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Bidentate Phosphorus Baskets by Intramolecular Phosphinidene Addition

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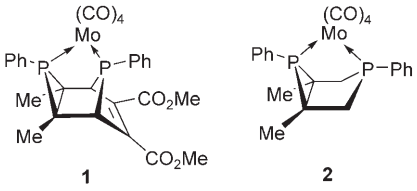
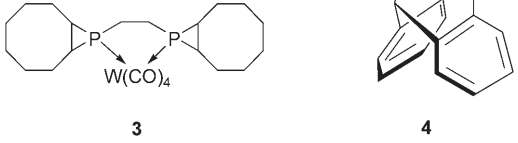
Abstract: Intramolecular phosphinidene addition to the C=C bond of Mo-complexed, seven-membered phosphorus heterocycles affords three novel [(diphos)Mo(CO)$_4$] complexes (**18**–**20**). The three bidentate phosphorus baskets differ in the composition of the seven-membered ring: one of the phosphorus atoms is flanked by CH_2, NCH_3, or O. The unsaturated tetrahydrophosphepine precursors are synthesized by either ring-closing metathesis (C and N derivatives) or by a cyclization sequence (O derivative). The crystal structures of the nitrogen- (**19**) and oxygen-containing (**20**) baskets have relatively small P-Mo-P angles of 76.240(13)° and 77.626(12)°, respectively, and complex **20** has slightly shortened Mo–P bond lengths.

Keywords: molybdenum · cage compounds · P ligands · phosphinidene complexes · phosphorus heterocycles

Introduction

Transition-metal complexes with polycyclic bidentate phosphane ligands are rare. They are of interest because the structural rigidity of the ligand can affect both the access to, and the electronic properties of, the transition metal, which are aspects relevant to the design of catalysts. Two such molybdenum complexes are known, one (**1**) with a tricyclic ligand and the other (**2**) with a bicyclic ligand.[1] Their phosphorus atoms are separated by two C_2 bridges. The crystal structure of **2** has an extremely small P–Mo–P bond angle of 69.732(16)°. Both these highly stable complexes have a chelating phosphirane ring, and they were synthesized by *intra*molecular cycloaddition of a transient phosphinidene ($RPML_n$) to the double bond of the five-membered phosphole ring (L) using the transition-metal in *cis*-[RPMo(CO)$_4$L] as template. Mathey et al.[2] have used a related double *inter*molecular cycloaddition (to cyclooctene) for the synthesis of **3**. The BABAR-Phos (**4**) system developed by Grützmacher et al.,[3] another polycyclic ligand with a phosphirane ring, has demonstrated its potential in catalysis. This very stable ligand has the advantage of being reformed from the metallaphosphetane, which otherwise usually leads to loss of catalyst.[4]





In the present study we report new molybdenum complexes with larger polycyclic bidentate phosphorus ligands that include N and O atoms embedded in the hydrocarbon frame that separates the phosphorus atoms. As starting

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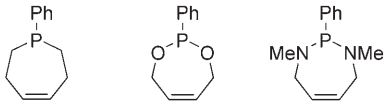
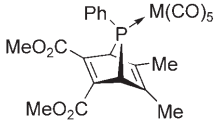
point we use the *P*-phenyl derivatives of the seven-membered rings (L) 2,3,6,7-tetrahydro-1*H*-phosphepine (**5**), 1,3-dimethyl-2,3,4,7-tetrahydro-1*H*-1,3,2-diazophosphepine (**6**), and 4,7-dihydro-1,3,2-dioxaphosphepine (**7**). Our strategy involves ligating the ring in a *cis* fashion in $[PMo(CO)_4L]$ and converting the P ligand to a terminal phosphinidene complex for subsequent *intra*molecular cycloaddition to the olefinic bond of the seven-membered ring (L) to build the new "baskets" **18**, **19**, and **20**. Relevant to the synthesis is whether the cycloaddition is influenced by the ring size of ligand L and whether heteroatoms will influence this process, for example, by competing ylide formation.



5 **6** **7**

Results and Discussion

The three systems are discussed separately, with each section starting with the synthesis of the seven-membered ring. Of the possible phosphinidene precursors,[5] we use the established 7-phosphanorbornadiene unit **8**.



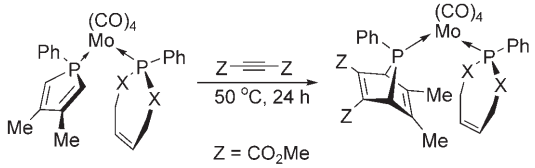
M = W, Mo, Cr

8

Diphos basket 18: The starting point is the synthesis of **5** (Scheme 1), the key step of which is the ring-closing metathesis (RCM) of diene **9** (obtained from reaction of phenylphosphonic dichloride with two equivalents of allylmagnesium bromide),[6] in the presence of 6% of the Grubbs' first-generation catalyst $[RuCl_2(PCy_3)_2{=}CHPh]$ (**11**).[7] Reduction of the resulting oxide **10** at 80°C with phenylsilane[8] gave the desired tetrahydrophosphepine **5** without side products, as shown by the clean conversion of the ^{31}P NMR resonance at $\delta = +41.7$ ppm of the starting material into one at $\delta = -13.5$ ppm.

Because **5** is sensitive toward oxidation it was not isolated, but was treated directly with *cis*-$[Mo(CO)_4(piperidine)_2]$[9] and 3,4-dimethyl-1-phenylphosphole. The expected mixed-chelate Mo complex **12** (44%; see Scheme 2) was formed together with smaller amounts of the bistetrahydrophosphepine (<10%) and bisphosphole complexes (<10%), as suggested by their resonances at $\delta = 25.1$ and 33.5 ppm, respectively, in the ^{31}P NMR spectrum. Product **12** shows two doublets at $\delta = 26.1$ and 32.7 ppm with a normal $^2J_{P,P}$ coupling constant of 24.0 Hz. The IR carbonyl frequencies at 2021, 1915, and 1890 cm^{-1} and the ^{13}C NMR carbonyl resonances at $\delta = 215.5$, 215.2, and 210.1 ppm confirm that the crucial *cis* configuration at the transition-metal center is maintained.

Next, the phosphole ring must be converted into the phosphinidene precursor for the critical cycloaddition to the olefinic bond of the seven-membered ring ligand. Precursor **15** was obtained (63%) in the usual manner by a Diels–Alder reaction with dimethylacetylene dicarboxylate (Scheme 2). Again, the complex maintains its *cis* configuration.



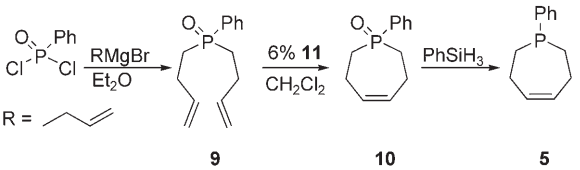
Z = CO_2Me

12	X = CH_2	**15**
13	X = NMe	**16**
14	X = O	**17**

Scheme 2. Synthesis of the 7-phosphanorbornadiene–Mo complexes.

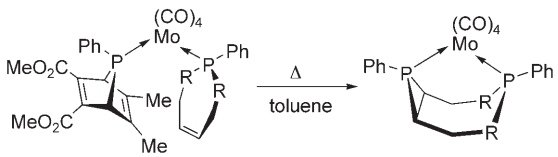
Product **15** shows two doublets in the ^{31}P NMR spectrum at $\delta = 25.7$ and 251.9 ppm for the phosphepine and 7-phosphanorbornadiene P atoms, respectively, with a normal $^2J_{P,P}$ coupling constant of 26.1 Hz. The large downfield shift from phosphole to 7-phosphanorbornadiene is normal.

Heating complex **15** in toluene at 80°C gave, after thermal decomposition of the 7-phosphanorbornadiene ligand to generate the transient phosphinidene complex, the desired cycloadduct **18** as the sole isolable, high-melting (m.p. 194–195°C) product in 66% yield (Scheme 3). The ^{31}P NMR spectrum exhibits two doublets ($^2J_{P,P} = 38.4$ Hz), one at $\delta = +16.5$ ppm for the phosphepane ring and one at $\delta = -150.5$ ppm for the phosphirane ring. $Mo(CO)_5$-complexed phosphiranes have more deshielded resonances in the range



9 **10** **5**

Scheme 1. Synthesis of tetrahydrophosphepine **5**.

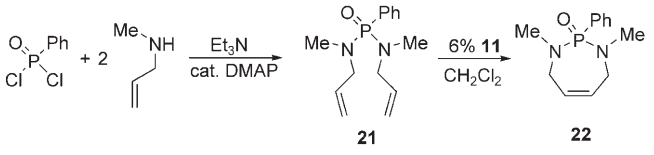


15	X = CH_2	**18**
16	X = NMe	**19**
17	X = O	**20**

Scheme 3. Phosphinidene addition to give novel diphos baskets **18**–**20**.

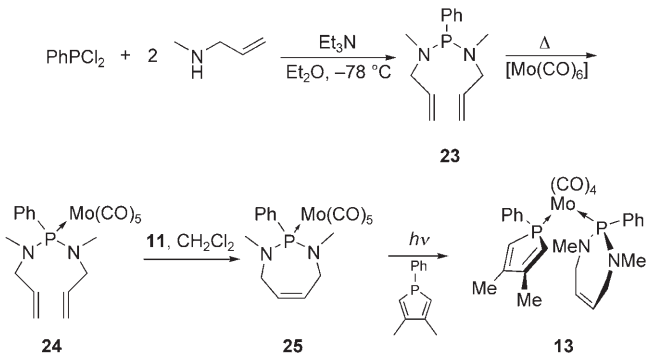
$\delta = -115$ to -135 ppm,[10,11] while those for **1** ($\delta = -101.7$ ppm) and **2** ($\delta = -79.7$ ppm) are at still lower field with no (**1**) or only a small $^2J_{P,P}$ coupling constant (**2**, 8.1 Hz). The ^{31}P NMR chemical shift of 15.4 ppm for the phospholane ring of **2** is similar to that of the phosphepane ring of **18**, but here also the ring-size effect seems to be present when comparing the chemical shifts of the "basket" and its precursor: **18** shows an upfield shift of 9.2 ppm compared to **15** and an *increase* of 12.3 Hz for $^2J_{P,P}$, while ring closure leading to **2** gives an 18.3-Hz *decrease* in $^2J_{P,P}$ and a smaller upfield shift of 4.2 ppm for the five-membered-ring phosphorus. No strain effects are evident from the ^{13}C NMR parameters of the hydrocarbon frame of **18** or in comparison with **2**.

Diphos basket 19: The synthesis of the seven-membered ring structure **6** was similar to that for **5** (Scheme 4), following a procedure described for the related phosphonamides.[12] While, N-methylallylamine (2 equiv) reacted with $PhP(O)Cl_2$ to give **21** (67%), and whereas ring-closing metathesis with the Grubbs' first-generation catalyst **11** yielded oxide **22** (78%), no reduction occurred with $PhSiH_3$ or $HSiCl_3/Et_3N$. Therefore, the approach outlined in Scheme 5 was followed. In this route, *N*-methylallylamine is treated with dichlorophenylphosphane, instead of the oxide, to give **23** (95%), and the stabilizing transition-metal group, using freshly prepared $[Mo(CO)_5(MeCN)]$ or $[Mo(CO)_6]$,[13] is added (**23** → **24** (30%)) before the RCM step (**24** → **25** (97%)). The ^{31}P NMR spectrum shows that the introduction of $Mo(CO)_5$ is frustrated by the formation of unidentified products (peaks at $\delta = 138$, 146, and 150 ppm) in a nearly equal combined ratio to the main product **23** ($\delta = 23.7$ ppm).



21 22

Scheme 4. Synthesis of phosphine oxide **22**.



23 24 25 13

Scheme 5. Synthesis of complex **13**.

The *cis* CO ligand was then exchanged for 3,4-dimethyl-1-phenylphosphole by UV irradiation (THF) to give the Mo complex **13** (28% yield, 51% conversion). Full conversion was not possible because of the limited stability of **13** under these reaction conditions. Diels–Alder reaction of the phosphole ligand with dimethylacetylene dicarboxylate yielded the phosphinidene precursor complex **16** (55%), and thermal decomposition of this complex at 70°C in toluene gave the diphosphane basket **19** in low yield (24%) as colorless crystals (m.p. 83–84°C) along with minor unidentified products ($\delta(^{31}P) = 135$ and 148 ppm). The much lower yield of **19** as compared to **18** indicates a lower selectivity for the cycloaddition, possibly due to the competing formation of an ylide due to interaction of the transient phosphinidene complex with the nitrogen atom. Related P,N-ylides are known as reactive intermediates[14] that are not amenable to isolation, and we expect this to be the case here too. The ring closure of **16** to **19** causes an upfield shift of only 2.4 ppm (to $\delta(^{31}P) = 140.0$ ppm) for the seven-membered heterocycle, although the 32.1-Hz increase in the $^2J_{P,P}$ coupling constant to 58.7 Hz is large. However, the NMR spectroscopic data provide little additional insight.

The formation of **19** was confirmed by a single-crystal X-ray structure determination (Figure 1). The distorted octahedral conformation around Mo, with a small Mo1-C22-O4 bond angle (170.42(16)°) and a larger than usual P2-Mo1-C22 bond angle (99.07(5)°) is due to interaction of the C5-methyl group at N1 with the C22-O4 carbonyl group. The P-Mo-P bite angle of 76.240(13)° is significantly larger than for the tighter **2** (69.732(16)°) and is only 2.6° smaller than

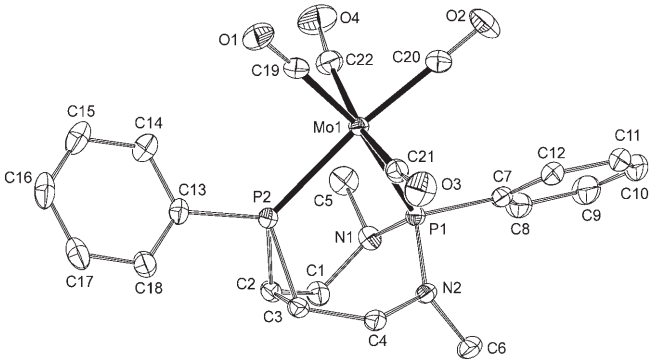


Figure 1. Structure of **19** (displacement ellipsoid plot drawn at the 50% probability level). Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å], angles, and torsion angles [°]: Mo1–P1 2.5079(4), Mo1–P2 2.4917(4), P1–N1 1.7144(13), P1–N2 1.6726(13), P2–C2 1.8538(15), P2–C3 1.8317(16), C1–N1 1.474(2), C4–N2 1.4760(19), C5–N1 1.470(2), C6–N2 1.4701(19), C1–C2 1.535(2), C2–C3 1.526(2), C3–C4 1.525(2); P1-Mo1-P2 76.240(13), P1-Mo1-C20 98.26(5), P1-Mo1-C21 92.30(4), P1-Mo1-C22 95.44(5), P2-Mo1-C19 91.82(5), P2-Mo1-C21 92.12(5), P2-Mo1-C22 99.07(5), Mo1-P1-N1 115.26(5), Mo1-P1-N2 114.10(5), Mo1-P1-C7 118.07(5), Mo1-P2-C13 125.31(5), N1-P1-N2 101.81(7), C2-P2-C3 48.90(7), P1-N1-C1 114.99(10), P1-N2-C4 121.49(10), P1-N1-C5 117.16(11), P1-N2-C6 121.21(11), P2-C2-C3 64.79(8), P2-C3-C2 66.30(8), P2-C2-C1 124.47(11), P2-C3-C4 118.81(11), N1-C1-C2 118.48(13), N2-C4-C3 117.41(13), P1-N1-C1-C2 43.94(18), P1-N2-C4-C3 39.03(18), N1-C1-C2-C3 −72.6(2), C2-C3-C4-N2 21.1(2), C1-C2-C3-P2 116.27(14), P2-C2-C3-C4 −110.09(15).

for the five-membered chelate [(dppe)Mo(CO)$_4$] (dppe = 1,2-bis(diphenylphosphino)ethane).[15] The Mo1–P1 and Mo1–P2 bond lengths of 2.5079(4) and 2.4917(4) Å, respectively, are in the normal range.[1,16] The steric congestion caused by the methyl group at N1 is also reflected in the seven-membered ring, where the P1–N1 bond (1.7144(13) Å) is slightly longer than the P1–N2 bond (1.6726(13) Å) and the bond angles around N1 are smaller (P1-N1-C1 114.99(10)° and P1-N1-C5 117.16(11)° versus P1-N2-C4 121.49(10)° and P1-N2-C6 121.21(11)°). While the nitrogen centers of the molecules in the crystal are chiral, the whole crystal is racemic (centrosymmetric space group); pyramidal inversion of the nitrogen atoms is rapid in solution.

Diphos basket 20: Phosphonite **7** was synthesized in a single step (75%) by condensing *cis*-but-2-ene-1,4-diol with dichlorophenylphosphane in the presence of triethylamine as base. Purification by distillation reduced the yield drastically.[17] Synthesis of **7** in a manner analogous to **5** is not a viable alternative as the sluggish RCM occurs in poor yield.[12] Reaction of **7** with *cis*-[Mo(CO)$_4$(piperidine)$_2$] and 3,4-dimethyl-1-phenylphosphole afforded **14** (30%), and the subsequent Diels–Alder reaction with dimethylacetylene dicarboxylate gave **17** (69%). Thermal decomposition at 80 °C in toluene gave the desired and very stable diphosphane basket **20** in reasonable yield (61%) as colorless crystals (m.p. 169–170 °C). As for **19**, ring closure causes essentially no deshielding (0.9 ppm) of the ^{31}P NMR signal for the seven-membered ring (**20**: $\delta = 140.0$ ppm), but the $^2J_{P,P}$ coupling constant (**20**: 66.8 Hz) increases more (34.2 Hz). The NMR spectroscopic data provide little additional insight in this case as well.

A single-crystal X-ray structure determination of **20** (Figure 2) shows the same features as for **19**, except that the octahedral conformation around Mo is less distorted, as reflected in the smaller *cis*-P-Mo-C bond angles. The P1-Mo1-P2 bond angle of 77.626(12)° is similar in magnitude to that of **19**. The two P–Mo distances of **20** (2.4624(4) and 2.4606(4) Å) are virtually identical and are about 0.04 Å shorter than those of **1, 2**, **19**, and other Mo(CO)$_n$-complexed phosphiranes,[1,16] but similar to those of [RO(R′)$_2$PMo(CO)$_5$] (2.436 Å) and [(RO)$_3$PMo(CO)$_5$] (2.485 Å);[18] we are not aware of structural data for molybdenum phosphonite complexes such as [(OC)$_5$MoP(OR)$_2$R′]. The P–O bonds (1.6122(11) and 1.6229(10) Å) are slightly longer than usual.[18]

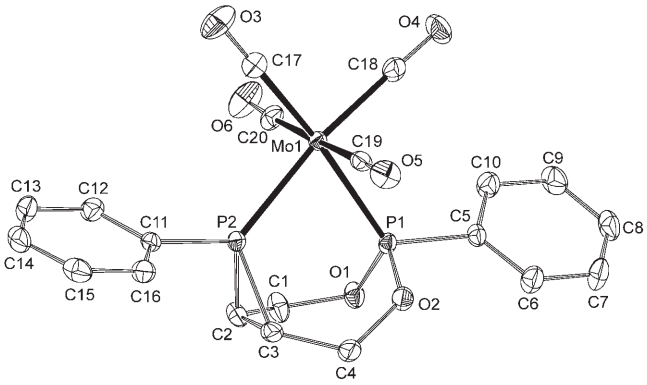


Figure 2. Structure of **20** (displacement ellipsoid plot drawn at the 50% probability level). Selected bond lengths [Å], angles, and torsion angles [°]: Mo1–P1 2.4624(4), Mo1–P2 2.4606(4), P1–O1 1.6122(11), P1–O2 1.6229(10), P2–C2 1.8309(15), P2–C3 1.8330(15), C1–O1 1.4457(18), C4–O2 1.4399(18), C1–C2 1.512(2), C2–C3 1.525(2), C3–C4 1.512(2); P1-Mo1-P2 77.626(12), P1-Mo1-C18 94.75(4), P1-Mo1-C19 85.92(4), P1-Mo1-C20 95.76(4), P2-Mo1-C17 96.32(5), P2-Mo1-C19 86.94(4), P2-Mo1-C20 93.38(4), Mo1-P1-O1 119.42(4), Mo1-P1-O2 110.58(4), Mo1-P1-C5 123.14(5), Mo1-P2-C11 129.20(5), O1-P1-O2 101.77(6), C2-P2-C3 49.20(7), P1-O1-C1 122.99(9), P1-O2-C4 119.99(9), P2-C2-C3 65.47(8), P2-C3-C2 65.32(8), P2-C2-C1 119.59(11), P2-C3-C4 125.06(11), O1-C1-C2 115.76(13), O2-C4-C3 118.32(12), P1-O1-C1-C2 −40.05(19), P1-O2-C4-C3 −30.58(19), O1-C1-C2-C3 −18.7(2), C2-C3-C4-O2 61.4(2), C1-C2-C3-P2 110.41(15), P2-C2-C3-C4 −116.67(15).

Conclusion

The synthesis of the novel Mo complexes **18**–**20** expands the access to a new class of unsymmetrical diphos chelates in which the chains (C-C-X versus C–C) connecting the phosphorus atoms and the substitution pattern (X = CH_2, NCH_3, O) around one of them can be varied, particularly to a small number of O- and N-containing diphos chelates. The novel "baskets" were obtained by metal-template-directed *intra*-molecular addition of the [Mo(CO)$_4$L] phosphinidene complex to the double bond of the seven-membered ring ligand L (L = 2,3,6,7-tetrahydro-1*H*-phosphepine (**5**), 1,3-dimethyl-2,3,4,7-tetrahydro-1*H*-1,3,2-diazophosphepine (**6**), and 4,7-dihydro-1,3,2-dioxaphosphepine (**7**)) Complex **18** and the dioxygen-containing **20** are very stable on heating, as opposed to the nitrogen homologue **19**, which may explain its lower yield of formation. The ^{31}P NMR resonances for the phosphirane ring are at similar high field (ca. $\delta = -150$ ppm) for all three complexes, but the already large $^2J_{P,P}$ coupling constants increase from 38.1 to 58.7 to 66.8 Hz for **18**, **19**, and **20**, respectively. The crystal structures of **19** and **20** show small P-Mo-P bite angles of 76.240(13)° and 77.626(12)°, respectively. The new compounds are strong chelating complexes: the transition-metal group cannot be liberated from the ligand by either heating with sulfur,[19] oxidation by iodine followed by ligand exchange,[20] or ligand displacement with bis(diphenylphosphanyl)ethane.[10]

Experimental Section

All experiments were performed under an atmosphere of dry nitrogen. Solids were dried in vacuo 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. Diethyl ether was distilled over $LiAlH_4$. CH_2Cl_2 was dried over P_2O_5. *cis*-[Mo(CO)$_4$(piperidine)$_2$][9] and 3,4-dimethyl-1-phenylphosphole[21] were prepared according to literature procedures. NMR spectra were recorded with a Bruker WM 250 spectrometer (^{1}H, ^{13}C) and internally referenced to residual solvent resonances or 85% H_3PO_4 (^{31}P) as external standard. IR spectra were recorded with a Mattson 6030 Galaxy FT-IR spectropho-

tometer and high-resolution mass spectra (HR-MS) with a Finnigan Mat 900 spectrometer. Melting points were measured for samples in unsealed capillaries and are uncorrected.

Synthesis of *cis*-tetracarbonyl(3,4-dimethyl-1-phenyl-1*H*-phosphole)(1-phenyl-2,3,6,7-tetrahydro-1*H*-phosphepine)molybdenum (12)

Synthesis of 1-phenyl-2,3,6,7-tetrahydro-1H-phosphepine 1-oxide (***10***): Grubbs' catalyst **11** (6 mol%) was added in three equal portions to a solution of diene **9** (2.5 g, 10.7 mmol) in dichloromethane (0.02 M). The reaction mixture was heated at reflux until full conversion of the starting material, as shown by ^{31}P NMR spectroscopy. The solvent was then evaporated and product **10** purified by column chromatography (silica gel, ethyl acetate/ethanol, 10:1) to yield a colorless solid (955 mg, 44%). A publication by Gouverneur et al. reports 89% isolated yield,[7] although product characterization was not included.

M.p. 75–76 °C; ^{1}H NMR ($CDCl_3$): δ = 1.85–2.09 (m, 4H; PCH_2), 2.15–2.40 (m, 2H; CH_2C=), 2.80–2.91 (m, 2H; CH_2C=), 7.46–7.51 (m, 3H; Ar), 7.69–7.77 ppm (m, 2H; Ar); ^{13}C NMR ($CDCl_3$): δ = 19.4 (d, $^2J_{P,C}$ = 5.0 Hz; CH_2), 29.3 (d, $^1J_{P,C}$ = 66.0 Hz; CH_2-P), 128.8 (d, $^2J_{P,C}$ = 11.2 Hz; *o*-Ph), 130.1 (d, $^3J_{P,C}$ = 9.0 Hz; *m*-Ph), 131.8 (d, $^4J_{P,C}$ = 2.7 Hz; *p*-Ph), 132.4 (s, = CH phosphepine), 134.1 ppm (d, $^1J_{P,C}$ = 94.5 Hz; *ipso*-Ph); ^{31}P NMR ($CDCl_3$): δ = 41.7 ppm (s); HR-MS calcd for $C_{12}H_{15}OP$: 206.0861; found 206.08671 (δ 2 × 10^{-3}).

Reduction of ***10*** *to phosphane* ***5***: 1-Phenyl-2,3,6,7-tetrahydro-1*H*-phosphepine 1-oxide (**10**; 500 mg, 2.43 mmol) was dissolved in phenylsilane (2.4 mL) and the mixture was heated for 4 h at 80 °C. Excess phenylsilane was evaporated off under reduced pressure and the resulting oil was extracted with hexane (2 × 10 mL). Product **5** is very sensitive towards oxygen and was used without further purification. ^{31}P NMR (hexane): δ = −13.5 ppm (s).

Synthesis of ***12***: A mixture of *cis*-[$Mo(CO)_4$(piperidine)$_2$] (0.925 g, 2.42 mmol) and 3,4-dimethyl-1-phenylphosphole (0.462 g, 2.42 mmol) was stirred in refluxing dichloromethane (20 mL) for 10 min. 1-Phenyl-2,3,6,7-tetrahydro-1*H*-phosphepine was then added and the mixture was stirred at reflux for an additional 2 h. Evaporation to dryness and column chromatography (silica gel; pentane/dichloromethane, 4:1) afforded **12** (600 mg, 41%) as a yellow solid. Recrystallization from dichloromethane/hexane gave yellow crystals. M.p. 104–105 °C; ^{1}H NMR ($CDCl_3$): δ = 2.02 (s, 6H; CH_3), 2.14–2.38 (m, 8H; CH_2 & CH_2P), 5.74 (m, 2H; phosphepine-CH), 6.15 (d, $^2J_{P,H}$ = 36.0 Hz, 2H; phosphole-CH), 7.26–7.36 ppm (m, 10H; Ar); ^{13}C NMR ($CDCl_3$): δ = 17.7 (d, $^3J_{P,C}$ = 9.9 Hz; CH_3), 23.4 (d, $^2J_{P,C}$ = 4.5 Hz; CH_2), 28.9 (dd, $^1J_{P,C}$ = 18.4, $^3J_{P,C}$ = 2.0 Hz; CH_2P), 128.6–131.3 (m, Ar), 131.1 (dd, $^1J_{P,C}$ = 35.4, $^3J_{P,C}$ = 1.8 Hz; PCH), 131.6 (s; CH_2C=), 133.5 (dd, $^3J_{P,C}$ = 1.7, $^1J_{P,C}$ = 16.0 Hz; phosphole *ipso*-Ph), 139.0 (dd, $^3J_{P,C}$ = 1.6, $^1J_{P,C}$ = 27.2 Hz; phosphepine *ipso*-Ph), 149.0 (d, $^2J_{P,C}$ = 7.8 Hz; CH*C*CH_3), 210.1 (t, $^2J_{P,C}$ = 9.2 Hz; CO_{ax}), 215.2 (dd, $^2J_{P,C}$ = 8.2, $^2J_{P,C}$ = 16.0 Hz; CO_{eq}), 215.5 ppm (dd, $^2J_{P,C}$ = 8.7, $^2J_{P,C}$ = 21.3 Hz; CO_{eq}); ^{31}P NMR ($CDCl_3$): δ = 26.1 (d, $^2J_{P,P}$ = 24.0 Hz; phosphepine), 32.7 ppm (d, $^2J_{P,P}$ = 24.0 Hz; phosphole); HR-MS calcd for $C_{28}H_{28}MoO_4P_2$: 588.0518; found 588.04955 (δ 2 × 10^{-3}); IR (CH_2Cl_2): $\tilde{\nu}$ = 2017 (m) (ν(CO)), 1907 (s) (ν(CO)), 1871 cm^{-1} (sh) (ν(CO)).

Synthesis of tetracarbonyl(3,4-dimethyl-1-phenyl-1*H*-phosphole)(1,3-dimethyl-2-phenyl-2,3,4,7-tetrahydro-1*H*-[1,3,2]diazaphosphepine)molybdenum (13)

Synthesis of N,N′-diallyl-N,N′-dimethyl-P-phenylphosphonic diamide (**21**): A solution of $PhP(O)Cl_2$ (975 mg, 5.0 mmol) and Et_3N (1.01 g, 10 mmol) in dichloromethane (25 mL) was slowly added to a stirred solution of methylallylamine (710 mg, 10 mmol) containing a catalytic amount of DMAP (31 mg, 0.05 mmol) in dichloromethane (50 mL) at 0 °C. After 2 h, the solvent was evaporated and diethyl ether (50 mL) was added to yield a yellow solution and pale yellow salts. The solution was filtered and the salts washed with diethyl ether (10 mL). Evaporation and column chromatography (silica gel; ethyl acetate/MeOH, 95:5) yielded **21** (890 mg, 67%) as a colorless oil.

^{1}H NMR ($CDCl_3$): δ = 2.58 (d, $^3J_{P,H}$ = 10.0 Hz, 6H; NCH_3), 3.57 (m, 4H; CH_2N), 5.10–5.19 (m, 4H; =CH_2), 5.63–5.77 (m, 2H; CH), 7.43–7.47 (m, 3H; Ar), 7.73–7.81 ppm (m, 2H; Ar); ^{13}C NMR ($CDCl_3$): δ = 33.1 (d, $^2J_{P,C}$ = 3.5 Hz; NCH_3), 51.5 (d, $^2J_{P,C}$ = 4.2 Hz; NCH_2), 117.6 (s; =CH_2), 128.5 (d, $^2J_{P,C}$ = 13.1 Hz; *o*-Ph), 131.3 (d, $^1J_{P,C}$ = 154.4 Hz; *ipso*-Ph), 131.5 (d, $^4J_{P,C}$ = 2.8 Hz; *p*-Ph), 132.2 (d, $^3J_{P,C}$ = 8.7 Hz; *m*-Ph), 134.9 ppm (d, $^3J_{P,C}$ = 5.1 Hz; CH=); ^{31}P NMR ($CDCl_3$): δ = 30.0 ppm (s); HR-MS calcd for $C_{14}H_{21}N_2OP$: 264.1391; found 264.13998 (δ 6 × 10^{-3}).

Synthesis of 1,3-dimethyl-2-phenyl-1,3,4,7-tetrahydro-[1,3,2]diazaphosphepine 2-oxide (***22***) *by ring-closing metathesis of* ***21***: Phosphane **21** (500 mg, 1.9 mmol) was dissolved in dichloromethane (100 mL), catalyst **11** (47 mg, 0.06 mmol) was added, and the purple solution was heated at reflux for 3 h. After evaporation of solvent and column chromatography (silica gel; ethyl acetate/methanol, 95:5), **22** (350 mg, 78%) was isolated as a colorless oil.

^{1}H NMR ($CDCl_3$): δ = 2.69 (d, $^3J_{P,H}$ = 9.5 Hz, 6H; NCH_3), 3.44–3.57 (m, 2H; CH_2N), 3.71–3.85 (m, 2H; CH_2N), 5.68 (t, $^3J_{H,H}$ = 2.4 Hz, 2H; = CH_2), 7.44–7.49 (m, 3H; Ar), 7.78–7.85 ppm (m, 2H; Ar); ^{13}C NMR ($CDCl_3$): δ = 36.1 (d, $^2J_{P,C}$ = 4.4 Hz; CH_3), 48.0 (d, $^2J_{P,C}$ = 2.8 Hz; CH_2), 127.6 (s; CH=), 128.6 (d, $^2J_{P,C}$ = 13.3 Hz; *o*-Ph), 130.2 (d, $^1J_{P,C}$ = 159.9 Hz; *ipso*-Ph), 131.7 (d, $^4J_{P,C}$ = 2.8 Hz; *p*-Ph), 132.5 ppm (d, $^3J_{P,C}$ = 8.8 Hz; *m*-Ph); ^{31}P NMR ($CDCl_3$): δ = 32.3 ppm (s); HR-MS calcd for $C_{12}H_{27}N_2OP$: 236.1078; found 236.10786 (δ 4 × 10^{-4}).

Synthesis of N,N′-diallyl-N,N′-dimethyl-P-phenyl phosphonous diamide (***23***): $PhPCl_2$ (0.712 mL, 5.2 mmol) was dissolved in dry diethyl ether (25 mL) and cooled to −78 °C. A mixture of allylmethylamine (1.00 mL, 10.5 mmol) and triethylamine (1.5 mL, 10.5 mmol) was then added slowly from a dropping funnel. The reaction mixture was slowly warmed up to room temperature and the salts were filtered off. Evaporation of the solvent yielded diaminophosphane **23** (1.23 g; 95%) of sufficient purity for further use. ^{1}H NMR ($CDCl_3$): δ = 2.61 (d, $^3J_{P,H}$ = 6.5 Hz, 6H; NCH_3), 3.63–3.69 (m, 4H; CH_2N), 5.13–5.23 (m, 4H; =CH_2), 5.80–5.91 (m, 2H; CH), 7.28–7.45 ppm (m, 5H; Ar); ^{31}P NMR ($CDCl_3$): δ = 102.3 ppm (s).

Synthesis of (N,N′-diallyl-N,N′-dimethyl-P-phenyl phosphonous diamide)-pentacarbonylmolybdenum (***24***): a) A solution containing [$Mo(CO)_5$(MeCN)] was prepared according to the literature procedure[22] from [$Mo(CO)_6$] (1.32 g, 5 mmol). A solution containing phosphane **23** (1.27 g, 5.0 mmol) in hexane (10 mL) was then slowly added. ^{31}P NMR spectroscopy showed the formation of several unidentified products. Column chromatography (silica gel, hexane) afforded complex **24** (470 mg, 0.97 mmol; 20% yield) as a thick oil.

b) A solution containing [$Mo(CO)_6$] (4.84 g, 18.5 mmol) and phosphane **23** (3.67 g, 14.8 mmol) was heated at 100 °C in methylcyclohexane (100 mL) for 3 h. ^{31}P NMR spectroscopy showed the formation of several products, most of which were identical to those obtained by method a). After the mixture had been cooled to room temperature, the unreacted [$Mo(CO)_6$] was filtered off and the remaining yellow solution was evaporated under reduced pressure. Column chromatography (silica gel, pentane) afforded the complexed phosphane **24** (2.15 g; 30%) as a thick oil, which solidified in the freezer. M.p. 31–32 °C; ^{1}H NMR ($CDCl_3$): δ = 2.72 (d, $^3J_{P,H}$ = 10.0 Hz, 6H; CH_3), 3.70–3.91 (m, 4H; CH_2N), 5.23–5.31 (m, 4H; =CH_2), 5.73–5.86 (m, 2H; CH), 7.26–7.60 ppm (m, 5H; Ar); ^{13}C NMR ($CDCl_3$): δ = 37.7 (d, $^2J_{P,C}$ = 1.8 Hz; CH_3), 56.7 (d, $^2J_{P,C}$ = 8.5 Hz; CH_2N), 118.2 (s; =CH_2), 129.2–130.8 (m; Ar), 135.8 (d, $^3J_{P,C}$ = 6.5 Hz; CH), 141.7 (d, $^1J_{P,C}$ = 61.7 Hz; phosphepine *ipso*-Ph), 205.7 (d, $^2J_{P,C}$ = 9.8 Hz; CO_{ax}), 211.4 ppm (d, $^2J_{P,C}$ = 27.6 Hz; CO_{eq}); ^{31}P NMR ($CDCl_3$): δ = 126.0 ppm (s); HR-MS calcd for $C_{19}H_{21}MoN_2O_5P$: 486.0242; found 486.02322 (δ 1 × 10^{-3}); IR (CH_2Cl_2): $\tilde{\nu}$ = 2071 (m) (ν(CO)), 1943 cm^{-1} (s) (ν(CO)).

Synthesis of pentacarbonyl(1,3-dimethyl-2-phenyl-1,3,4,7-tetrahydro-[1,3,2]diazaphosphepine)molybdenum (***25***) *by ring-closing metathesis of* ***24***: Complex **24** (470 mg, 0.97 mmol) was dissolved in dichloromethane (25 mL). RCM-catalyst **11** (2 mol%; 16 mg, 0.02 mmol) was added and the mixture was heated at reflux temperature for 10 min. After evaporation of the solvent and column chromatography (silica gel, *n*-hexane), complex **25** (430 mg, 97%) was isolated as a white solid. M.p. 136–137 °C (decomp); ^{1}H NMR ($CDCl_3$): δ = 3.07 (d, $^3J_{P,H}$ = 14.5 Hz, 6H; CH_3), 3.13–3.27 (m, 2H; CH_2N), 4.26–4.35 (m, 2H; CH_2N), 6.10–6.15 (m, 2H; CH), 7.36–7.68 ppm (m, 5H; Ar); ^{13}C NMR ($CDCl_3$): δ = 41.1 (d, $^2J_{P,C}$ = 14.34 Hz; CH_3), 48.8 (d, $^2J_{P,C}$ = 7.2 Hz; CH_2N), 129.5–130.6 (m, Ar), 135.1 (s, CH), 141.8 (d, $^1J_{P,C}$ = 63.7 Hz; *ipso*-Ph), 205.8 (d, $^2J_{P,C}$ = 9.9 Hz; CO_{ax}), 211.5 ppm (d, $^2J_{P,C}$ = 27.1 Hz; CO_{eq}); ^{31}P NMR ($CDCl_3$): δ = 135.1 ppm

(s); HR-MS calcd for $C_{17}H_{27}MoN_2O_5P$: 457.9929; found 457.99393 (δ 1×10^{-3}); IR(CH_2Cl_2): $\tilde{\nu}$ = 2072 (w) (ν(CO)), 1944 cm^{-1} (s) (ν(CO)).

*Synthesis of **13** by irradiation of **25** in the presence of phenylphosphole*: A solution of complex **25** (1.55 g, 3.4 mmol) and 3,4-dimethyl-1-phenylphosphole (637 mg, 3.4 mmol) in THF (100 mL) was prepared. This mixture was irradiated for 5 h with light from a high-pressure Philips Hg lamp (0.9 A, Type 93110E), while N_2 was bubbled through the solution at a slow rate. Evaporation of THF and subsequent column chromatography starting with pentane and gradually changing to pentane/dichloromethane (4:1) resulted in the isolation of complex **13** (580 mg, 28%) as a yellow solid. Furthermore, compound **25** (700 mg, 45%) was recovered and could be re-used. The yields are calculated based on the amount of starting material used (3.4 mmol) and are not corrected for recovery of **25**. Recrystallization of **13** from DCM/hexane gave yellow crystals. M.p. 142–143 °C; ^{1}H NMR ($CDCl_3$): δ = 2.07 (s, 6H; phosphole-CH_3), 2.92 (d, $^3J_{P,H}$ = 14.1 Hz, 6H; NCH_3), 3.11–3.25 (m, 2H; CH_2N), 4.14–4.23 (m, 2H; CH_2N), 6.00 (m, 2H; phosphepine HC=), 6.40 (d, $^2J_{P,H}$ = 35.3 Hz, 2H; phosphole HC=), 7.26–7.60 ppm (m, 10H; Ar); ^{13}C NMR ($CDCl_3$): δ = 17.6 (d, $^3J_{P,C}$ = 10.1 Hz; phosphole-CH_3), 40.0 (dd, $^4J_{P,C}$ = 2.0, $^2J_{P,C}$ = 15.0 Hz; NCH_3), 49.0 (d, $^2J_{P,C}$ = 6.8 Hz; CH_2N), 128.7–131.6 (m, Ar), 131.3 (dd, $^3J_{P,C}$ = 11.6, $^1J_{P,C}$ = 46.7 Hz; phosphole-CH), 133.4 (d, $^1J_{P,C}$ = 32.2 Hz; phosphole *ipso*-Ph), 134.6 (s; phosphepine-CH), 141.7 (d, $^1J_{P,C}$ = 55.7 Hz; phosphepine *ipso*-Ph), 148.7 (d, $^2J_{P,C}$ = 8.11 Hz; P–CH=*C*), 209.3 (dd, $^2J_{P,C}$ = 8.5, $^2J_{P,C}$ = 10.3 Hz; CO_{ax}), 215.0 (dd, $^2J_{P,C}$ = 9.8, $^2J_{P,C}$ = 21.1 Hz; CO_{eq}), 216.2 ppm (dd, $^2J_{P,C}$ = 8.6, $^2J_{P,C}$ = 30.4 Hz; CO_{eq}); ^{31}P NMR ($CDCl_3$): δ = 32.3 (d, $^2J_{P,P}$ = 25.5 Hz; phosphole), 138.2 ppm (d, $^2J_{P,P}$ = 25.5 Hz; phosphepine); HR-MS calcd for $C_{28}H_{30}MoN_2O_4P_2$: 618.0735; found 618.07009 (δ 2×10^{-3}); IR(CH_2Cl_2): $\tilde{\nu}$ = 2022 (m) (ν(CO)), 1908 (s) (ν(CO)), 1875 cm^{-1} (sh) (ν(CO)).

Synthesis of tetracarbonyl(3,4-dimethyl-1-phenyl-1*H*-phosphole)(2-phenyl-4,7-dihydro-[1,3,2]dioxaphosphepine)molybdenum (14)

*Synthesis of 2-phenyl-4,7-dihydro-1,3,2-dioxaphosphepine (**7**)*: $PhPCl_2$ (3.58 g, 20.0 mmol) in 50 mL of diethyl ether was slowly added to a solution of triethylamine (4.55 g, 40.0 mmol) and *cis*-but-2-ene-1,4-diol (1.84 g, 20.0 mmol) in 150 mL of diethyl ether at 0 °C and stirred for 1 h before warming to room temperature. ^{31}P NMR spectroscopy showed an excellent conversion to the desired product. After filtration of the salts and evaporation of solvent, 3.00 g of **7** (>90% pure by ^{31}P NMR) was obtained as a colorless oil, which could be used without further purification. A minor side product (<10% by ^{31}P NMR) at δ = 21.6 ppm was observed. During distillation, a gummy material was formed that reduced the yield dramatically. After distillation at 80 °C/2×10^{-4} mbar, **7** (830 mg; 24%) was obtained as an air-sensitive colorless oil.

^{1}H NMR ($CDCl_3$): δ = 4.45–4.66 (m, 4H; CH_2), 5.75 (t, $^2J_{H,H}$ = 1.9 Hz, 2H; CH_2CH), 7.44–7.48 (m; 3H; Ar), 7.68–7.74 ppm (m; 2H; Ar); ^{13}C NMR ($CDCl_3$): δ = 64.0 (s; CH_2), 128.2 (d, $^4J_{P,C}$ = 4.9 Hz; *m*-Ph), 129.6 (d, $^3J_{P,C}$ = 20.6 Hz; *o*-Ph), 130.0 (s; phosphepine HC=), 131.3 (s; *p*-Ph), 140.8 ppm (d, $^1J_{P,C}$ = 32.0 Hz; *ipso*-Ph); ^{31}P NMR ($CDCl_3$): δ = 161.1 ppm (s).

*Synthesis of **14***: A mixture of *cis*-[$Mo(CO)_4$(piperidine)$_2$] (2.1 g, 5.6 mmol) and 2-phenyl-4,7-dihydro-1,3,2-dioxaphosphepine (**7**; 1.1 g, 5.6 mmol) was stirred in refluxing dichloromethane (20 mL) for 10 min. 3,4-Dimethyl-1-phenylphosphole (1.0 g, 5.6 mmol) in dichloromethane (10 mL) was added and the mixture was stirred at reflux for an additional 3 h. Evaporation to dryness and column chromatography (silica gel; pentane/dichloromethane, 4:1) gave complex **14** (0.841 g; 30%) as a yellow solid. Recrystallization from diethyl ether/hexane afforded yellow crystals. M.p. 111–112 °C; ^{1}H NMR ($CDCl_3$): δ = 2.05 (s, 6H; CH_3), 4.41–4.62 (m, 4H; CH_2), 5.70 (s, 2H; CH, phosphepine), 6.41 (d, $^2J_{P,H}$ = 36.3 Hz, 2H; CH phosphole), 7.29–7.54 ppm (m, 10H; Ar); ^{13}C NMR ($CDCl_3$): δ = 17.7 (d, $^3J_{P,C}$ = 10.3 Hz; CH_3), 64.6 (d, $^2J_{P,C}$ = 6.0 Hz; CH_2), 128.5–131.5 (m; Ph), 129.4 (s; phosphepine HC=), 131.2 (d, $^1J_{P,C}$ = 35.0 Hz; phosphole HC=), 133.8 (d, $^1J_{P,C}$ = 33.0 Hz; phosphole *ipso*-Ph), 141.2 (d, $^1J_{P,C}$ = 33.8 Hz; phosphepine *ipso*-Ph), 148.9 (d, $^2J_{P,C}$ = 8.2 Hz; CH*C*CH_3), 209.0 (dd, $^2J_{P,C}$ = 8.8, $^2J_{P,C}$ = 12.1 Hz; CO_{ax}), 213.7 (dd, $^2J_{P,C}$ = 11.5, $^2J_{P,C}$ = 19.4 Hz; CO_{eq}), 214.0 ppm (dd, $^2J_{P,C}$ = 8.2, $^2J_{P,C}$ = 36.6 Hz; CO_{eq}); ^{31}P NMR ($CDCl_3$): δ = 33.0 (d, $^2J_{P,P}$ = 29.0 Hz; phosphole-P), 190.9 ppm (d, $^2J_{P,P}$ = 29.0 Hz; O-P); HR-MS calcd for $C_{26}H_{24}MoO_6P_2$: 592.0103; found 592.00659 (δ 1×10^{-3}); IR (CH_2Cl_2): $\tilde{\nu}$ = 2025 (m) (ν(CO)), 1913 cm^{-1} (s) (ν(CO)).

Synthesis of *cis*-tetracarbonyl(dimethyl 5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate)(1-phenyl-2,3,6,7-tetrahydro-1*H*-phosphepine)molybdenum (15): A mixture of complex **12** (0.500 g, 0.85 mmol) and dimethylacetylene dicarboxylate (2.5 mL, 20 mmol) was stirred at 50 °C for 22 h. Column chromatography over silica gel, starting with pentane as eluent and gradually changing to dichloromethane, gave recovered dimethylacetylene dicarboxylate first, followed by compound **15** (390 mg, 63%) as a yellow oil. Crystallization from dichloromethane/hexane gave yellow crystals. M.p. 131–132 °C; ^{1}H NMR ($CDCl_3$): δ = 1.88 (d, $^4J_{P,H}$ = 0.9 Hz, 6H; CH_3), 2.19–2.35 (m, 8H; CH_2-P & CH_2), 3.39 (d, $^2J_{P,H}$ = 2.9 Hz, 2H; phosphanorbornadiene-CH), 3.61 (s, 6H; OCH_3), 5.73 (m, 2H; =CH), 7.26–7.49 ppm (m, 10H; Ar); ^{13}C NMR ($CDCl_3$): δ = 16.2 (d, $^3J_{P,C}$ = 1.8 Hz; CH_3), 23.3 (d, $^2J_{P,C}$ = 5.2 Hz; *C*H$_2$C=), 29.2 (dd, $^3J_{P,C}$ = 1.8, $^1J_{P,C}$ = 19.9 Hz; *C*H$_2$P), 52.4 (s, OCH_3), 60.0 (dd, $^3J_{P,C}$ = 2.0, $^1J_{P,C}$ = 14.3 Hz; phosphonorbornadiene-CH), 128.1–130.4 (m; Ar), 131.7 (s; =CH), 137.7 (d, $^1J_{P,C}$ = 17.4 Hz; phosphanorbornadiene *ipso*-Ph), 139.3 (dd, $^3J_{P,C}$ = 2.4, $^1J_{P,C}$ = 27.4 Hz; phosphepine *ipso*-Ph), 142.3 (d, $^2J_{P,C}$ = 3.0 Hz; CH*C*CH_3), 146.2 (d, $^2J_{P,C}$ = 3.5 Hz; *C*CO_2CH_3), 165.6 (d, $^3J_{P,C}$ = 2.3 Hz; *C*O_2CH_3), 209.3 (dd, $^2J_{P,C}$ = 8.0, $^2J_{P,C}$ = 9.8 Hz; CO_{ax}), 214.8 (dd, $^2J_{P,C}$ = 8.8, $^2J_{P,C}$ = 12.4 Hz; CO_{eq}), 215.3 ppm (dd, $^2J_{P,C}$ = 5.7, $^2J_{P,C}$ = 8.8 Hz; CO_{eq}); ^{31}P NMR ($CDCl_3$): δ = 25.7 (d, $^2J_{P,P}$ = 26.1 Hz; phosphepine), 251.9 ppm (d, $^2J_{P,P}$ = 26.1 Hz; phosphanorbornadiene-P); IR (CH_2Cl_2): $\tilde{\nu}$ = 2021 (m) (ν(CO)), 1915 (s) (ν(CO)), 1890 cm^{-1} (sh) (ν(CO)). Compound **15** was too unstable for HR-MS; formation of **18** was observed.

Synthesis of *cis*-tetracarbonyl(dimethyl 5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylte)(1,3-dimethyl-2-phenyl-2,3,4,7-tetrahydro-1*H*-[1,3,2]diazaphosphepine)molybdenum (16): A solution of complex **13** (500 mg, 0.81 mmol) and dimethylacetylene dicarboxylate (3 mL; 24 mmol) in dichloromethane (1 mL) was heated for 28 h at 45 °C. Column chromatography, starting with hexane and gradually changing to dichloromethane as eluent, afforded complex **16** (330 mg; 55%) as an orange solid. Recrystallization (CH_2Cl_2/hexane) resulted in the formation of orange needles. M.p. 71–72 °C; ^{1}H NMR ($CDCl_3$): δ = 1.96 (d, $^4J_{P,H}$ = 1.0 Hz, 6H; CH_3), 2.96 (d, $^3J_{P,H}$ = 14.1 Hz, 6H; NCH_3), 3.13–3.20 (m, 2H; CH_2N), 3.59 (s, 2H; phosphanorbornadiene-CH), 3.61 (s, 6H; OCH_3), 4.16–4.20 (m, 2H; CH_2N), 6.00 (m, 2H; phosphepine-CH), 7.04–7.49 ppm (m, 10H; Ar); ^{13}C NMR ($CDCl_3$): δ = 16.2 (d, $^3J_{P,C}$ = 2.1 Hz; CH_3), 40.0 (d, $^2J_{P,C}$ = 14.1 Hz; NCH_3), 49.0 (d, $^2J_{P,C}$ = 6.9 Hz; CH_2N), 52.3 (s, OCH_3), 60.5 (dd, $^3J_{P,C}$ = 1.4, $^1J_{P,C}$ = 14.2 Hz; phosphonorbornadiene-CH), 127.9–131.2 (m; Ar), 134.7 (s; =CH), 138.1 (d, $^1J_{P,C}$ = 17.4 Hz; phosphanorbornadiene *ipso*-Ph), 141.7 (dd, $^3J_{P,C}$ = 1.5, $^1J_{P,C}$ = 57.0 Hz; phosphepine *ipso*-Ph), 141.9 (d, $^2J_{P,C}$ = 2.8 Hz; CH*C*CH_3), 146.7 (d, $^2J_{P,C}$ = 3.6 Hz; *C*CO_2CH_3), 165.7 (d, $^3J_{P,C}$ = 2.1 Hz; *C*O_2CH_3), 208.9 (dd, $^2J_{P,C}$ = 8.2, $^2J_{P,C}$ = 10.5 Hz; CO_{ax}), 215.0 (dd, $^2J_{P,C}$ = 10.8, $^2J_{P,C}$ = 28.9 Hz; CO_{eq}), 215.8 ppm (dd, $^2J_{P,C}$ = 10.0, $^2J_{P,C}$ = 28.2 Hz; CO_{eq}); ^{31}P NMR ($CDCl_3$): δ = 250.5 (d, $^2J_{P,P}$ = 26.6 Hz; 7-phosphanorbornadiene), 137.6 ppm (d, $^2J_{P,P}$ = 26.6 Hz; phosphepine); IR (CH_2Cl_2): $\tilde{\nu}$ = 2024 (m) (ν(CO)), 1918 (s) (ν(CO)), 1889 cm^{-1} (sh) (ν(CO)). Compound **16** was too unstable for HR-MS; formation of compound **19** was observed.

Synthesis of *cis*-tetracarbonyl(dimethyl 5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate)(2-phenyl-4,7-dihydro-[1,3,2]dioxaphosphepine)molybdenum (17): A mixture of complex **14** (0.72 g, 1.2 mmol) and dimethylacetylene dicarboxylate (2.5 mL, 20 mmol) was stirred at 45 °C for 22 h. Column chromatography over silica gel, starting with pentane as eluent and gradually changing to dichloromethane, gave dimethylacetylene dicarboxylate first, followed by complex **17** (0.61 g; 69%) as a yellow oil. Crystallization from dichloromethane/hexane gave yellow crystals. M.p. 139–140 °C; ^{1}H NMR ($CDCl_3$): δ = 1.97 (d, $^4J_{P,H}$ = 0.8 Hz, 6H; CH_3), 3.63 (s, 6H; OCH_3), 3.77 (d, $^2J_{P,H}$ = 2.6 Hz, 2H; phosphanorbornadiene-CH), 4.45–4.56 (m, 4H; CH_2), 5.75 (s, 2H; =CH), 7.09–7.59 ppm (m, 10H; Ar); ^{13}C NMR ($CDCl_3$): δ = 16.3 (d, $^3J_{P,C}$ = 1.8 Hz; CH_3), 52.4 (s, OCH_3), 60.4 (dd, $^3J_{P,C}$ = 2.0, $^1J_{P,C}$ = 15.4 Hz; phosphonorbornadiene-CH), 64.8 (d, $^2J_{P,C}$ = 6.1 Hz; OCH_2), 128.1–129.5 (m; Ar), 131.0 (s; =CH), 138.0 (d, $^1J_{P,C}$ = 17.4 Hz; phosphanorbornadiene *ipso*-Ph), 141.3 (d, $^1J_{P,C}$ = 34.9 Hz; phosphepine

ipso-Ph), 142.4 (d, $^2J_{P,C}=4.6$ Hz; CH*C*CH$_3$), 146.4 (d, $^2J_{P,C}=3.7$ Hz; *C*CO$_2$CH$_3$), 165.7 (d, $^3J_{P,C}=2.3$ Hz; *C*O$_2$CH$_3$), 208.4 (dd, $^2J_{P,C}=8.3$, $^2J_{P,C}=12.1$ Hz; CO$_{ax}$), 213.2 (dd, $^2J_{P,C}=11.2$, $^2J_{P,C}=26.7$ Hz; CO$_{eq}$), 213.9 ppm (dd, $^2J_{P,C}=9.9$, $^2J_{P,C}=33.7$ Hz; CO$_{eq}$); ^{31}P NMR (CDCl$_3$): $\delta=190.8$ (d, $^2J_{P,P}=32.6$ Hz; phosphepine), 248.8 ppm (d, $^2J_{P,P}=32.6$ Hz; phosphanorbornadiene); HR-MS calcd for $C_{32}H_{30}MoO_{10}P_2$: 734.0369; found 734.03273 (δ 2×10^{-2}); IR (CH_2Cl_2): ν(CO)=2029 (w) (ν(CO)), 1923 cm^{-1} (s) (ν(CO)).

Synthesis of tetracarbonyl(4,8-diphenyl-4,8-diphospha-bicyclo-[5.1.0]octane)molybdenum (18) by thermal decomposition of 15: A solution of **15** (0.35 g, 0.48 mmol) in toluene (5 mL) was stirred at 80 °C for 3 h. Evaporation to dryness, column chromatography (silica gel; dichloromethane/pentane, 2:1), and recrystallization from dichloromethane/hexane gave **18** (0.160 g, 66 %) as colorless crystals. M.p. 194–195 °C (decomp); ^{1}H NMR: (CDCl$_3$): $\delta=2.07$–2.38 (m, 6H; CH & CH$_2$P), 2.43–2.72 (m, 2H; CHC*H*$_2$), 2.78–2.98 (m, 2H; CHC*H*$_2$) , 7.37–7.60 ppm (m, 10H; Ar); ^{13}C NMR: (CDCl$_3$): $\delta=21.9$ (d, $^2J_{P,C}=3.4$ Hz; CH*C*H$_2$), 26.7 (dd, $^1J_{P,C}=20.5$, $^3J_{P,C}=4.0$ Hz; CH$_2$P), 26.8 (dd, $^3J_{P,C}=4.8$, $^1J_{P,C}=15.4$ Hz; CHP), 128.9–131.4 (m; Ar), 135.8 (dd, $^3J_{P,C}=4.2$, $^1J_{P,C}=11.8$ Hz; phosphirane *ipso*-Ph), 138.5 (dd, $^3J_{P,C}=8.4$, $^1J_{P,C}=30.2$ Hz; phosphepane *ipso*-Ph), 209.7 (dd, $^2J_{P,C}=9.5$, $^2J_{P,C}=11.4$ Hz; CO$_{ax}$), 214.6 (dd, $^2J_{P,C}=9.2$, $^2J_{P,C}=31.3$ Hz; CO$_{eq}$), 216.4 ppm (dd, $^2J_{P,C}=10.0$, $^2J_{P,C}=22.3$ Hz; CO$_{eq}$); ^{31}P NMR: (CDCl$_3$): $\delta=-150.5$ (d, $^2J_{P,P}=38.4$ Hz; phosphirane), 16.46 ppm (d, $^2J_{P,P}=38.4$ Hz; phosphepane); HR-MS calcd. for $C_{22}H_{20}MoO_4P_2$: 507.9892; found 507.98926 (δ 2×10^{-3}); IR(CH_2Cl_2): $\tilde{\nu}=$ 2019 (m) (ν(CO)), 1901 (s) (ν(CO)), 1884 cm^{-1} (sh) (ν(CO)); EI-MS: *m/z* (%): 508 (18) [M^+], 480 (2) [M^+−CO], 452 (24) [M^+−2CO], 424 (15) [M^+−3CO], 396 (100) [M^+−4CO].

Synthesis of tetracarbonyl(3,5-dimethyl-4,8-diphenyl-3,5-diaza-4,8-diphosphabicyclo[5.1.0]octane)molybdenum (19) by thermal decomposition of 16: A solution of **16** (146 mg, 0.19 mmol) in 3 mL of toluene was stirred at 70 °C for 5 h. Evaporation to dryness, chromatography (silica gel; dichloromethane/pentane, 2:1), and recrystallization from dichloromethane/hexane gave complex **19** (25 mg; 24 %) as colorless crystals. A second fraction contained starting material **16** (46 mg; 32 %). M.p. 83–84 °C; ^{1}H NMR (CDCl$_3$): $\delta=2.32$ (m, 2H; CH), 2.42 (d, $^3J_{P,H}=8.8$ Hz, 6H; NCH$_3$), 3.60–3.80 (m, 2H; CH$_2$N), 4.02–4.11 (m, 2H; CH$_2$N), 7.40–7.69 ppm (m, 10H; Ar); ^{13}C NMR (CDCl$_3$): $\delta=25.8$ (dd, $^1J_{P,C}=14.0$, $^3J_{P,C}=4.8$ Hz; CH), 40.7 (d, $^2J_{P,C}=2.5$ Hz; NCH$_3$), 51.0 (dd, $^2J_{P,C}=7.4$, $^2J_{P,C}=2.5$ Hz; CH$_2$N), 128.1–131.2 (m; Ar), 133.8 (dd, $^3J_{P,C}=7.7$, $^1J_{P,C}=9.6$ Hz; phosphirane *ipso*-Ph), 136.3 (dd, $^3J_{P,C}=5.8$, $^1J_{P,C}=43.7$ Hz; phosphepane *ipso*-Ph), 210.5 (dd, $^2J_{P,C}=10.1$, $^2J_{P,C}=11.4$ Hz; CO$_{ax}$), 214.0 (dd, $^2J_{P,C}=10.1$, $^2J_{P,C}=31.7$ Hz; CO$_{eq}$), 216.2 ppm (dd, $^2J_{P,C}=10.3$, $^2J_{P,C}=26.4$ Hz; CO$_{eq}$); ^{31}P NMR (CDCl$_3$): $\delta=-149.1$ (d, $^2J_{P,P}=58.7$ Hz; phosphirane), 140.4 ppm (d, $^2J_{P,P}=58.7$ Hz; phosphepane); HR-MS: calcd for $C_{22}H_{22}MoN_2O_4P_2$: 538.0109; found 538.00991 (δ 6×10^{-3}); IR (CH_2Cl_2): $\tilde{\nu}=$2017 (m) (ν(CO)), 1900 (s) (ν(CO)); EI-MS: *m/z* (%): 538 (10) [M^+], 510 (8) [M^+−CO], 482 (10) [M^+−2CO], 454 (10) [M^+−3CO], 426 (45) [M^+−4CO], 374 (45) [M^+−2CO−PPh], 318 (45) [M^+−phosphepine].

Synthesis of tetracarbonyl(4,8-diphenyl-3,5-dioxa-4,8-diphosphabicyclo-[5.1.0]octane)molybdenum (20) by thermal decomposition of 17: A solution of **17** (0.35 g, 0.47 mmol) in toluene (3 mL) was stirred at 80 °C for 3 h. Evaporation to dryness and column chromatography (silica gel; dichloromethane/pentane, 2:1) followed by recrystallization from dichloromethane/hexane yielded **20** (0.15 g, 61 %) as colorless crystals. M.p. 169–170 °C (decomp); ^{1}H NMR (CDCl$_3$): $\delta=2.62$ (d, $^2J_{P,H}=5.6$ Hz, 2H; phosphirane-CH), 4.75–5.30 (m, 4H; CH$_2$), 7.44–7.78 ppm (m, 10H; Ar); ^{13}C NMR (CDCl$_3$): $\delta=28.6$ (dd, $^1J_{P,C}=11.7$, $^3J_{P,C}=7.6$ Hz; CH), 65.0 (dd, $^2J_{P,C}=2.0$, $^2J_{P,C}=2.9$ Hz; CH$_2$), 128.6–132.0 (m; Ar), 132.9 (dd, $^1J_{P,C}=10.2$, $^3J_{P,C}=6.7$ Hz; phosphirane *ipso*-Ph), 140.1 (dd, $^1J_{P,C}=51.6$, $^3J_{P,C}=4.9$ Hz; phosphepane *ipso*-Ph), 207.8 (m; CO$_{ax}$), 212.9 (dd, $^2J_{P,C}=10.2$, $^2J_{P,C}=29.8$ Hz; CO$_{eq}$), 215.5 ppm (dd, $^2J_{P,C}=10.6$, $^2J_{P,C}=32.7$ Hz; CO$_{eq}$); ^{31}P NMR (CDCl$_3$): $\delta=-150.6$ (d, $^2J_{P,P}=66.8$ Hz; phosphirane), 191.7 ppm (d, $^2J_{P,P}=66.8$ Hz; phosphepane); HR-MS calcd for $C_{20}H_{16}MoO_6P_2$: 511.9477; found 511.94668 (δ 2×10^{-3}); IR (CH_2Cl_2): $\tilde{\nu}=$2031 (w) (ν(CO)), 1919 cm^{-1} (s) (ν(CO)); EI-MS: *m/z* (%): 512 (40) [M^+], 484 (4) [M^+−CO], 456 (16) [M^+−2CO], 428 (28) [M^+−3CO], 400 (100) [M^+−4CO].

X-ray crystal structure determinations: X-ray intensities were measured with a Nonius Kappa CCD diffractometer with rotating anode and graphite monochromator ($\lambda=0.71073$ Å) at a temperature of 150(2) K up to a resolution of $(\sin\theta/\lambda)_{max}=0.65$ Å^{-1}. The structures were solved with automated Patterson methods[23] and refined with SHELXL-97[24] on F^2 of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. All hydrogen atoms were located in the difference Fourier map. Methyl and phenyl H-atoms were refined with a riding model; all other H-atoms were refined freely with isotropic displacement parameters. Geometry calculations, drawings, and checking for higher symmetry were performed with the PLATON package.[25]

Crystal structure determination of ***19***: $C_{22}H_{22}MoN_2O_4P_2$, Fw=536.30, colorless block, 0.42×0.36×0.18 mm^3, orthorhombic, *Pbca* (no. 61), $a=$ 16.48859(15), $b=15.3260(9)$, $c=18.2133(4)$ Å, $V=4602.6(3)$ Å^3, $Z=8$, $\rho_{calcd}=1.548$ g cm^{-3}; 110857 reflections were measured. An absorption correction based on multiple measured reflections was applied ($\mu=$ 0.74 mm^{-1}, 0.72–0.88 correction range); 5283 reflections were unique ($R_{int}=0.029$); 306 parameters were refined with no restraints. *R*1/*wR*2 [$I>2\sigma(I)$]: 0.0200/0.0457. *R*1/*wR*2 (all refl.): 0.0287/0.0504. $S=1.092$. Residual electron density between −0.29 and 0.47 e Å^{-3}.

Crystal structure determination of ***20***: $C_{20}H_{16}MoO_6P_2$, Fw=510.21, colorless block, 0.45×0.42×0.36 mm^3, triclinic, $P\bar{1}$ (no. 2), $a=7.5410(1)$, $b=$ 9.6907(1), $c=14.8771(2)$ Å, $\alpha=96.2156(11)°$, $\beta=101.7812(10)°$, $\gamma=$ 106.0581(10)°, $V=1006.95(2)$ Å^3, Z=2, $\rho_{calcd}=1.683$ g cm^{-3}; 16625 reflections were measured. An absorption correction based on multiple measured reflections was applied ($\mu=0.85$ mm^{-1}, 0.67–0.74 correction range); 4598 reflections were unique ($R_{int}=0.016$); 286 parameters were refined with no restraints. *R*1/*wR*2 [$I>2\sigma(I)$]: 0.0175/0.0416. *R*1/*wR*2 (all reflections): 0.0218/0.0428. $S=1.065$. Residual electron density between −0.27 and 0.36 e Å^{-3}.

CCDC-291538 (**19**) and CCDC-291539 (**20**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

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