(CO) = 1911 (vs); ν(NO) = 1559 (s) cm^{-1}.

Preparation of *trans*-$\overline{Mo[CH_2CH_2C(O}$$)CH_2CH_3](C_2H_4)(NO)(PMePh_2)_2$ (4). A 555 mg (0.734 mmol) sample of **3** was placed in a Fischer-Porter pressure bottle along with 15 mL of toluene and 50 psi of C_2H_4. The solution was stirred and heated at 50 °C for 48 h, and then the solution was cooled to room temperature and the pressure was vented. The dark brown solution was transferred via cannula into a flask which

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(18) For an analogous example of migratory insertion of an orthometalated arylphosphine to a CO ligand, see: Kaesz, H. D.; McKinney, R. J. *J. Am. Chem. Soc.* **1975**, *97*, 3066.

(19) For insertion reactions of substituted styrene substrates to give a family of η^3-π-benzyl complexes of Pd, see: Rix, F. C.; Brookhart, M.; White, P. S. *J. Am. Chem. Soc.* **1996**, *118*, 2436.

was then fitted to a frit assembly under argon counterflow. The whole assembly was evacuated, the volume of solution was reduced to 5 mL, and Et_2O (~5 mL) was added to this solution by vacuum transfer. Hexane (10 mL) was then added to cause a sticky dark brown solid to precipitate. The mixture was filtered, and the filtrate was removed under vacuum.. The residue was extracted with a minimum amount of Et_2O, and then $[(CH_3)_3Si]_2O$ was added to precipitate the yellow-brown solids. The product was filtered and washed with $[(CH_3)_3Si]_2O$. The sticky dark brown solids were subsequently extracted with Et_2O, and the extract was worked up by the same method described above. The process was repeated five times to give an overall yield of 0.28 g (58.5 %) of **4**. Anal. Calcd for $C_{33}H_{39}NO_2P_2Mo$: C, 61.97; H, 6.15; N, 2.19. Found: C, 61.78; H, 6.09; N, 1.89. ^1H NMR (C_6D_6): δ 7.70−7.53 (m, 8 H, *Ph*), 7.19−6.92 (m, 12 H, *Ph*), 2.18−2.16 (dm, 2 H, C_2H_4, $^2J_{HH} = 9$ Hz), 1.99 (t, 6 H, PCH_3, $^2J_{PH} = 2.6$ Hz), 1.95 (t, 2 H, CH_2, $^3J_{HH} = 7.3$ Hz), 1.89−1.86 (dm, 2 H, C_2H_4, $^2J_{HH} = 9$ Hz), 1.54 (hept, 2 H, $MoCH_2$, $^3J_{HH} = 7.3$ Hz, $^3J_{PH} = 14.6$ Hz), 1.02 (q, 2 H, CH_2, $^3J_{HH} = 7.3$ Hz), 0.11 (t, 3 H, CH_3, $^3J_{HH} = 7.3$ Hz). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 35.6 (s). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 234.8 (s, *C*O), 47.0 (s, CH_2), 39.2 (t, C_2H_4, $^2J_{CP} = 3.1$ Hz), 33.2 (s, CH_2), 15.9 (t, CH_2, $^2J_{CP} = 12.1$ Hz), 13.4 (t, PCH_3, $^1J_{CP} = 11.4$ Hz), 6.8 (s, CH_3). IR: ν(CO) = 1640 (m); ν(NO) = 1520 (s) cm^{-1}. ***trans*-$Mo\{CH_2CH_2{}^{13}C(O)CH_2CH_3\}(C_2H_4)(NO)(PMePh_2)_2$ ([^{13}C]-4** was analogously prepared from [^{13}C]-**3**. IR: ν(CO) = 1620; ν(NO) = 1520 cm^{-1}. ***trans*-$Mo\{CH_2CH_2C(O)C_2H_4{}^2H\}(C_2H_4)(NO)(PMePh_2)_2$ (4-*d*)** was analogously prepared as a mixture of isomers (see text) from **3**-*d*.

Reaction of 4 with CO. A 10 mg (0.016 mmol) sample of **4** and 2 mg of $Fe(C_5H_5)_2$ (internal standard) were placed in a 5 mm sealable NMR tube attached to a needle valve adapter, and the assembly was evacuated on a vacuum line. C_6D_6 (~0.5 mL) was transferred into the tube, the contents were frozen at −78 °C, and the tube was charged with 1 atm of CO. The needle valve above the tube was closed, and then the tube was frozen in N_2(l) and subsequently sealed under vacuum (this gave a final pressure of ~2.5 atm of CO). The contents were allowed to thaw at ambient temperature, and the reaction was periodically monitored by using ^1H NMR spectroscopy. Over the period of days, several unidentified intermediates appeared, and after three days, complex **4** had completely disappeared to give 3-pentanone (80%) and C_2H_4 as the major organic products.

Thermolysis of 4. A sealed-tube NMR experiment was carried out as described above for the reaction of **4** with CO except that no carbon monoxide was sealed in the tube with **4**. The NMR tube was heated at 70 °C for ~2 h, during which time **4** had disappeared to give 3-pentanone (95%) and C_2H_4 as the major organic products.

Reaction of 4 with H_2. The reaction was carried out in a fashion analogous to that described above (for CO) except that H_2 was sealed in the tube. After 19 days at ambient temperature, ^1H NMR spectrum indicated that complex **4** had completely decomposed to give a 55% yield of 3-pentanol (by comparison to an authentic sample) and ethane as the major organic products. $^{31}P\{^1H\}$ NMR spectroscopy showed many phosphorus-containing metal products.

Reaction of 4 with HCl. The reaction was monitored in a fashion analogous to that described above (for CO), except that a 5 mm NMR tube with an open-faced screw cap equipped with a Teflon-backed septum was charged with 10 mg (0.016 mmol) of **4** and ~0.5 mL of C_6D_6. Excess concentrated HCl(aq) was injected into the tube via a syringe, and the tube was shaken vigorously. The ^1H NMR spectrum showed that the starting material was completely consumed. Black solids precipitated from solution, and the major organic products, as determined by ^1H NMR, were 3-pentanone (85%, based on **4**) and ethylene.

Preparation of *mer*-$Mo\{\eta^2\text{-}C(O)CH_2CH_2CH_3\}(NO)(PMePh_2)_3$ (5) and *mer*-$Mo\{\eta^2\text{-}C(O)CH(CH_3)_2\}(NO)(PMePh_2)_3$ (6). A 30 mg (0.04 mmol) sample of **3** was placed in a 5 mm sealable NMR tube along with 0.4 mL of C_6D_6. The tube was placed on a vacuum line via a needle valve adapter. The contents were frozen at −196 °C, and then propylene (0.048 mmol) was condensed from a calibrated volume onto the frozen solution. The tube was sealed under vacuum and the contents were allowed to thaw at room temperature. The tube was then heated at 50 °C, and the reaction was periodically monitored by ^1H and ^{31}P NMR spectroscopies over a period of a few days. Complex **3** was slowly consumed, and two new compounds **5** and **6** were formed. After two days, the maximum yield of **5** and **6** was ~60% (**5**:**6** ~ 3:2). Prolonged heating could not drive the reaction to completion and higher pressure of propylene resulted in increased decomposition. The two isomers could not be separated, and attempts to isolate these compounds free from the starting hydride **3** were unsuccessful. For **5**: ^1H NMR (C_6D_6, aryl protons omitted): δ 2.56 (t, 2 H, CH_2, $^3J_{HH} = 7.7$ Hz), 1.42 (m, 2 H, CH_2, $^3J_{HH} = 7.6$ Hz), 0.61 (t, 3 H, CH_3, $^3J_{HH} = 7.5$ Hz), 1.51 (t, 6 H, PCH_3, $^2J_{PH} = 2.6$ Hz), 1.48 (d, 3 H, PCH_3, $^2J_{PH} = 5.1$ Hz). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 26.3 (t, $PMePh_2$(cis), $^2J_{PP} = 12.2$ Hz), 22.1 (d, $PMePh_2$(trans), $^2J_{PP} = 12.2$ Hz). For **6**: ^1H NMR (C_6D_6, aryl protons omitted): δ 2.30 (hept, 1 H, CH, $^3J_{HH} = 7.3$ Hz), 0.95 (d, 6 H, CH_3, $^3J_{HH} = 7.3$ Hz), 1.57 (t, 6 H, PCH_3, $^3J_{HH} = 2.5$ Hz), 1.49 (d, 3 H, PCH_3, $^3J_{HH} = 5.1$ Hz). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 25.8 (t, $PMePh_2$(cis), $^2J_{PP} = 12.2$ Hz), 20.5 (d, $PMePh_2$(trans), $^2J_{PP} = 12.2$ Hz). The ^{13}C-labeled compounds *mer*-$Mo\{\eta^2\text{-}{}^{13}C(O)CH_2CH_2CH_3\}(NO)(PMePh_2)_3$ ([^{13}C]-**5**) and *mer*-$Mo\{\eta^2\text{-}{}^{13}C(O)CH(CH_3)_2\}(NO)(PMePh_2)_3$ ([^{13}C]-**6**) were formed analogously in the reaction of [^{13}C]-**3** with propylene. $^{13}C\{^1H\}$ NMR of the acyl carbons (C_6D_6): [^{13}C]-**5**, δ 307 (qt, $^2J_{CP} = 13.4$ Hz); [^{13}C]-**6**, δ 309 (qt, $^2J_{CP} = 13.4$ Hz) assigned by relative intensities in comparison with ^1H data.

Preparation of *mer*-$MoCl(\eta^1\text{-}O{=}CHCH_2CH_2CH_3)(NO)(PMePh_2)_3$ (7) and *mer*-$MoCl\{\eta^1\text{-}O{=}CHCH(CH_3)_2\}(NO)(PMePh_2)_3$ (8). A C_6D_6 solution of **5** and **6** was placed in a NMR tube with an open-faced screw cap equipped with a Teflon-backed septum. Excess anhydrous HCl was added into the tube via a syringe. The ^1H NMR spectrum indicated that the acyl ligands in **5** and **6** were cleanly transformed by the acid to give the coordinated aldehyde complexes **7** and **8**, respectively. The resonances of the aldehyde protons are at δ 12.80 for **7** and at δ 12.63 for **8**. $^{31}P\{^1H\}$ NMR (C_6D_6) for **7**: δ 13.7 (d, $PMePh_2$(trans), $^2J_{PP} = 19.8$ Hz), δ −0.4 (t, $PMePh_2$(cis), $^2J_{PP} = 19.8$ Hz); for **8**: δ 13.3 (d, $PMePh_2$(trans), $^2J_{PP} = 19.8$ Hz), δ −4.3 (t, $PMePh_2$(cis), $^2J_{PP} = 19.8$ Hz).

Reaction of CO with 7 and 8 To Give Butyraldehyde and Isobutyraldehyde. A C_6D_6 solution of **7** and **8** was placed in a sealable NMR tube attached to a needle-valve adapter. The contents were frozen at −78 °C, and the assembly was evacuated. The tube was charged with 1 atm of CO, the needle valve above the tube was closed, and the tube was frozen in N_2(l), and subsequently sealed under vacuum to give ~2.5 atm of CO upon thawing. When the contents were thawed at room temperature, the NMR spectra were acquired. The $^{31}P\{^1H\}$ NMR spectrum showed that the two AB_2 spin patterns of **7** and **8** gradually disappeared in favor of three singlets that grew in at δ 17.5 (complex **9**), 15.5 (complex **10**), and −26 (free $PMePh_2$). The ^1H NMR showed that two new aldehyde protons appeared at δ 14.45 and 14.35 for **9** and **10**, respectively. The spectroscopic data indicated that one $PMePh_2$ ligand was displaced by the CO ligand in each complex. Over a 24 h period, a second CO displaced the aldehyde ligands in complexes **9** and **10** to give **11**, butyraldehyde, and isobutyraldehyde, identified by comparison to authentic samples.

Preparation of *trans*-$Mo[PMePh\{C_6H_4C(O)CH_2CH_2C_6H_4\}](NO)(PMePh_2)_2$ (12). A 0.50 g (0.662 mmol) sample of **3** and 35 mL of benzene were placed in a 100 mL Schlenk tube having a Teflon valve. Excess styrene (6 equiv) was vacuum transferred into the reaction tube, and the reaction mixture was heated at 50 °C for five days. During this time, the color of the solution changed from orange to dark green. After five days, the solution was cannula transferred into a 100 mL two-necked flask which was attached to frit assembly. The solution was filtered and concentrated to 10 mL, and 5 mL of diethyl ether and 20 mL of pentane were added to give an emerald-green precipitate. The mixture was filtered and solids were washed with 5 mL of pentane to give 0.47 g (83% yield) of emerald-green **12**. Anal. Calcd for $C_{48}H_{46}NO_2P_3Mo$: C, 67.21; H, 5.41, N, 1.63. Found: C, 67.94; H, 5.44, N, 1.63. ^1H NMR (C_6D_6): δ 7.51−7.32 (m, 15 H, *Ph*), 7.18−7.09 (m, 4 H, *Ph*), 7.02−6.90 (m, 9 H, *Ph*), 6.85−6.78 (m, 4 H, *Ph*), 6.50 (d, 1 H, *Ph*), 3.09 (m, 2 H, C*H*$_2$), 2.77 (m, 2 H, C*H*$_2$), 1.53 (t, 6 H, PC*H*$_3$, $^2J_{PH} = 2.9$ Hz), 1.47 (d, 3 H, PC*H*$_3$, $^2J_{PH} = 4.8$ Hz). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 18.6 (d, *P*MePh$_2$, $^2J_{PP} = 24.4$ Hz), 10.7 (t, *P*MePh, $^2J_{PP} = 24.4$ Hz). $^{13}C\{^1H\}$ NMR (C_6D_6, aryl carbons omitted): δ 189.9 (d, *C*O, $^3J_{CP} = 9.8$ Hz), 40.0 (s, C(O)*C*H$_2$), 33.9 (s, C_6H_4*C*H$_2$), 14.9 (d, P*C*H$_3$, $^1J_{CP} = 19.5$ Hz), 10.6 (t, P*C*H$_3$, $^1J_{CP} = 9.8$ Hz). IR: ν(NO) = 1514 (s); ν(CO) = 1464 (m) cm^{-1}.

***trans*-Mo[PMePh$\{C_6H_4{}^{13}C(O)CH_2CH_2C_6H_4\}$](NO)(PMePh$_2$)$_2$ ([^{13}C]-12)** was analogously prepared from styrene and [^{13}C]-**3**. $^{31}P\{^1H\}$ NMR (C_6D_6): δ 18.6 (d, *P*MePh$_2$, $^2J_{PP} = 24.4$ Hz), 10.7 (td, *P*MePh-, $^2J_{PP} = 24.4$ Hz, $^3J_{CP} = 10$ Hz). $^{13}C\{^1H\}$ NMR (C_6D_6, aryl carbons omitted): δ 189.9 (d, *C*O, $^3J_{CP} = 9.8$ Hz), 40.0 (d, C(O)*C*H$_2$, $^1J_{CC} = 41.5$ Hz), 33.9 (s, *C*H$_2$), 14.9 (d, P*C*H$_3$, $^1J_{CP} = 19.5$ Hz), 10.6 (t, P*C*H$_3$, $^1J_{CP} = 9.8$ Hz). IR: ν(NO) = 1514 (s); ν(CO) = 1447 (m) cm^{-1}.

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