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Decomplexation of Phosphirane and Phosphirene Complexes

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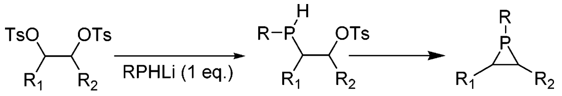
Novel transient phosphinidene complex Ph−P═Mo(CO)$_4$PMe$_3$, generated from a 7-phosphanorbornadiene precursor, adds to C═C and C≡C bonds to give Mo(CO)$_4$PMe$_3$-complexed phosphiranes and phosphirenes. The *cis*-PMe$_3$ ligand weakens the interaction between the molybdenum complex and the three-membered ring. Under mild CO pressure the Mo(CO)$_4$PMe$_3$ transition metal group detaches from the phosphorus center of the ring structure by selective CO substitution. The resulting byproduct Mo(CO)$_5$PMe$_3$ can be reused in the synthesis of the phosphinidene precursor.

Introduction

Phosphirane (**1**), the phosphorus homologue of cyclopropane, has received much attention in the past two decades as new synthetic routes became available that made use of the stabilization rendered by transition metal groups.[1] Whereas uncomplexed phosphiranes can be obtained, for example, from the reaction of a metal phosphide and a diol ditosylate (see Scheme 1),[2] their limited thermal stability and sensitivity toward oxidation not only complicates their isolation but also restricts the versatility of the reaction. Phosphiranes have also been synthesized by carbene addition to a phosphaalkene, by salt elimination from the reaction of RPX$_2$ with 1,2-dimetallic derivatives of alkanes, and by cyclization of C−P−C units.[3] The stability of phosphiranes improves with bulky substituents on the phosphorus atom, but they remain photolytically labile[4] and subject to [2+1] cycloreversion,[5] retro-electrocyclization,[6] and ring−chain rearrangement.[7]

Scheme 1. Synthesis of Uncomplexed Phosphiranes



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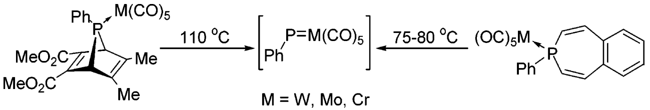
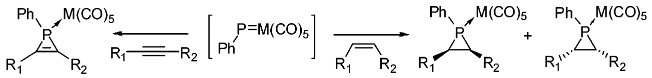
Scheme 2. Two Phosphinidene Precursors



2 **3**

Scheme 3. Addition Reactions of a Phosphinidene Transition Metal Complex



4 **5a** **5b**

Phosphiranes with a transition metal complex coordinated to the phosphorus center are intrinsically more stable. Several methods have been reported to obtain these complexed heterocycles. A popular method is the addition of a transient electrophilic phosphinidene R−P═M(CO)$_5$ (M = Cr, Mo, W) to the C═C bond of a suitable substrate. The most widely used precursor, 7-phosphanorbornadiene complex **2**, generates this phosphinidene through thermal cheletropic elimination.[8] Recently, a new precursor was developed, 3*H*-3-benzophosphepine complex **3** (Scheme 2),[9] that offers more flexibility in the choice of the transition metal complex. It has also been shown that transient R$_2$N−P═Fe(CO)$_4$, generated from Collman's reagent, adds to double bonds, albeit only to terminal ones.[10] Still other precursors have been reported that are capable of transferring (trapping) electrophilic phosphinidene complexes by addition to olefins and alkynes to generate isomeric phosphiranes **5** and phosphirenes **4** (Scheme 3). Azaphosphirene complexes[11] and 1-amino-phosphirane and -phosphirene complexes[12] have also been used to generate electrophilic phosphinidenes.

There are only a few methods to remove a transition metal complex from the three-membered heterocycles, but none works reliably and consistently for all systems, possibly in part due to the perceived sensitivity of the uncomplexed products. Decom-

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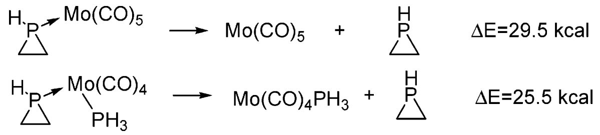
plexation of the $W(CO)_5$ group has been explored most. One approach is the selective oxidation with iodine to weaken the W−P bond followed by ligand exchange with *N*-methylimidazole.[13] In a variation of this method, pyridinium tribromide is used for the oxidation of W(0) to W(II) and 2,2′-bipyridine for the displacement of the phosphine.[14] The use of this method for the decomplexation of sensitive compounds such as phosphiranes is very limited, and to the best of our knowledge, only one such example has been reported.[15]

Direct exchange for a bidentate diphosphine ligand has been reported to work only for very stable phosphiranes, as high temperatures (∼150 °C) are needed.[16a] With this method, phospholes and 1-chlorophosphirenes can also be demetalated.[16b,c] Trimethylamine *N*-oxide has been reported as a reagent for oxidative decomplexation of a $P-W(CO)_5$ complex to the corresponding phosphoryl compound.[17] Finally, the electrochemical decomplexation of phosphine−$W(CO)_5$ complexes has been reported for phosphole compounds.[18]

Photodissociation of the transition metal group has received little attention, probably because the reverse process is used to exchange CO for phosphine ligands in metal carbonyl complexes.[19] However, TD-DFT calculations on $(C_2H_4)PH-Cr(CO)_5$ and $H_3P-Cr(CO)_5$ suggested that photochemical decomplexation may be a viable option.[20] PB88/TZP calculations also indicated that the phosphirane−$Mo(CO)_5$ complex weakens by 4 kcal/mol on replacing a CO for a PH_3 ligand.

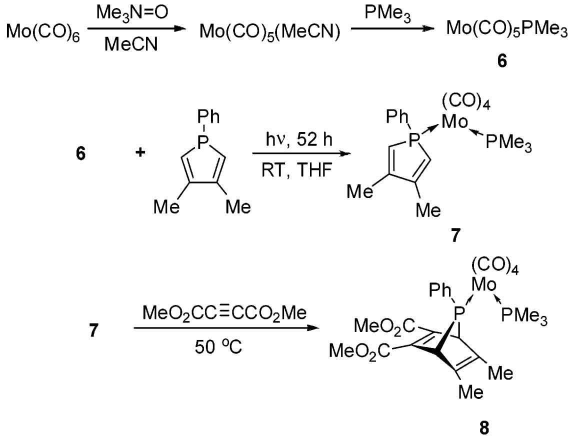


To expand the access to metal-free phosphorus heterocycles, which have potential in asymmetric catalysis,[21] we report on a decomplexation procedure that is based on pressurized reactions in a CO atmosphere. As proof of principle, we use as substrates phosphirene and phosphirane molybdenum carbonyl complexes carrying one additional phosphine ligand.

Results and Discussion

The first step is the synthesis of phosphinidene precursor **8**, based on the 7-phosphanorbornadiene unit, having a $Mo(CO)_4PMe_3$ group coordinated to the phosphorus atom. Next this phosphinidene will be added to olefins and alkynes. Such phosphiranes coordinated to a transition metal carbonyl complex carrying an additional phosphine ligand are rare. We are aware of only a phosphirane Fe complex with a bidentate diphosphine ligand[22] and bidentate phosphine Mo complexes in which the second phosphine is linked to the phosphirane ring.[23] Finally, the demetalation from the phosphiranes and phosphirenes will be discussed.

Scheme 4. Synthesis of a Novel Phosphinidene Precursor



Synthesis of Phosphinidene Precursor 8. This phosphanorbornadiene derivative can be obtained by cycloaddition of an acetylene derivative and 3,4-dimethylphosphole-$Mo(CO)_4PMe_3$ complex **7**. The synthesis of **7** was pursued first by the addition of both phosphorus ligands 1-phenyl-3,4-dimethylphosphole and PMe_3 to *cis*-$Mo(CO)_4(piperidine)_2$, but surprisingly this reaction yielded mostly bis-trimethylphosphine complex *cis*-$Mo(CO)_4(PMe_3)_2$. Sequential addition, starting with the phosphole followed by PMe_3, gave mixtures of phosphine complexes with *cis*-$Mo(CO)_4(PMe_3)_2$ as the major product. A more successful procedure started with the synthesis of $Mo(CO)_5PMe_3$, **6** (75% yield), from $Mo(CO)_6$ by oxidation with trimethylamine *N*-oxide, followed by replacement of the in-situ-formed acetonitrile complex with trimethylphosphine. Exchange of a *cis*-CO ligand for 1-phenyl-3,4-dimethylphosphole by UV irradiation in THF gave the desired Mo complex **7** (61% yield). Its ^{31}P NMR spectrum shows doublets ($^2J(P,P) = 24.5$ Hz) at +33.6 ppm for the phosphole ligand and at −15.3 ppm for the PMe_3 ligand. Diels−Alder reaction of **7** with dimethyl acetylenedicarboxylate yielded phosphinidene precursor **8** in 50% isolated yield (Scheme 4).

Phosphinidene Additions. Heating a toluene solution of phosphanorbornadiene complex **8** and diphenylacetylene at 70 °C results in the rapid addition of transient $PhP{=}Mo(CO)_4PMe_3$ to the C≡C bond to give the Mo-complexed phosphirene **9** in 39% yield (Scheme 5). This yield is slightly higher than the 29% yield reported for the addition of transient $PhP{=}Mo(CO)_5$, which is generated at 120 °C.[14] Generally, because of the stronger W−P bond, higher yields are obtained with tungsten phosphinidene complexes. Only very recently was a higher yield of 66% reported by using a benzophosphepine phosphinidene precursor (Scheme 2, M = Mo) at 75−80 °C.[9] However, we could not use this precursor because it lacks the additional PMe_3 ligand. The ^{31}P NMR resonance at −130.0 ppm is normal for

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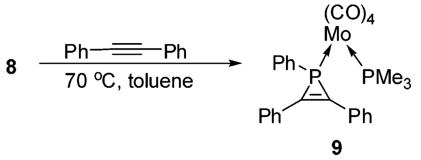
Scheme 5. Synthesis of a Phosphirene Complex



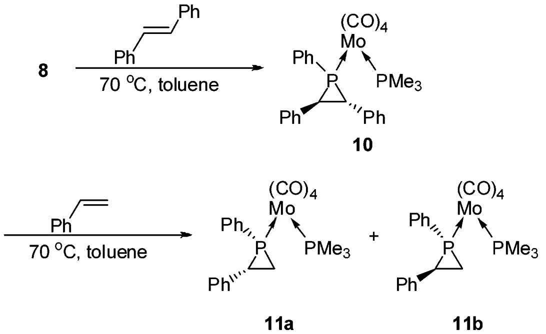
a Mo-complexed phosphirene, and that at −14.2 ppm for PMe_3 is similar to that of **8**; the ^2J(P,P) coupling constant of 32.4 Hz is normal for *cis*-diphosphine compounds.

The reaction of **8** with the C═C bond of *trans*-stilbene gave phosphirane complex **10**, but in low isolated yield (21%) due to product decomposition during the reaction. Reaction of **8** with styrene resulted in the formation (51%) of a mixture of diastereomeric phosphiranes **11a** and **11b** (ratio 8:1) in which the $Mo(CO)_4PMe_3$ group is oriented respectively *anti* and *syn* to the phenyl substituent of the ring. The products could be separated by crystallization. The *anti* assignment of the major isomer is based on steric considerations, as we were unable to grow suitable crystals for an X-ray crystal structure determination. Addition reactions to sterically more hindered alkenes, such as $Ph_2C{=}CH_2$ and ^{t}BuCH═CH_2, did not result in the formation of the desired phosphiranes. The ^{31}P NMR resonances of phosphirane complexes **10** (−89.5) and **11** (**a** −125.6; **b** −124.6) are similar to those of the $W(CO)_5$ complexes.[24] During the synthesis of **10** and **11** small amounts (<5%) of the demetalated products were detected by their ^{31}P NMR resonances at −147 and −182 ppm, respectively. This suggests that mild heating may suffice to remove the transition metal group, which can be captured by CO under pressurized condition.

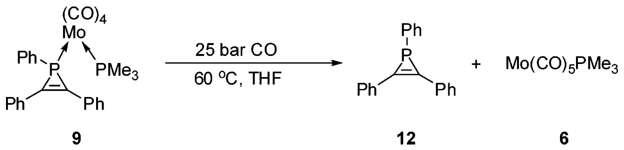
Demetalation. The decomplexation of Mo complex **9** occurs already at 60 °C to give over 48 h the known free triphenylphosphirene **12**[15] in 94% isolated yield. Also the metal fragment is nearly quantitatively recovered as $Mo(CO)_5PMe_3$ (**6**) and can be reused in the synthesis of **8**. Removal of the transition metal group results in a 57 ppm shielding of the ^{31}P NMR chemical shift to −187.4. ppm. Free PMe_3 is not observed under the reaction conditions.

Decomplexation of phosphirane **10** occurs likewise, but more care has to be exercised because of the sensitivity of the product to oxygen. Thus, heating **10** ($\delta(^{31}P)$ −88.6 and −15.2 ppm, ^2J(P,P) 30.5 Hz) at 60 °C for 24 h resulted in the near quantitative formation of free triphenylphosphirane **13** ($\delta(^{31}P) = -147.5$ ppm) and $Mo(CO)_5PMe_3$ ($\delta(^{31}P) = -15.1$ ppm). Also complex **11a** ($\delta(^{31}P)$ −125.6 and −14.6 ppm, $^2J(P,P) = 31.4$ Hz) is converted at 60 °C to the free phosphirane (**14**, $\delta(^{31}P)$ −182.2 ppm) without isomerization. Monitoring the decomplexing of a **11a**,**b** mixture by ^{31}P NMR shows the formation of both phosphirane isomers **14** ($\delta(^{31}P) = -182.2$ and −197.2 ppm) in the same ratio. Phosphirane **14** is thermally not very stable and undergoes slow degradation at 60 °C, thereby lowering the observed ratio of phosphirane to $Mo(CO)_5PMe_3$. Decomplexation of phosphiranes **10** and **11** was performed on a 5 mg scale. Due to the instability of the free phosphiranes, we reduced the reaction time by increasing the ratio of CO to phosphirane complex. In our experimental setup, suited for monitoring the reactions, this could be achieved only by reducing the amount of phosphirane complex to 5 mg. An autoclave and higher CO pressures are recommended for larger scale reactions.

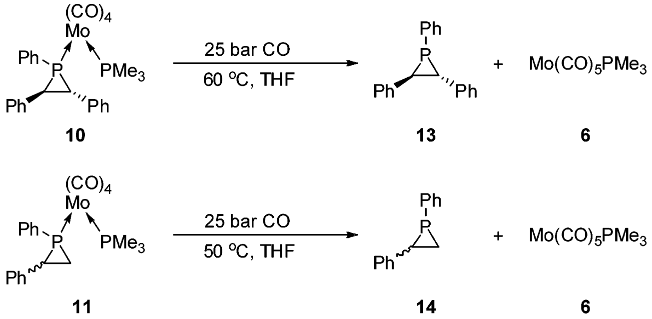
Scheme 6. Synthesis of Phosphirane Complexes



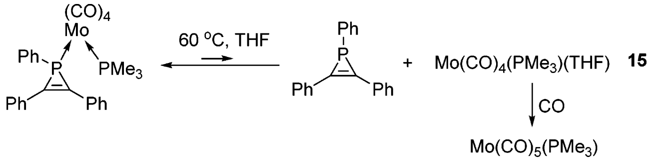
Scheme 7. Phosphirene Decomplexation



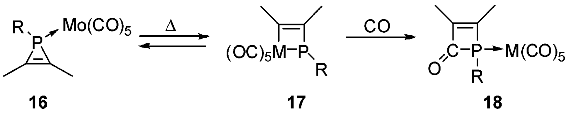
Scheme 8. Phosphirane Decomplexation



Scheme 9. Possible Reaction Path for Decomplexation



Scheme 10. Thermolysis of Phosphirene−Transition Metal Complexes



A possible explanation for the mild decomplexation of the $Mo(CO)_4PMe_3$ group at 60 °C could be the existence of an equilibrium between the complex of the three-membered heterocycle and its free form. Indicative is the rapid formation of small amounts of the decomplexed phosphirene and phosphiranes at the slightly higher temperature of 80 °C. The presence of CO dissolved in the reaction mixture is apparently capable of capturing the possible intermediate **15**, thereby driving the decomplexation to completion.

The reaction is remarkable, as thermolysis of $M(CO)_5$-complexed phosphirene **16** (M = Cr, Mo, W) has been reported by Mathey et al.[14] to give ring enlargement via carbonylation of a phosphorus−carbon bond (Scheme 10). The mechanism involves intermediate 1-phospha-2-metallacyclobutene **17**, which is carbonylated in modest yield (8−43%) to phosphete complex **18**. We did not observe this reaction with the $Mo(CO)_4PMe_3$-complexed phosphirene, which illustrates that the PMe_3 ligand contributes to the weakened coordination of the transition metal to the heterocycle.

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Conclusions

Transient phosphinidene complex Ph−P═Mo(CO)$_4$PMe$_3$ is generated at only 70 °C from its 7-phosphanorborandiene precursor and adds to olefinic and acetylenic bonds to form Mo(CO)$_4$PMe$_3$-complexed phosphiranes and phosphirenes, respectively. The phosphine ligand reduces the P═Mo bond strength as compared to the all-carbonyl complex. The transition metal group is readily removed under mild CO pressure by selective replacement of the three-membered PCC rings for CO. Byproduct Mo(CO)$_5$PMe$_3$ of this reaction is used photochemically to generate Mo(CO)$_4$PMe$_3$-complexed phosphole **7**, from which phosphinidene precursor **8** is obtained in a mild Diels−Alder reaction with dimethyl acetylenedicarboxylate.

Experimental Section

All experiments were performed under an atmosphere of dry nitrogen. Solids were dried in a vacuum, and liquids were distilled under N$_2$ prior to use. Toluene was distilled over sodium, and THF was dried by successive distillation over LiAlH$_4$ and sodium/benzophenone. CH$_2$Cl$_2$ was dried over P$_2$O$_5$. 1-Phenyl-3,4-dimethylphosphole[25] was prepared according to literature procedures. NMR spectra were recorded on a Bruker WM 250 spectrometer (^{1}H, ^{13}C), internally referenced to residual solvent resonances and 85% H$_3$PO$_4$ (^{31}P) as external standard. IR spectra were recorded on a Mattson 6030 Galaxy FT-IR spectrophotometer and high-resolution mass spectra (HR-MS) on a Finnigan Mat 900 spectrometer (EI, 70 eV). Fast atom bombardment (FAB) mass spectrometry was carried out using a JEOL JMS SX/SX 102A four-sector mass spectrometer, coupled to a JEOL MS-MP9021D/UPD system program. Samples were loaded in a matrix solution (3-nitrobenzyl alcohol) onto a stainless steel probe and bombarded with xenon atoms with an energy of 3 keV. During the high-resolution FAB-MS measurements a resolving power of 10 000 (10% valley definition) was used. Column chromatography was performed using silica gel (SiliaFlash P60, Silicycle) using indicated solvents as determined with TLC. Thin-layer chromatography was performed using silica gel plates (silica gel 60 F254 plates, Merck). Melting points were measured on samples in unsealed capillaries and are uncorrected.

Synthesis of (Trimethylphosphine)pentacarbonylmolybdenum, 6. Mo(CO)$_6$ (3.00 g, 11.4 mmol) and Me$_3$N$^+$O$^-$·2H$_2$O (1.27 g, 11.5 mmol) were added to 50 mL of a 1:1 mixture of dichloromethane and acetonitrile. The reaction mixture was stirred for 1.5 h at room temperature. A 11.4 mL portion of 1 M PMe$_3$ in toluene was slowly added to the reaction mixture. Stirring was continued for 1.5 h at room temperature. Evaporation to dryness and column chromatography (silica gel, pentane/dichloromethane, 5:1) gave **6** (2.80 g, 79%) as a white solid.

^{31}P NMR (CDCl$_3$): δ −15.3 (s, P(CH$_3$)$_3$). The ^{1}H and ^{13}C NMR data are identical to those in ref 26.

Synthesis of *cis*-(Trimethylphosphine)(3,4-dimethyl-1-phenylphosphole)tetracarbonylmolybdenum, 7. Mo(CO)$_5$PMe$_3$ (**6**) (2.40 g, 8.01 mmol) was dissolved in 200 mL of dry THF. Nitrogen was bubbled through the solution, and 1.65 g (9.00 mmol) of 1-phenylphosphole was added. The reaction mixture was stirred for 44 h while being irradiated with a high-pressure Philips Hg lamp (0.9 A, Type 93110E). UV light was filtered out using a 0.1 cm thick glass plate. Evaporation to dryness, column chromatography (silica gel, pentane/dichloromethane, 5:1), and recrystallization from dichloromethane/hexane gave 2.32 g (61%) of **7** as yellow crystals.

Mp: 69−70 °C. ^{31}P NMR (CDCl$_3$): δ −15.3 (d, ^2J(P,P) = 24.5 Hz; P(CH$_3$)$_3$), 33.6 (d, ^2J(P,P) = 24.5 Hz; phosphole). ^{1}H NMR (CDCl$_3$): δ 1.28 (d, ^2J(P,H) = 7.0 Hz; 9H, P(CH$_3$)$_3$), 2.10 (s, 6H, CH$_3$), 6.52 (d, ^2J(P,H) = 36.0 Hz; 2H, C═CH), 7.28−7.54 (m, 5H, Ph). ^{13}C NMR (CDCl$_3$): δ 17.3 (d, ^3J(C,P) = 9.7 Hz; CH$_3$), 20.5 (dd, ^1J(C,P) = 22.6 Hz; ^3J(C,P) = 2.0 Hz; P(CH$_3$)$_3$), 128.4 (d, ^3J(C,P) = 9.4 Hz; *m*-Ph), 129.3 (d, ^4J(C,P) = 2.0 Hz; *p*-Ph), 131.0 (dd, ^1J(C,P) = 34.3 Hz; ^3J(C,P) = 8.1 Hz; P−C═), 131.1 (d, ^2J(C,P) = 12.0 Hz; *o*-Ph), 133.2 (dd, ^1J(C,P) = 33.1 Hz; ^3J(C,P) = 2.8 Hz; *ipso*-Ph), 148.8 (d, ^3J(C,P) = 7.7 Hz; CH*C*CH$_3$), 209.8 (dd, ^2J(C,P) = 10.4 Hz; ^2J(C,P) = 9.2 Hz; *cis*-CO), 214.6 (dd, ^2J(C,P) = 23.9 Hz; ^2J(C,P) = 8.4 Hz; *trans*-CO), 215.0 (dd, ^2J(C,P) = 22.1 Hz; ^2J(C,P) = 9.0 Hz; *trans*-CO). IR (CH$_2$Cl$_2$): ν(CO) = 2017 (w), 1903 (vs), 1880 (sh) cm^{-1}. HR-MS: calcd for C$_{19}$H$_{22}$O$_4$P$_2$Mo 474.0047, found 474.0046.

Synthesis of *cis*-(Trimethylphosphine)(5,6-dimethyl-2,3-bis(methoxycarbonyl)-7-phenyl-7-phosphanorbornadiene)tetracarbonylmolybdenum, 8. A mixture of complex **7** (1.60 g, 3.39 mmol) and dimethyl acetylenedicarboxylate (10 mL, 82.6 mmol) was stirred at 50 °C for 22 h. Column chromatography (silica gel, starting with pentane and gradually converting to dichloromethane) gives a yellow solid. Recrystallization from dichloromethane/hexane resulted in 1.02 g (49%) of **8** as orange crystals.

Mp: 120−121 °C (dec). ^{31}P NMR (CDCl$_3$): δ −14.6 (d, ^2J(P,P) = 27.7 Hz; P(CH$_3$)$_3$), 253.2 (d, ^2J(P,P) = 27.7 Hz; 7-phosphanorbornadiene). ^{1}H NMR (CDCl$_3$): δ 1.34 (d, ^2J(P,H) = 6.8 Hz; 9H, P(CH$_3$)$_3$), 2.02 (s, 6H, CH$_3$), 3.63 (s, 6H, CO$_2$CH$_3$), 3.85 (d, ^2J(P,H) = 3.5 Hz; 2H, ═C−CH−C═), 7.14−7.30 (m, 5H, Ph). ^{13}C NMR (CDCl$_3$): δ 15.9 (d, ^3J(C,P) = 1.7 Hz; CH$_3$), 21.5 (dd, ^1J(C,P) = 23.1 Hz; ^3J(C,P) = 2.5 Hz; P(CH$_3$)$_3$), 51.6 (s, OCH$_3$), 60.5 (dd, ^1J(C,P) = 14.1 Hz; ^3J(C,P) = 2.3 Hz; P−*C*H−C═), 127.9 (d, ^3J(C,P) = 6.3 Hz; *m*-Ph), 128.6 (d, ^2J(C,P) = 9.3 Hz; *o*-Ph), 128.7 (s, *p*-Ph), 137.3 (d, ^1J(C,P) = 17.4 Hz; *ipso*-Ph), 142.2 (d, ^2J(C,P) = 3.5 Hz; *C*═*C*−CH$_3$), 145.6 (d, ^2J(C,P) = 17.4 Hz; *C*═*C*−CO$_2$CH$_3$), 165.2 (d, ^3J(C,P) = 2.2 Hz; *C*O$_2$CH$_3$), 208.7 (dd, ^2J(C,P) = 10.4 Hz; ^2J(C,P) = 8.1 Hz; *cis*-CO), 214.1 (dd, ^2J(C,P) = 11.5 Hz; ^2J(C,P) = 2.5 Hz; *trans*-CO), 214.5 (dd, ^2J(C,P) = 9.2 Hz; ^2J(C,P) = 4.5 Hz; *trans*-CO). IR (CH$_2$Cl$_2$): ν(CO) = 2021 (w), 1913 (vs), 1889 (sh) cm^{-1}. HR-MS (FAB+): calcd for C$_{25}$H$_{28}$O$_8$P$_2$Mo 616.0313, found 616.0296.

Synthesis of *cis*-(Trimethylphosphine)(1,2,3-triphenylphosphirene)tetracarbonylmolybdenum, 9. A mixture of **8** (500 mg, 0.81 mmol) and diphenylacetylene (470 mg, 2.64 mmol) dissolved in 15 mL of dry toluene was stirred at 70 °C for 5.25 h. Column chromatography (silica gel, pentane/dichloromethane, 7:3) and recrystallization from dichloromethane/hexane gave **9** (190 mg, 39%) as yellow crystals.

Mp: 143−144 °C. ^{31}P NMR (CDCl$_3$): δ −130.0 (d, ^2J(P,P) = 32.4 Hz; phosphirene), −14.2 (d, ^2J(P,P) = 34.2 Hz; P(CH$_3$)$_3$). ^{1}H NMR (CDCl$_3$): δ 1.24 (d, ^2J(P,H) = 6.8 Hz; 9H, P(CH$_3$)$_3$), 7.43−7.93 (m, 15H, Ph). ^{13}C NMR (CDCl$_3$): δ 20.7 (dd, ^1J(C,P) = 22.7 Hz; ^3J(C,P) = 2.8 Hz; P(CH$_3$)$_3$), 127.9 (d, ^3J(C,P) = 6.3 Hz; *m*-Ph), 128.6 (d, ^2J(C,P) = 9.3 Hz; *o*-Ph), 128.2−31.4 (m, Ph), 140.0 (d, ^1J(C,P) = 6.1 Hz; *ipso*-Ph), 209.7 (dd, ^2J(C,P) = 10.5 Hz; ^2J(C,P) = 11.4 Hz; *cis*-CO), 213.9 (dd, ^2J(C,P) = 35.6 Hz; ^2J(C,P) = 8.9 Hz; *trans*-CO), 214.5 (dd, ^2J(C,P) = 23.3 Hz; ^2J(C,P) = 10.1 Hz; *trans*-CO). IR (CH$_2$Cl$_2$): ν(CO) = 2020 (w), 1908 (vs), 1882 (sh) cm^{-1}. HRMS (70 eV): *m*/*z* (%)572 (2) [M$^+$], 516 (1) [M$^+$ − 2CO], 488 (1) [M$^+$ − 3CO], 460 (4) [M$^+$ − 4CO], 384 (6) [M$^+$ − 4CO − P(CH$_3$)$_3$], 314 (18) [PhPMo(CO)$_4$], 286 (22) [M$^+$ − Mo(CO)$_4$P(CH$_3$)$_3$], 178 (100) [PhCCPh]. HR-MS: calcd for C$_{27}$H$_{24}$O$_4$P$_2$Mo, 572.02039; found, 572.01932.

Synthesis of *cis*-(Trimethylphosphine)(1,2,3-triphenylphosphirane)tetracarbonylmolybdenum, 10. A mixture of **8** (500 mg, 0.81 mmol) and *trans*-stilbene (517 mg, 2.87 mmol) dissolved in 15 mL of dry toluene was stirred at 70 °C for 5.75 h. ^{31}P NMR spectroscopy showed that the precursor-to-product ratio was ca.

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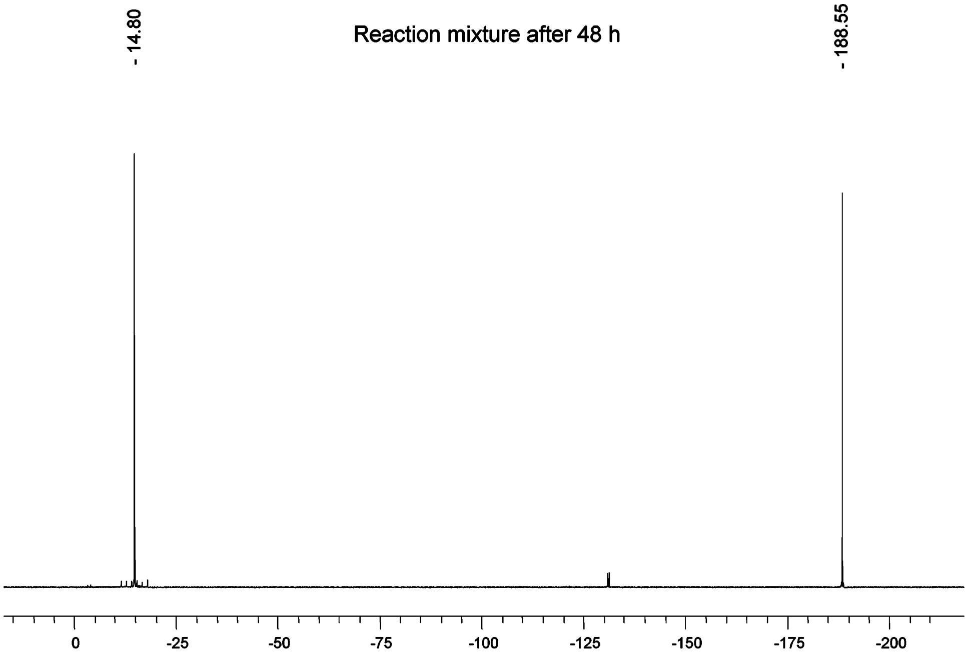


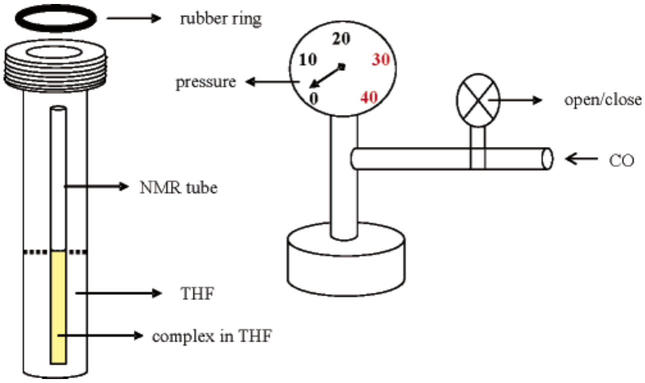
Figure 1. ^{31}P NMR spectrum of phosphirene decomplexation.

1:1. Column chromatography (silica gel, pentane/dichloromethane, 7:3) and recrystallization from dichloromethane/hexane gave **10** (99 mg, 21%) as colorless crystals. Mp: 127−128 °C. ^{31}P NMR ($CDCl_3$): δ −89.5 (d, $^2J(P,P) = 30.0$ Hz; phosphirane), −15.3 (d, $^2J(P,P) = 30.0$ Hz; $P(CH_3)_3$). ^1H NMR ($CDCl_3$): δ 1.19 (d, $^2J(P,H) = 6.9$ Hz; 9H, $P(CH_3)_3$), 3.45 (dd, $^2J(P,H) = 3.1$ Hz; $^3J(H,H) = 10.0$ Hz; 1H, P−CHPh), 3.85 (dd, $^2J(P,H) = 7.5$ Hz; $^3J(H,H) = 10.0$ Hz; 1H, P−CHPh), 7.00−7.50 (m, 15H, Ph). ^{13}C NMR ($CDCl_3$): δ 20.7 (dd, $^1J(C,P) = 23.0$ Hz; $^3J(C,P) = 2.7$ Hz; $P(CH_3)_3$), 33.4 (dd, $^1J(C,P) = 20.4$ Hz; $^3J(C,P) = 1.6$ Hz; P−CHPh), 35.7 (dd, $^1J(C,P) = 21.9$ Hz; $^3J(C,P) = 3.9$ Hz; P−CHPh), 126.2−133.2 (m, Ph), 135.7 (d, $^3J(C,P) = 7.0$ Hz; *ipso*-Ph), 137.4 (s; *ipso*-Ph), 208.7 (t, $^2J(C,P) = 10.3$ Hz; *cis*-CO), 214.2 (m; *trans*-CO). IR (CH_2Cl_2): ν(CO) = 2022 (w), 1913 (vs), 1881 (sh) cm^{-1}. HRMS (70 eV): *m/z* (%) 574 (2) [M^+], 394 (3) [$PhPMo(CO)_4P(CH_3)_3$], 366 (4) [$PhPMo(CO)_3P(CH_3)_3$], 338 (4) [$PhPMo(CO)_2P(CH_3)_3$], 310 (7) [$PhPMo(CO)P(CH_3)_3$], 288 (10) [$M^+ - Mo(CO)_4P(CH_3)_3$], 179 (100) [PhCHCHPh]. HR-MS: calcd for $C_{27}H_{26}O_4P_2Mo$, 574.03601; found, 574.03559.

Synthesis of *cis*-(Trimethylphosphine)(1,2-diphenylphosphirane)tetracarbonylmolybdenum, 11. A mixture of **8** (400 mg, 0.65 mmol) and styrene (0.75 mL, 6.50 mmol) dissolved in 15 mL of dry toluene was stirred at 70 °C for 9.5 h. Column chromatography (silica gel, pentane/dichloromethane, 7:3) and recrystallization from dichloromethane/hexane gave **11** (165 mg, 51%) as colorless crystals. Two diastereomers were formed in a 8:1 ratio. The two isomers can be separated by slow recrystallization from dichloromethane/hexane. The minor isomer was not obtained in pure form.

Major isomer: mp 66−67 °C. ^{31}P NMR ($CDCl_3$): δ −125.6 (d, $^2J(P,P) = 31.4$ Hz; phosphirane), −14.6 (d, $^2J(P,P) = 31.4$ Hz; $P(CH_3)_3$). ^1H NMR ($CDCl_3$): δ 1.34 (d, $^2J(P,H) = 6.8$ Hz; 9H, $P(CH_3)_3$), 1.74−1.82 (m, 1H, P−CH), 2.22−2.32 (m, 1H, P−CH), 2.89−2.96 (m, 1H, P−CH), 6.81−6.85 (m; 2H, Ph), 7.00−7.15 (m, 8H, Ph). ^{13}C NMR ($CDCl_3$): δ 14.3 (dd, $^1J(C,P) = 16.1$ Hz; $^3J(C,P) = 2.0$ Hz; PCH_2), 21.0 (dd, $^1J(C,P) = 22.9$ Hz; $^3J(C,P) = 2.8$ Hz; $P(CH_3)_3$), 30.8 (dd, $^1J(C,P) = 20.8$ Hz; $^3J(C,P) = 3.6$ Hz; P−CHPh), 126.1−133.4 (m, Ph), 133.8 (d, $^1J(C,P) = 15.9$ Hz; *ipso*-Ph), 136.0 (d, $^2J(C,P) = 5.5$ Hz; *ipso*-Ph), 209.0 (t, $^2J(C,P) = 10.4$ Hz; *cis*-CO), 214.5 (dd, $^2J(C,P) = 24.3$ Hz, $^2J(C,P) = 11.0$ Hz; *trans*-CO), 214.5 (dd, $^2J(C,P) = 34.3$ Hz, $^2J(C,P) = 8.8$ Hz; *trans*-CO). IR (CH_2Cl_2): ν(CO) = 2021 (w), 1907 (vs), 1889 (sh) cm^{-1}. HR-MS: calcd for $C_{21}H_{22}O_4P_2Mo$ 498.0047, found 498.0043.

Chart 1. Schematic View of Equipment for Decomplexation Reactions



Minor isomer: ^{31}P NMR ($CDCl_3$) δ −124.6 (d, $^2J(P,P) = 31.4$ Hz; phosphirane), −14.9 (d, $^2J(P,P) = 31.4$ Hz; $P(CH_3)_3$).

Decomplexation of Phosphirene−$Mo(CO)_4PMe_3$, 9. A NMR tube was charged with phosphirene complex **9** (89 mg, 0.15 mmol) and 1.5 mL of dry THF. The tube was pressurized at 25 bar of CO and heated for 48 h at 60 °C. ^{31}P NMR showed complete conversion of the complex to the free phosphirene (see Figure 1). The reaction mixture was filtered over a short silica gel column. Recrystallization from pentane gave **12** (40 mg, 94%). Mp: 76−77 °C (lit. 73 °C). ^{31}P NMR ($CDCl_3$): δ −187.2 (s). ^1H NMR ($CDCl_3$): δ 7.19−7.25 (m, 3H; Ph), 7.40−7.51 (m, 8H; Ph), 7.84−7.88 (m, 4H; Ph). The spectroscopic data are identical to those of ref 15.

Decomplexation of Phosphirane−$Mo(CO)_4PMe_3$, 10. A NMR tube was charged with phosphirane complex **10** (5 mg, 9 μmol) and 0.75 mL of dry THF. The tube was pressurized at 25 bar of CO and heated for 24 h at 60 °C. ^{31}P NMR showed complete conversion of the complex to the free phosphirane **13**. Upon prolonged heating, thermal degradation of the phosphirane was observed.

^{31}P NMR [intensity] (THF): δ −147.5 (s, phosphirane) [0.995], −15.1 (s, $Mo(CO)_5PMe_3$) [1.000].

Decomplexation of Phosphirane−$Mo(CO)_4PMe_3$, 11a. A NMR tube was charged with phosphirane complex **11a** (5 mg, 10 μmol) and 0.75 mL of dry THF. The tube was pressurized at 25 bar of CO and heated for 10 h at 60 °C. ^{31}P NMR showed clean conversion of the complex to the free phosphirane. The conversion of complex to free phosphine was 1:3, but without formation of byproducts. Upon prolonged heating, thermal degradation of the phosphirane **14** was observed.

^{31}P NMR [intensity] (THF): δ −182.2 (s, free phosphirane) [1.00], −125.7 (d, ^{2}J(P,P) = 31.4 Hz; complex) [0.35], −14.9 (s, $Mo(CO)_5PMe_3$) [1.05], −14.5 (d, ^{2}J(P,P) = 31.4 Hz; complex) [0.37].

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Supporting Information Available: NMR spectra (^{31}P, ^{1}H, and ^{13}C) for compounds **7**, **8**, **9**, **10**, and **11a/b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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