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One-Pot Synthesis of Mo^0 Dinitrogen Complexes Possessing Monodentate and Multidentate Phosphine Ligands

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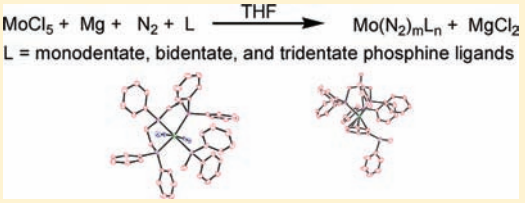
Supporting Information

ABSTRACT: Mo^0 dinitrogen complexes bearing electron-rich mono- and bidentate phosphines can be synthesized in good yields from inexpensive and readily accessible $MoCl_5$ via a one-step mild reduction with Mg metal. *trans*-$[(N_2)_2Mo(PMePh_2)(PPh(CH_2CH_2PPh_2)_2)]$ can also be obtained via this strategy. However, in the presence of tri- and tetradentate ligands that are sterically restrictive, the analogous reduction leads to either (η^6-arene) formation or $[Mo(multidentate\ phosphine)_m]_n$ oligomer complexes that have no dinitrogen ligands. One such η^6-arene complex, where the Mo^0 center is ligated by 1,1,1-tris(diphenylphosphinomethyl)ethane, was isolated and characterized via X-ray crystallography.



INTRODUCTION

Mo^0 complexes with phosphine ligands have attracted a considerable amount of attention in inorganic, organometallic, and catalytic chemistry. Because of the electron-rich nature of the multiphosphine ligand environments, subsets of these compounds, such as those containing dinitrogen or (η^6-C_6H_5) ligands, have been explored as potential catalysts for dinitrogen fixation[1,2] and other catalytic processes.[3−8] However, these complexes were often synthesized using multistep sequences that involve the preparation of intermediate $Mo^{II/III/IV}$ complexes from high oxidation state $Mo^{V/VI}$ salts followed by further reduction to Mo^0 (see Scheme 1 and further discussion below). A variety of reducing agents has been employed in these syntheses but with significant drawbacks such as high flammability (Na,[9,10] $AlEt_3$,[11] $Al(^iPr)_3$[11]), toxicity (Na/Hg[12−22]), long reaction times ($AlEt_3$, $Al(^iPr)_3$),[11] and/or low yields ($AlEt_3$, $Al(^iPr)_3$).[11] Herein, we report a study on how Mo^0 dinitrogen complexes possessing a wide range of monodentate to multidentate phosphine ligands can be prepared directly from $MoCl_5$ using Mg^0 as a safe and mild reducing agent. While this process is generally efficient for electron-rich mono- and bidentate phosphines, extending it to tri- and tetradentate ligands requires a careful consideration of the spatial arrangement of the chelating motif. Multidentate ligands with sterically restricted chelating motifs often lead to either (η^6-C_6H_5) complexes that lack dinitrogen ligands[6] or unidentifiable precipitates. The former observation can be explained by the labile nature of the Mo^0−N_2 moiety, which cannot compete with the thermodynamically favored Mo-arene bond-formation. The precipitates in the latter case are most likely $[Mo(multidentate\ phosphine)_m]_n$ oligomers where the multidentate phosphines are bridging across multiple metal centers.

RESULTS AND DISCUSSION

The majority of reported synthetic routes to phosphine-containing Mo^0 dinitrogen complexes are labor-intensive, multistep procedures. Typical procedures start with the preparation of a commercially unavailable precursor, such as Mo^{III}(acetylacetonate)$_3$,[11] $MoCl_4(PR_3)_2$,[17,23] $MoCl_3(THF)_3$ (THF = tetrahydrofuran),[9,10,12,14,15,17,19] $MoCl_2(dmpe)_2$ (dmpe = 1,2-bis(dimethylphosphino)ethane),[20] $MoCl_3$(triphos I) (triphos I = bis(diphenylphosphinoethyl)-phenylphosphine),[14,18,21,22,24−26] and $MoCl_3$(trident) (trident = $(Ph_2PCH_2CH_2)_2O$, $(Ph_2PCH_2CH_2)_2NR$, $(Ph_2PCH_2CH_2CH_2)_2S$, and $(Ph_2PCH_2CH_2CH_2)_2PPh$))[13] followed by reduction to the desired phosphine-containing Mo^0 species. Thus, direct reductive syntheses of Mo^0 dinitrogen compounds from $MoCl_5$,[27] one of the most affordable and commercially available Mo sources, would be highly attractive. However, to date there exist only a few one-pot syntheses[15,28−30] that utilize $MoCl_5$ as the starting material, and most of these are limited to specific mono and bidentate ligands (Scheme 2). We hypothesize that such a strategy can be generalized to a wider range of phosphine ligands in the presence of Mg metal as a safe reductant.[31]

Mo^0 Dinitrogen Complexes of the Type $Mo(N_2)_2(L)_4$ (L = Monodentate Phosphine Ligands). Mo^0 bis(dinitrogen) complexes of $PMePh_2$ and PMe_3 ligands have been isolated as pure *trans*-$Mo(N_2)_2(PMePh_2)_4$[12,14,15,17,23,28] and *cis*-$Mo(N_2)_2(PMe_3)_4$, respectively.[9] On the other hand, *cis*-$Mo(N_2)_2(PMePh_2)_4$ and *trans*-$Mo(N_2)_2(PMe_3)_4$ are unknown, the former presumably because of steric issues and the latter presumably because of electronic reasons.[12] As such, we chose *trans*-$Mo(N_2)_2(PMePh_2)_4$ and *cis*-$Mo(N_2)_2(PMePh_2)_4$ to test

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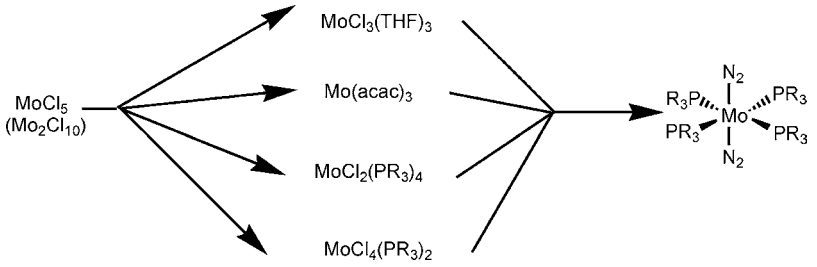
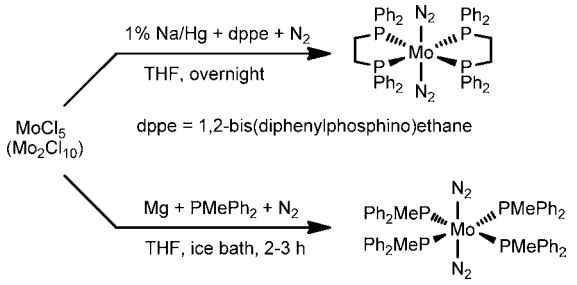
Scheme 1. Traditional Multi-Steps Synthesis of Mo^0 Dinitrogen Complexes with Phosphine Ligands



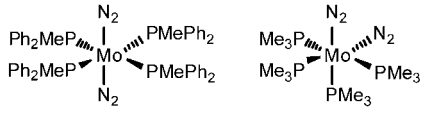
Scheme 2. Previously Reported One-Pot Syntheses of Mo^0 Complexes with Mono and Bidentate Phosphine Ligands[15,28,29]



the feasibility of our proposed one-pot Mg^0-reduction of $MoCl_5$ (eq 1).

$$2\ MoCl_5 + 5\ Mg + 4\ N_2 + 8\ L \xrightarrow{THF} 2\ Mo(N_2)_2L_4 + 5\ MgCl_2 \quad (1)$$

L = $PMePh_2$(**1**), PMe_3 (**2**)



1 **2**

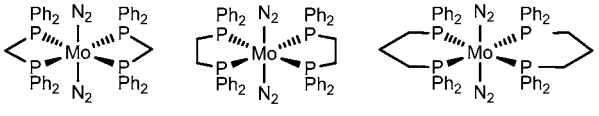
cis-$Mo(N_2)_2(PMe_3)_4$ has been previously synthesized from $Mo(THF)_3Cl_3$[32] and $Mo(PMe_3)_3Cl_3$.[9] However, Na was employed as the reducing agent, and the described experimental protocols were quite tedious. In our hands, treatment of $MoCl_5$ with an excess amount of magnesium in the presence of 4.4 equiv of PMe_3 in THF under a dinitrogen atmosphere for 17 h gave *cis*-$Mo(N_2)_2(PMe_3)_4$ (**1**) in 58% in one step. Comparing to the overall 35% yield previously obtained from $MoCl_4(THF)_2$ in three steps,[9,32] this is a good improvement.

trans-$Mo(N_2)_2(PMePh_2)_4$ (**2**) has been made by various routes,[12,14,15,17,23,28] one of which involved recrystallizing of the product from a large-scale (8.3 mmol) reduction of $MoCl_5$ by Mg^0.[28] In our hands, this reduction could be carried out on a twenty-times-smaller scale with a 60% yield after recrystallization, suggesting that this one-pot strategy could be easily scaled down in the modern academic laboratory without a great sacrifice in yield. Thus, we also attempted to extend it to prepare $Mo^0(N_2)_2$ complexes with other monodentate tertiary phosphines. As the reported syntheses of $Mo(N_2)_2(PMe_2Ph)_4$ invariably give a mixture of *cis*- and *trans*- isomers,[12,14,17,19,23] and attempts to synthesize $Mo(N_2)_2(PPh_3)_4$ via direct reduction of Mo^{III}(acetylacetonate)$_3$ have only yielded arene dimer,[8,11] we did not pursue these compounds. Unfortunately, our remaining attempts have proven to be unsuccessful. Reduction in the presence of PBu_3 proceeded readily and yielded some *trans*-$Mo(N_2)_2(PBu_3)_4$, as indicated by ^{31}P NMR spectroscopy, along with an unidentified species but no *cis*-product. Attempts to isolate the *trans*-$Mo^0(N_2)_2$ isomer failed to afford any solid, presumably because of the high solubility afforded by the PBu_3 ligand. Reduction in the presence of PCy_3 and $P(OMe)_3$ did not occur readily and left a lot of starting materials, presumably because of the bulky nature of PCy_3 and the insufficient electron-donating properties of $P(OMe)_3$. We note that $Mo(P(OMe)_3)_6$ has been successfully obtained from the direct reduction of $MoCl_5$ but with K or K/Hg as the reducing agent,[33] suggesting the need to balance low ligand nucleophilicity with a good reducing agent in these types of one-pot reductions. These observations indicate that, for a moderate reducing agent such as Mg^0, the one-pot synthesis is best suited to phosphines of the type R_nPPh_{3-n} having moderate steric and nucleophilic properties.

Mo^0 Dinitrogen Complexes of the Type $Mo(N_2)_2(L_2)_2$ (L = Bidentate Phosphine Ligands). Numerous Mo^0 phosphine dinitrogen complexes of the type $Mo(N_2)_2(L_2)_2$ (L_2 = dppe,[11,17] dmpe,[20] dppm (1,2-bis(diphenylphosphino)-methane),[11] dppp (1,2-bis(diphenylphosphino)propane),[11] dippe (1,2-bis(diisopropylphosphino)ethane),[10] diars (*o*-phenylenebis(dimethylarsine),[17] dpae (1,2-bis(diphenylarsino)-ethane),[17] arphos (1-diphenylarsino-2-diphenylphosphino-ethane)[15,17]) have been reported. As mentioned in the introduction, the syntheses of these compounds generally employ commercially unavailable precursors such as $MoCl_4$(dppe),[17] Mo^{III}(acetylacetonate)$_3$,[11] $MoCl_3(THF)_3$,[15,17] or $MoCl_2$(dmpe)$_2$.[20] We were curious to see if the Mg^0-reduction of $MoCl_5$ could be extended to include the bidentate phosphine ligands dppm, dppe, and dppp (eq 2), with increasing ligand bite angles. The $Mo(N_2)_2(L_2)_2$ complexes in this series have all been made from the Na/Hg-reduction of Mo^{III}(acetylacetonate)$_3$;[11] however, these reductions were slow and the yields were negligible (5% for dppm, 13% for dppe, and 4% for dppp).

$$2\ MoCl_5 + 5\ Mg + 4\ N_2 + 4\ L_2 \xrightarrow{THF} 2\ Mo(N_2)_2(L_2)_2 + 5\ MgCl_2 \quad (2)$$

L_2 = dppm(**3**), dppe (**4**), dppp(**5**)



3 **4** **5**

In our hands, treatment of $MoCl_5$ with an excess of magnesium under an N_2 atmosphere and in the presence of 2.1 equiv of dppm or dppe in THF gave *trans*-$Mo(N_2)_2$(dppm)$_2$ (**3**) or *trans*-$Mo(N_2)_2$(dppe)$_2$ (**4**) in good to moderate yields (43% for dppm or 29% for dppe) after 17 h at

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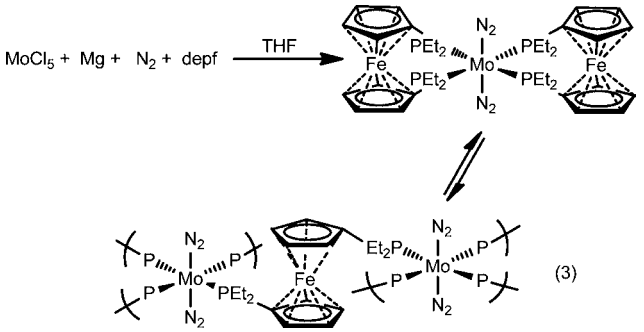
room temperature. However, the analogous synthesis of *trans*-$Mo(N_2)_2(dppp)_2$ (**5**) required an additional period of overnight heating at 80 °C to afford the product in 9% isolated yield. Without this additional heating, the solution remained light in color throughout the room-temperature period of reaction and only yielded a greenish-yellow precipitate, which we suspected to be a mixture of $[Mo(N_2)_2(dppp)_2]_n$ and $[Mo(dppp)_m]_n$[34] oligomers. The heating caused the reaction solution, as well as the surface of the precipitate, to become progressively more orange-red in color, presumably by breaking apart the aforementioned oligomers and forming the desired monomeric product. Unfortunately, heating longer (24 h) did not improve the yield, presumably because of the low thermal sensitivity of **5**. Curiously, heating the reaction immediately from the beginning did not lead to the darkening of the reaction solution and gave no observable products. This suggests a delicate balance between the reduction of Mo^V versus the formation of the N_2-containing Mo^0 product **5**, which should be formed most easily from the $[Mo(N_2)_2(dppp)_2]_n$ oligomer. However, this oligomer is more thermally sensitive than $[Mo(dppp)_m]_n$ and does not form in large amounts if the reaction is heated too early.

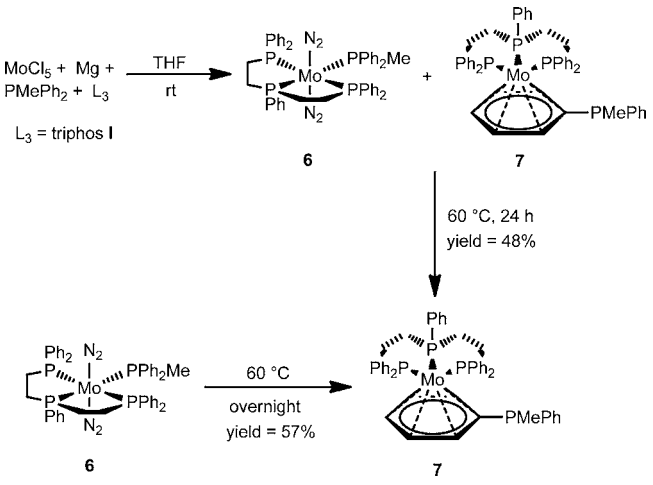
While the one-pot Mg^0-reduction-of-$MoCl_5$ strategy can clearly be extended to the synthesis of $Mo(N_2)_2$(bidentate phosphine)$_2$ complexes, the yields of the isolable monomeric products (dppm > dppe > dppp) are inversely proportional to the ligand bite angle (dppm < dppe < dppp).[16,29,35,36] This observation can be explained by the increased formation of insoluble oligomeric byproducts as the bite angle of the bidentate phosphine increases. When the chelate bite angle becomes as large as that in dppp, it makes sense that phosphine-bridging oligomers such as $[Mo(N_2)_2(dppp)_2]_n$ and $[Mo(dppp)_m]_n$, where the bidentate phosphines span more than one metal center, can become major kinetic side products. Thus, additional thermal treatment is needed to break such oligomers up into the desired monomeric products, as the synthetic conditions that we discussed (see preceding paragraph) seem to indicate. Unfortunately, the insolubility of these oligomers prevented us from obtaining spectroscopic evidence for their formation. We note that the competition by oligomer formation (eq 3) may explain why the reported one-step synthesis of $Mo(N_2)_2(depf)_2$ (depf = 1,1′-bis(diethylphosphino)ferrocene) from $MoCl_5$ with Mg^0 as the reducing agent only resulted in low isolated yield (13%).[29]



Mo^0 Complexes of the Type $Mo(N_2)_x(L_3)L$ and $Mo(\eta^6$-Arene)$(L_3)L$ (L_3 = Tridentate Phosphine Ligands). To date, many Mo^0 dinitrogen complexes bearing tridentate phosphine ligands have been reported. These include complexes of triphos **I** and monodentate phosphines, such as $Mo(N_2)_x$(triphos **I**)$(PR_3)_{(3-x)}$ (PR_3 = $P(OMe)_3$,[24] PMe_3,[24] PMe_2Ph,[18,25,26] PPh_3,[14,25] $PMePh_2$,[14,25]); complexes of triphos **I** and bidentate phosphines such as $Mo(N_2)$(triphos)(L_2) (L_2 = dppe,[13,21] diars,[18] dppm,[13,22] dmpm (1,2-bis(dimethylphosphino)methane),[18] depe (1,2-bis(diethylphosphino)ethane),[21] dppp[21]); and other tridentate phosphine complexes of the type $Mo(N_2)_2(L_3)(PR_3)$[13] (L_3 = $(Ph_2PCH_2CH_2)_2O$, $(Ph_2PCH_2CH_2)_2NR$, $(Ph_2PCH_2CH_2CH_2)_2S$, and $(Ph_2PCH_2CH_2CH_2)_2PPh$). As in the cases for $Mo(N_2)_2(L)_4$ and $Mo(N_2)_2(L_2)_2$ discussed above, most of these syntheses start with presynthesized Mo^{III} compounds such as $MoCl_3$(triphos)[14,18,25,26] or $MoCl_3(L_3)$[13] where the L_3 chelating ligand has been precoordinated. Ligand exchange between triphos **I** and monodentate complexes such as $Mo(N_2)_2(PMePh_2)_4$ was observed to be quite slow on the NMR scale,[14] presumably because of the slow dissociation of the monodentate ligand; thus, ligand exchange has not been attempted as a viable route to Mo^0 dinitrogen complexes possessing triphos **I**, to the best of our knowledge. In addition, the strong chelating effect of triphos **I** and **II** (1,1,1-tris(diphenylphosphinomethyl)ethane), we speculated that a one-pot direct reduction of $MoCl_5$ in the combined presence of $PMePh_2$ and a tridentate ligand would afford Mo^0 complexes of the type $Mo(N_2)_x(L_3)(PMePh_2)_{(3-x)}$. Given the high preference of triphos **II** to act as a tripodal ligand, disfavoring any equatorial arrangement of the phosphine moieties,[37] would favor *cis*-$Mo(N_2)_x$(triphos **II**)$(PMePh_2)_{(3-x)}$.

Under a dinitrogen atmosphere, treatment of $MoCl_5$ with an excess amount of magnesium in the presence of 1 equiv of triphos **I** and a slight excess of $PMePh_2$ in THF for 17 h gave a soluble reaction mixture that primarily contained unreacted $PMePh_2$, *trans*-$Mo(N_2)_2$(triphos **I**)$(PMePh_2)$ (**6**), and (η^6-C_6H_5PMePh)Mo(triphos **I**) (**7**) (top reaction in Scheme 3), as

Scheme 3. One-Pot Synthesis of Mo^0 Complexes 6 and 7 with a Tridentate Phosphine Ligand



analyzed by ^1H and ^{31}P NMR spectroscopies (see Supporting Information). In contrast to the aforementioned synthesis of *trans*-$Mo(N_2)_2(dppp)_2$, solid polymeric precipitates were not observed, presumably because of the preference of triphos **I** to function as a monometallic chelating ligand rather than bridging across multiple metal centers.[38,39] Because of the similar solubilities of **6** and **7**, isolation of **6** by recrystallization from a wide variety of solvent mixtures (toluene/hexane, THF/methanol, toluene/methanol, and THF/hexane) was not successful. Repeated recrystallization from THF/MeOH eventually afforded pure **6** in low isolated yield (4%).

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Suspecting that **6** is unstable during the in situ reduction and can be converted into **7** via N_2 elimination, we repeated the aforementioned synthesis with an additional heating step (at 60 °C for 24 h, Scheme 3). ^{1}H and ^{31}P NMR analyses of the resulting reaction mixture (Supporting Information, Figures S8 and S9) revealed the complete conversion to unreacted $PMePh_2$ and (η^6-C_6H_5PMePh)Mo (triphos **I**) (**7**), which was isolated in 48% yield. Thus, the low yield of **6** at room temperature is a consequence of its facile conversion into **7** via elimination of the N_2 ligand. Additional support for this hypothesis is obtained by heating **6** to 60 °C to produce **7** in 57% yield after 17 h (bottom reaction in Scheme 3).[5] Consistent with our results, η^6-arene complex analogue of **7**, [(η^6-4-$CH_3OC_6H_4$)P(4-$CH_3OC_6H_4$)$_2$]Mo(triphos **I**), has been obtained by Davies and George from the reduction of $MoCl_3$(triphos **I**) under Ar.[6] We note that arene complexes have been observed as side products in the reductive syntheses of Mo^0 dinitrogen complexes bearing monodentate phosphines,[34,40] suggesting that these are low-energy side products in the reduction of molybdenum halides.

The molecular structure of **6** was determined using single-crystal X-ray diffraction (Figure 1). The structure features a six-coordinate molybdenum center in a slightly distorted octahedral geometry, with the two dinitrogen ligands occupying axial positions (N−Mo−N = 175.46(10)°) and the four phosphorus atoms occupying equatorial positions around the Mo center (the sums of the P−Mo−P angles are 359.77°). This structure of **7** was assigned based on a combination of ^{1}H, ^{31}P, and ^{13}C NMR spectroscopic data that are similar to those for analogous complexes prepared via the thermal reaction of triphos with Mo(η^6-arene)$_2$ complexes.[3,4,7] The η^6-C_6H_5 group exhibits five distinct resonances between δ 4.4 to 3.5 in the ^{1}H NMR spectrum and six different signals (δ 85.2, 84.9, 80.5, 77.6, 73.2, and 71.3) in the ^{13}C NMR spectrum (Supporting Information, Figure S7). Additionally, ^{31}P NMR spectrum shows four equal intensity signals: one at δ −26.6 for the noncoordination phosphine moiety in the (η^6-C_6H_5PMePh) ligand and three for the coordinating phosphines from triphos **I** (δ 106.3, 86.3 and 83.5) (Supporting Information, Figure S7).

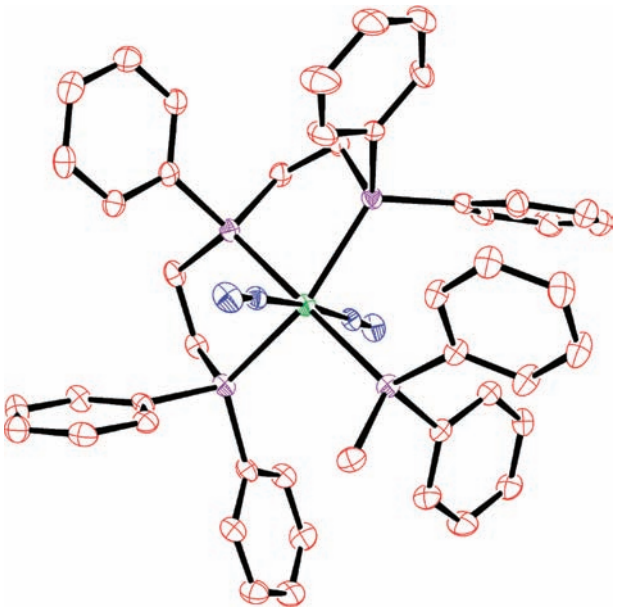
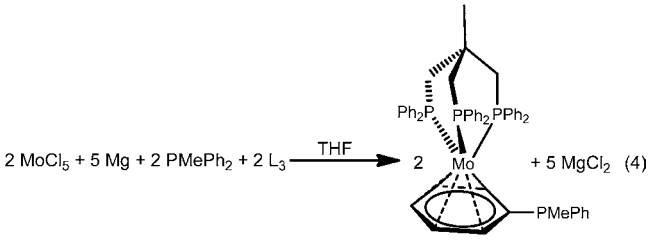


Figure 1. ORTEP depiction of the crystal structure of **6**. Thermal ellipsoids are drawn at 50% probability. Hydrogens are omitted for clarity.



8

The reduction of $MoCl_5$ in the presence of triphos **II**, yielded only (η^6-C_6H_5PMePh)Mo(triphos **II**) (**8**) as a single product in 64% yield (eq 4). The molecular structure of **8** was unambiguously established by X-ray crystallography (Figure 2) where the Mo center in **8** exhibits a distorted octahedral coordination environment, with the σ-bonded triphos **II** ligand on one face and the η^6-bonded phenyl ring on the other face. The structure also features Mo−C(arene) (2.271(3)−2.357(3) Å) distances that are similar to those reported for analogous arene complexes.[40] Numerous modifications of reaction conditions (temperature and reaction time) were attempted to effect the formation of *cis*-Mo(N_2)$_2$(triphos **II**)($PMePh_2$) but were unsuccessful. Attempts to carry out the reduction of $MoCl_5$ in the presence of triphos **II** and a nonaromatic phosphine such as PMe_3 resulted also in unidentifiable precipitates. In retrospect, these results are not surprising given the strong η^6-arene bond to Mo^0 and the facially restricted chelating environment of triphos **II**.

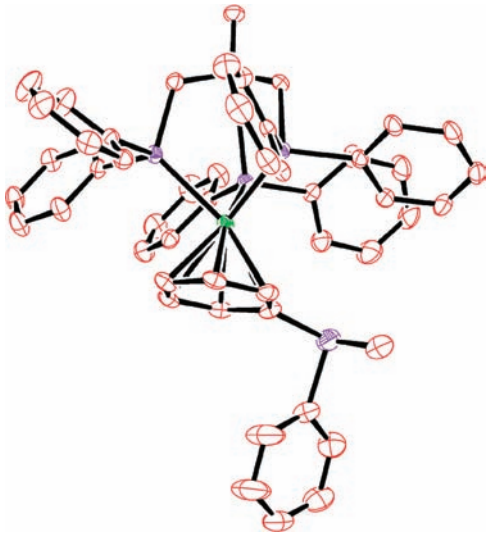


Figure 2. ORTEP depiction of the crystal structure of **8**. Thermal ellipsoids are drawn at 50% probability. Hydrogens are omitted for clarity.

Attempts to Synthesize Mo^0 Complexes of the Type Mo(N_2)$_2$(L_4). Attempts to reduce $MoCl_5$ with Mg^0 in the presence of the tetradentate phosphine ligands (1*R*,2*R*)-*N*,*N*′-bis[2-(diphenylphosphino)benzyl]cyclohexane-1,2-diamine (PNNP) and tris[2-(diphenylphosphino)ethyl]phosphine (P_3P) did not produce any identifiable products. Reduction of $MoCl_5$ in the presence of the PNNP ligand, either at room temperature or on heating to 100 °C, produced large amounts

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of precipitates that we attributed to oligomer formation;[34] however, we could not rule out the possibility of decomposition of an $Mo(N_2)_2(L_4)$ intermediate via loss of N_2 ligands or one coordination arm in the tetradentate ligand.[16] The reaction involving the P_3P ligand resulted in a dark brown suspension that we interpreted as evidence of oligomer formation. However, the ^{31}P NMR spectrum of the filtered mother liquor of the reaction mixture still shows a significant amount of soluble species, with a signal at δ −8.4 that is very close to the chemical shift of uncoordinated P_3P and five signals at δ 112.4, 88.0, 85.3, 67.8, 65.4 that are similar to those in **6**, **7**, and **8**. These data are consistent with species where there is an incomplete coordination of the tetradentate phosphine ligand P_3P to a single Mo^0 center, as has been reported for complex $Mo(P_3P)_2$,[41] and this is a potential pathway for oligomer formation.

Taken together with the results presented in the previous sections, the aforementioned observations reinforce the importance of having a stable monometallic phosphine-coordination environment during the in situ reduction of $MoCl_5$ with Mg^0. For this reaction to be successful in producing an isolable, soluble product from a multidentate ligand, such a ligand must be able to coordinate solely to a single metal center instead of undergoing bridging. While this can be enforced via either ligand geometry (as in the case of dppm) or via reversible depolymerization (as in the case of dppp), a careful balance between ligand coordination environment and steric demand must be maintained or facile rearrangement into more stable complex (as in the case of triphos **I** and **II**) will be more favored. Indeed, Tuczek and co-workers have recently reported a successful synthesis of both *trans* and *cis*-$[(N_2)_2Mo^0(prP_4)]$ complexes from the Mg-reduction of $MoCl_5$ in the presence of N_2 and the linear tetradentate phosphine ligand prP_4 (prP_4 = $Ph_2P(CH_2CH_2)PPh(CH_2CH_2CH_2)PPh(CH_2CH_2)PPh_2$).[30] Presumably, the linear arrangement of the coordinating phosphine moieties in this ligand as well as its flexible ethyl and propyl spacers allows it to completely enfold the Mo center and stabilize it well enough during the reduction so that the desired product can eventually be formed.

CONCLUSION

In conclusion, we have mapped out the reaction scope for the one-pot synthesis of Mo^0 dinitrogen complexes possessing a range of monodentate to multidentate phosphine ligands using Mg metal as a reductant. In the cases using monodentate and bidentate ligands where this strategy was most successful, it enables the safe and facile production of the desired product from inexpensive, commercially accessible starting materials. The use of Mg^0 as a reductant avoided a number of drawbacks that other strategies had, not only with safety, but also with relative reaction kinetics and low nitrogen solubility in organic media. With a kinetically slower reducing agent such as Mg metal, overpressures of nitrogen[12,13] are not required because nitrogen has time to be replenished in solution during reaction. In the cases of tridentate and tetradentate phosphines, successful syntheses of the desired dinitrogen Mo^0 species can be achieved if the ligand is flexible enough to stabilize the Mo center during the reduction both sterically and spatially.[30] If the ligand chelating motif is too rigid or spatially too restrictive, facile rearrangement into more stable η^6-arene complexes and/or oligomerization will become competitive.

EXPERIMENTAL SECTION

Materials, Reagents, Methods, and Instrumentation. All syntheses and manipulations of air- and moisture-sensitive materials were carried out in oven-dried Schlenk-type glassware, either on a dual-manifold Schlenk line or in a nitrogen-filled glovebox.

Hexanes, toluene, tetrahydrofuran (THF), and methanol are obtained by passing HPLC-grade solvents (VWR Scientific) over a column of activated neutral alumina in a Dow-Grubbs solvent system. Benzene-d_6 (Cambridge Isotope Laboratories) was dried over sodium/benzophonone, vacuum-transferred into a Strauss flask, and stored over activated (heated at 210 °C under reduced pressure for 20 h) Davison 4 Å molecular sieves before use. Methylene chloride-d_2 (Cambridge Isotope Laboratories) was dried and distilled over calcium hydride and stored over activated Davison 4 Å molecular sieves before use. Deionized water was obtained from a laboratory source provided by Northwestern University.

Molybdenum(V) chloride, methyldiphenylphosphine, trimethylphosphine, 1,2-bis(diphenylphosphino)methane (dppm), 1,2-bis(diphenylphosphino)ethane (dppe), 1,2-bis(diphenylphosphino)propane (dppp), 1,1,1-tris(diphenylphosphinomethyl)ethane, and (1*R*,2*R*)-*N*,*N*-bis[2-(diphenylphosphino)benzyl]cyclohexane-1,2-diamine (PNNP) were purchased from Strem Chemicals. Benzophonone, tris[2-(diphenylphosphino)ethyl]phosphine (P_3P), and calcium hydride were purchased from VWR Scientific. Bis(diphenylphosphinoethyl)phenylphosphine, magnesium, and iodine were purchased from Aldrich. Magnesium was activated by iodine vapor under static vacuum overnight at 50 °C. All other chemicals were used as received.

NMR spectra were recorded on either a Bruker Avance III 500 NMR spectrometer (500 MHz for ^1H, 125 MHz for ^{13}C) or a Varian Mercury 400 FT-NMR spectrometer (400.6 MHz for ^1H, 121.6 MHz for ^{31}P). Chemical shifts for ^1H and ^{13}C spectra were referenced to internal solvent resonances and were reported as parts per million relative to $SiMe_4$, whereas ^{31}P NMR spectra were referenced to external H_3PO_4 (85%).

Inductively coupled plasma optical emission spectroscopy (ICP-OES) was conducted on a Varian Vista-MDX (Varian, Walnut Creek, CA) ICP-OES spectrometer equipped with simultaneous CCD to cover the 175−785 nm spectral range. The instrument was controlled by ICP expert software (version 4.1.0) and calibrated using deionized water and mixtures containing Mo (2, 8, 15, and 25 ppm) and P (3, 15, 25, and 40 ppm) that were prepared from commercially available ICP standard solutions.

In a typical ICP-OES experiment, sample (around 10 mg) of a molybdenum complex was weighed into a VWR microwave vial (2−5 mL, Cat No 89079-404) inside a nitrogen-filled glovebox. After the vial was taken outside, a magnetic stirbar was added and an aliquot (2 mL) of a freshly prepared mixture of conc. H_2SO_4:H_2O_2 (30 wt % in H_2O) (3:1 v/v) was added. The resulting orange sample vial was crimped before being placed into a Biotage (Uppsala, Sweden) SPX microwave reactor (software version 2.3, build 6250). Digestion was carried out at 180 °C (the reactor tunes the microwave power to obtain desired temperature and keeps it stable during course of the reaction depending on the headspace available in the vial) while the content of the vial was magnetically stirred during irradiation using the built-in magnetic stirrer. When the solution became clear and colorless and no further vapor was produced (1/2 h or more), the irradiation was stopped and the vial was allowed to cool down. This acidic solution was diluted to either 100 or 250 mL by the addition of deionized H_2O and analyzed for Mo (202.032, 203.846, and 204.598 nm) and P (185.827, 185.878, and 214.914 nm) content using standard solutions. We note that the aforementioned digestion protocol does not work for *trans*-$Mo(N_2)_2(dppm)_2$ (**3**) and *trans*-$Mo(N_2)_2(dppp)_2$ (**5**), both of which left behind insoluble residues.

Synthesis of *cis*-$Mo(N_2)_2(PMe_3)_4$ (1). Under a N_2 atmosphere, a 100-mL Schlenk flask containing $MoCl_5$ (1.0 g, 3.64 mmol, 1 equiv), and a Teflon-coated magnetic stir bar were cooled in an acetone/dry ice bath. A precooled (−78 °C) solution of PMe_3 (1.24 g, 16.1 mmol, 4.42 equiv) in THF (40 mL) and activated magnesium (3.0 g, excess)

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were added sequentially. The bath was removed after 30 min, and the resulting dark orange reaction mixture was allowed to stir overnight. The next day, the reaction mixture was evaporated to dryness under reduced pressure. The remaining brown solid was taken into the glovebox, extracted with hexanes (30 mL), and vacuum-filtered through a plug of Celite. The filtrate was evaporated to dryness under reduced pressure to remove the solvents and PMe_3. The remaining dark-yellow solid was redissolved in hexanes (15 mL) and filtered through a syringe filter (PFTE, 0.45 μm). The collected solution was concentrated to 10 mL and kept at −30 °C overnight to crystallize out a light yellow powder, which was isolated by filtration, washed with cold methanol (2−3 mL), and dried under reduced pressure. This recrystallization protocol was repeated two times to afford the pure product as a light yellow powder (0.96 g, 58%). ^{1}H NMR (400.6 MHz, C_6D_6): δ 1.32 (t, 18H, J = 20.0 Hz, PMe_3), 1.08 (t, 18H, J = 20.0 Hz, PMe_3). ^{31}P NMR (121.6 MHz, C_6D_6): δ −6.5 (t, 2P, J = 18.0 Hz, PMe$_3$), −4.4 (t, 2P, J = 18.0 Hz, PMe$_3$). ICP-OES: calc. = 25.24 wt % Mo, found =26.30 wt %; calc. = 32.52 wt % P, found =31.03 wt %.

Synthesis of *trans*-Mo(N$_2$)$_2$(PMePh$_2$)$_4$ (2). *trans*-Mo(N$_2$)$_2$(PMePh$_2$)$_4$ was synthesized using a modification of the reported procedure by Lazarowich et al.[28] Under a N_2 atmosphere, a 100-mL Schlenk flask containing $MoCl_5$ (0.1 g, 0.37 mmol, 1 equiv), and a Teflon-coated magnetic stir bar were cooled in an ice bath. A precooled (0 °C) solution of $PMePh_2$ (0.32 g, 1.58 mmol, 4.33 equiv) in THF (50 mL) and activated magnesium (1.5 g, excess) were added sequentially. The reaction mixture was allowed to stir for 100 min at 0 °C, and the resulting golden yellow solution was cannula-transferred into a 100-mL Schlenk flask and evaporated to dryness under reduced pressure. The remaining yellow solid was taken into the glovebox, extracted with toluene (30 mL), and filtered through Celite. The collected solution was evaporated to dryness under reduced pressure to afford an orange solid residue. This solid was redissolved in toluene (8 mL) and kept at −30 °C overnight to crystallize out the product, which was isolated by filtration, washed with methanol (3 mL), and dried under reduced pressure. Further recrystallization of the mother liquor afforded a second crop that is combined with the first to yield the final product as an orange powder (0.21 g, 61% yield). ^{1}H NMR (400.6 MHz, C_6D_6): δ 7.26 (br s, 16 H, C_6H_5), 6.87 (br s, 24 H, C_6H_5), 1.85 (s, 12H, CH_3). ^{31}P{^{1}H} NMR (121.6 MHz, C_6D_6): δ 19.9 ppm. ICP-OES: calc. = 10.07 wt % Mo, found = 9.54 wt %; calc. = 12.98 wt % P, found =12.97 wt %.

Synthesis of *trans*-Mo(N$_2$)$_2$(dppm)$_2$ (3). Under a N_2 atmosphere, a 250-mL Schlenk flask containing $MoCl_5$ (0.13 g, 0.48 mmol, 1 equiv), dppm (0.4 g, 1.0 mmol, 2.08 equiv), and a Teflon-coated magnetic stir bar were cooled in an acetone/dry ice bath. Precooled (−78 °C) THF (70 mL) and activated magnesium (1.5 g, excess) were added sequentially. The bath was removed after 30 min, and the reaction mixture was allowed to stir overnight. The next day, the reaction mixture was evaporated to dryness under reduced pressure. The resulting brown solid was taken into the glovebox, extracted with toluene (40 mL), and filtered through a plug of Celite. The collected solution was evaporated to dryness under reduced pressure. The remaining dark red solid was redissolved in THF (10 mL), layered with methanol (10 mL), and kept at −30 °C for several days. The precipitated product was isolated by filtration, washed with methanol (5 mL), and dried under reduced pressure to afford a dark red powder (0.19 g, 43%). ^{1}H NMR (400.6 MHz, C_6D_6): δ 7.51 (br s, 8 H, C_6H_5), 6.97−6.67 (m, 32 H, C_6H_5), 5.01 (br s, 4H, CH_2). ^{31}P{^{1}H} NMR (121.6 MHz, C_6D_6): δ 16.7 ppm. ICP-OES data could not be obtained for this compound because of our inability to digest it.

Synthesis of *trans*-Mo(N$_2$)$_2$(dppe)$_2$ (4). Under a N_2 atmosphere, a 250-mL Schlenk flask containing dppe (0.50 g, 1.24 mmol, 2.1 equiv), $MoCl_5$ (0.16 g, 0.58 mmol, 1 equiv), and a Teflon-coated magnetic stir bar were cooled in an acetone/dry ice bath. Precooled (−78 °C) THF (100 mL) and activated magnesium (1.5 g, excess) were added sequentially. The bath was removed after 30 min, and the reaction mixture was allowed to stir for 17 h . The next day, the resulting dark-orange suspension was evaporated to dryness under reduced pressure. The remaining dark-orange solid was taken into the glovebox, extracted with toluene (70 mL), and filtered through a plug of Celite. The collected filtrate was evaporated to dryness under reduced pressure, redissolved in THF (10 mL), layered with methanol (8 mL), and kept at −30 °C for several days. The precipitated product was isolated by filtration, washed with methanol (5 mL), and dried under reduced pressure to afford an orange powder (0.16 g, 29%). ^{1}H NMR (400.6 MHz, C_6D_6): δ 7.21 (br s, 16 H, C_6H_5), 7.01 (br s, 24 H, C_6H_5), 2.28 (t, 8H, J = 8.5 Hz, CH_2). ^{31}P{^{1}H} NMR (121.6 MHz, C_6D_6): δ 66.1 ppm. ICP-OES: calc. = 10.11 wt %, found = 9.95 wt % Mo; calc. = 13.03 wt % P, found = 13.52 wt %.

Synthesis of *trans*-Mo(N$_2$)$_2$(dppp)$_2$ (5). Under a N_2 atmosphere, a 250-mL Schlenk flask containing dppp (0.40 g, 0.95 mmol, 2.1 equiv), $MoCl_5$ (0.124 g, 0.45 mmol, 1 equiv), and a Teflon-coated magnetic stir bar were cooled in an acetone/dry ice bath. Precooled (−78 °C) THF (80 mL) and activated magnesium (1.5 g, excess) were added sequentially. The bath was removed after 30 min, and the reaction mixture was allowed to stir for 24 h before a water-cooled reflux condenser was attached to the flask. The resulting brown reaction mixture was heated up to 80 °C and kept at that temperature for 17 h. The next day, the reaction mixture was evaporated to dryness under reduced pressure. The remaining dark-yellow solid was taken into the glovebox, extracted with with toluene (40 mL), and filtered through a plug of Celite. The collected solution was evaporated to dryness under reduced pressure, redissolved in THF (8 mL), layered with methanol (5 mL) and kept at −30 °C for several days. The precipitated product was isolated by filtration, washed with methanol (5 mL), and dried under reduced pressure to afford an orange powder (0.04 g, 9%). ^{1}H NMR (400.6 MHz, C_6D_6): δ 7.17 (br s, 16 H, C_6H_5), 6.99 (br s, 24 H, C_6H_5), 2.41 (t, 8H, J = 5.6 Hz, CH_2), 1.72 (q, 4H, J = 5.6 Hz, CH_2). ^{31}P{^{1}H} NMR (121.6 MHz, C_6D_6): δ 25.5 ppm. ICP-OES data could not be obtained for this compound because of our inability to digest it.

Synthesis of *trans*-Mo(N$_2$)$_2$(triphos I)(PMePh$_2$) (6). Under a N_2 atmosphere, a 100-mL Schlenk flask containing bis(diphenylphosphinoethyl)phenylphosphine (0.87 g, 1.58 mmol, 1.01 equiv), $MoCl_5$ (0.43 g, 1,57 mmol, 1 equiv), and a Teflon-coated magnetic stir bar were cooled in an acetone/dry ice bath. A precooled (−78 °C) solution of $PMePh_2$ (0.34 g, 1.68 mmol, 1.07 equiv) in THF (70 mL) and activated magnesium (1.5 g, excess) were added sequentially. The bath was removed after 30 min, and the reaction mixture was allowed to stir for 17 h. The next day, the resulting dark-orange reaction mixture was evaporated to dryness under reduced pressure. The remaining dark-orange solid was taken into the glovebox, extracted with toluene (50 mL), and filtered through a plug of Celite. The collected solution was evaporated to dryness under reduced pressure, redissolved in THF (8 mL), layered with methanol (8 mL), and kept at −30 °C for 2 days.

The precipitated product was again redissolved in THF (15 mL), layered with methanol (8 mL), and kept at −30 °C for 3 days. The precipitated product was isolated by filtration to afford purified **6** as a yellow-orange powder (50 mg, 4%) after being washed with methanol (2 mL) and dried under reduced pressure. ^{1}H NMR (400.6 MHz, C_6D_6): δ 7.26 (br s, 14 H, C_6H_5), 7.06 (br s, 14 H, C_6H_5), 6.97 (br s, 7 H, C_6H_5), 2.85 (br d, 2H, CH_2), 2.37 (br s, 2H, CH_2), 2.10 (br s, 2H, CH_2), 1.78 (s, 3H, PMePh$_2$), 1.67 (br s, 2H, CH_2). ^{31}P{^{1}H} NMR (121.6 MHz, C_6D_6): δ 103.9 (d, 1P, J = 101.7 Hz, PPh$_2$$P$PhPPh$_2$), 65.6 (d, 2P, J = 13.8 Hz, PPhPPh$_2$), 23.8 (dt, 1P, J_1= 101.7 Hz, J_2= 13.8 Hz, PMePh$_2$). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6): δ 142.6, 142.4, 141.1 (td, 1C, J_1 = 9.7 Hz, J_2 = 3.1 Hz), 140.7 (t, 1C, J = 10.9 Hz), 138.0, 137.8, 133.2 (t, J = 5.4 Hz), 133.0 (t, J = 5.4 Hz), 132.3, 132.2, 132.0, 131.9, 129.4, 128.8, 128.5, 128.3 (Ph carbons), 142.1 (pentet, 1C, J_{P-C} = 8.9 Hz, =CH), 141.8 (pentet, 1C, J_{P-C} = 7.4 Hz, =CPh$_2$), 36.3 (m, 2C, CH_2), 27.0 (t, 1C, J_{P-C} = 8.6 Hz, CH_2), 26.8 (t, 1C, J_{P-C} = 8.6 Hz, CH_2), 17.8 (t, 2C, J_{P-C} = 18.9 Hz, PCH_3).

Single crystals suitable for X-ray diffraction analysis were grown by dissolving purified **6** (40 mg) in THF (3 mL) and layering the resulting solution with methanol (3 mL) at −30 °C inside the glovebox freezer. Yellow crystals were formed after a few days and structurally characterized by X-ray diffraction analysis.

Synthesis of (η^6-C$_6$H$_5$PMePh)Mo(triphos I) (7). Under a N_2 atmosphere, a 100-mL Schlenk flask containing bis(diphenyl-

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phosphinoethyl)phenylphosphine (0.5 g, 0.907 mmol, 1 equiv), $MoCl_5$ (0.249 g, 0.907 mmol, 1 equiv), and a Teflon-coated magnetic stir bar were cooled in an acetone/dry ice bath. A precooled (−78 °C) solution of $PMePh_2$ (0.185 g, 0.915 mmol, 1.01 equiv) in THF (50 mL) and activated magnesium (1.5 g, excess) were added sequentially. The bath was removed after 30 min, and the reaction mixture was allowed to stir for 17 h before a water-cooled reflux condenser was attached to the flask. The resulting dark-orange suspension was then heated to 60 °C and kept at this temperature for 24 h. The next day, the reaction mixture was evaporated to dryness under reduced pressure. The remaining dark-orange solid was taken into the glovebox, extracted with toluene (40 mL), and filtered through a plug of Celite. The collected solution was evaporated to dryness under reduced pressure, and the resulting yellow-orange solid was stirred in methanol (30 mL) for 1 h before being filtered over a fine-fritted funnel. This washing and filtration process was repeated two more times with the collected solid to remove all methanol-soluble impurities. The purified product was a yellow powder (0.36 g, 48%) after being dried under reduced pressure. ^{1}H NMR (400.6 MHz, C_6D_6): δ 7.83 (t, 2 H, J = 8.3 Hz, C_6H_5), 7.55 (t, 2 H, J = 7.6 Hz, C_6H_5), 7.49 (t, 2 H, J = 6.9 Hz, C_6H_5), 7.35 (m, 5 H, C_6H_5), 7.26−6.84 (m, 24 H, C_6H_5), 4.42 (br d, 1H, C_6H_5), 4.31, 3.80, 3.71, 3.67 (br s, 4H, C_6H_5), 2.36−1.70 (br m, 6H, CH_2), 1.26 (br d, 3H, P*Me*Ph_2), 0.91, 0.73 (br s, 2H, CH_2). ^{31}P{^{1}H} NMR (121.6 MHz, C_6D_6): δ 106.25 (td, 1P, J_1 = 15.1 Hz, J_2 = 4.0 Hz, PPh_2*P*PhPPh_2), 86.3 (t, 1P, J = 16.4 Hz, PPh*P*Ph_2), 83.5 (t, 1P, J_1= 16.5 Hz, PPh*P*Ph_2), −26.6 (d, P, J = 3.8 Hz, *P*$MePh_2$). ^{13}C{^{1}H} NMR (125 MHz, C_6D_6): δ 134.2, 134.1, 133.75, 133.71, 133.67, 133.62, 133.5, 133.3, 133.8, 132.7, 132.1, 132.0, 131.8, 131.7, 131.5, 131.4 (Ph carbons), 85.2, 84.9, 80.5, 77.6, 73.2 (d, J = 10.0 Hz), 71.3 (arene-Ph carbons), 34.1 (t, J = 21.5 Hz, CH_2), 32.3 (m, 2C, CH_2), 31.5 (t, J = 20.5 Hz, CH_2), 13.1 (d, J = 14.5 Hz, P*Me*Ph_2). ICP-OES: calc. = 11.07 wt % Mo, found = 10.23 wt %; calc. = 14.27 wt % P, found = 12.98 wt %.

Synthesis of (η^6-C_6H_5PMePh)Mo(triphos II) (8). Under a N_2 atmosphere, a 100-mL Schlenk flask containing 1,1,1-tris-(diphenylphosphinomethyl)ethane (1.55 g, 2.41 mmol, 1 equiv), $MoCl_5$ (0.66 g, 2.41 mmol, 1 equiv), and a Teflon-coated magnetic stir bar under N_2 were cooled in an acetone/dry ice bath. A precooled (−78 °C) solution of $PMePh_2$ (0.51 g, 2.52 mmol, 1.05 equiv) in THF (70 mL) and activated magnesium (1.5 g, excess) were added sequentially. The resulting dark red reaction mixture was allowed to stir for 17 h, over which time it slowly warmed up to room temperature. The next day, the reaction mixture was evaporated to dryness under reduced pressure. The resulting dark-red solid was taken into the glovebox, extracted with toluene (35 mL), and filtered through a plug of Celite. The collected solution was evaporated to dryness under reduced pressure. The remaining solid was resuspended in THF (30 mL) and filtered over a fine-fritted funnel. The remaining solid residue was washed on-frit with THF (1−2 mL) and methanol (20 mL) before being dried under reduced pressure to give the first crop of product as an orange-red powder. The combined filtrates were concentrated to ∼10 mL, layered with methanol (5 mL), and kept at −30 °C for 2 days to produce the second crop, which was isolated using a similar protocol as described above for the first crop. Combining both crops afforded purified **8** as an orange-red powder (1.40 g, 64% yield). ^{1}H NMR (400.6 MHz, C_6D_6): δ 7.61 (m, 2H, C_6H_5), 7.20−6.81 (m, 33 H, C_6H_5), 4.82 (d, 1H, J = 5.0, C_6H_5), 4.72 (t, 1H, J = 5.0, C_6H_5), 4.54 (br s, 1H, C_6H_5), 4.34 (t, 1H, J = 5.0, C_6H_5), 4.13 (t, 1H, J = 5.0, C_6H_5), 2.28, 2.24, 2.11, 2.08 (br s, 6H, CH_2), 1.22 (d, 3H, J = 4.5, PPh_2*Me*), 1.08 (br s, 3H, CH_3). ^{31}P{^{1}H} NMR (121.6 MHz, C_6D_6): δ 46.1 (s, 3P, *P*-Mo), −29.0 (br s, 1P, η^6-Ph-*P*-MePh). ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2): δ 133.4, 133.3, 132.8, 131.9, 129.5, 128.7, 128.6, 127.9, 127.8, 127.7, 127.5, 125.8 (Ph carbons), 84.9, 78.3, 75.8, 75.0, 74.2, 73.6 (η^6-*Ph*-P-MePh), 45.7 (m, PCH_2), 37.6 ($(CH_2)_3CCH_3$), 21.7 (CH_3), 14.0 (br s, PCH_3). ICP-OES: calc. = 10.42 wt % Mo, found =9.70 wt %; calc. = 13.43 wt % P, found =14.10 wt %.

Single crystals suitable for X-ray diffraction analysis were grown by dissolving purified **8** (10 mg) in THF (1.5 mL) in a 5-mm NMR tube and layering the resulting solution with methanol (2 mL). After being kept at room temperature inside the glovebox for a few days, single crystals were formed and structurally characterized by X-ray diffraction analysis.

X-ray Crystallographic Analyses of 6 and 8. Single crystals of complexes **6** and **8** were mounted using oil (Infineum V8512) on a glass fiber. Single X-ray crystallography data were collected on a Bruker APEX-II CCD diffractometer (Bruker AXS Inc., Madison, WI) equipped with an Apex II CCD detector using graphite monochromated Mo$K\alpha$ radiation at a temperature of 100(2) K with a θ range of 1.95 to 29.15° for **6** or 1.31 to 31.60° for **8** and in 0.5° oscillations with 20 s exposures. The crystal-to-detector distance was 60.00 mm.

The structure was solved by direct methods and expanded using Fourier techniques.[42] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The disordered methanol solvent molecules were found in the crystal lattice of **8** and refined with rigid bond restraints (esd 0.01) on the displacement parameters as well as restraints on similar amplitudes (esd 0.05) separated by less than 1.7 Å. The carbon atoms on the solvent molecules of **8** were restrained esd (0.01) that its U_{ij} components approximate to isotropic.

■ ASSOCIATED CONTENT

Supporting Information

Digital images of NMR spectra and X-ray crystallography analysis of **6** and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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