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Synthesis of 1-Molybda-2-phosphatriazoline and -aziridine Derivatives via 1,3-Dipolar Cycloaddition of Aryl Azides to σ^3,λ^4-Phosphanediyl Complexes

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Summary: The reaction of $[(2,4,6\text{-}{}^tBu_3C_6H_2O)(HC{\equiv}CCH_2)]P{=}MoCp(CO)_2$ *(**1**; R =* $2,4,6\text{-}{}^tBu_3C_6H_2O$*) with aryl azides* $R'N_3$ *(**2a**, R′ =* C_6H_5*; **2b**, R′ =* $2,4,6\text{-}Me_3C_6H_2$*) affords the triazoline derivatives* $[(2,4,6\text{-}{}^tBu_3C_6H_2O)(HC{\equiv}CCH_2)]P{-}N{=}N{-}NR'{-}MoCp(CO)_2$ *(**3**) via a 1,3-dipolar cycloaddition reaction. Thermally induced dinitrogen elimination from **3** yields the 1-molybda-2-phosphaaziridines* $[(2,4,6\text{-}{}^tBu_3C_6H_2O)(HC{\equiv}CCH_2)]P{-}NR'{-}MoCp(CO)_2$ *(**4**). Compounds **1**, **3**, and **4** each contain a 2-propynyl unit. Reaction of each with* $Co_2(CO)_8$ *(**5**) gives* $(R)[(\eta^2\text{-}CH_2C{\equiv}CH)Co_2(CO)_6]P{=}MoCp(CO)_2$ *(**8**),* $(R)[(\eta^2\text{-}CH_2C{\equiv}CH)Co_2(CO)_6]P{-}N{=}N{-}NR'{-}MoCp(CO)_2$ *(**6**), and* $(R)[(\eta^2\text{-}CH_2C{\equiv}CH)Co_2(CO)_6]P{-}NR'{-}MoCp(CO)_2$ *(**7**), respectively. Complex **7** is also formed by thermal treatment of **6**. The steric influence of the dicobaltatetrahedrane cluster unit in **8** toward the addition of* $R'N_3$ *(**2**) to the P—Mo π system is discussed. The identities of all new compounds have been documented by analytical as well as by spectroscopic (IR, MS, and* ^1H*,* ^{31}P*, and* ^{13}C *NMR) data; the X-ray structure of* $\{(R)[(\eta^2\text{-}CH_2C{\equiv}CH)Co_2(CO)_6]\}P{-}N{=}N{-}N(R'){-}MoCp(CO)_2$ *(**6b**; R′ =* $2,4,6\text{-}Me_3C_6H_2$*) is reported.*

Introduction

σ^3,λ^4-Phosphanediyl complexes of the type $RR'P{=}ML_n$ (ML_n = 15-electron organometallic building block; R, R′ = singly bonded organic ligand) react with diazomethane or with organometallic fragments isolobal with carbene to yield the three-membered cycles $RR'P{-}E{-}ML_n$ (E = CH_2, $Fe(CO)_4$, ...).[1,2] Recently, we showed that CH_2N_2 adds to the phosphorus–metal π bond by a 1,3-dipolar cycloaddition reaction, forming 1-molybda-2-phosphapyrazoline derivatives.[2a] So far, no reaction between σ^3,λ^4-phosphanediyl compounds with other 1,3-dipoles such as $R'N_3$ have been reported. In this context we report the stepwise formation of 1-molybda-2-phosphaaziridines via a 1,3-dipolar cycloaddition of $R'N_3$ to the formal P=Mo double bond in σ^3,λ^4-phosphanediyl complexes.

Results and Discussion of Reaction Chemistry

An overview of all reactions described is given in Scheme I.

Triazolines of the type $(R)(HC{\equiv}CCH_2)P{-}N{=}N{-}N(R'){-}MoCp(CO)_2$ (R = $2,4,6\text{-}{}^tBu_3C_6H_2O$; R′ = C_6H_5 (**3a**), $2,4,6\text{-}Me_3C_6H_2$ (**3b**)) were prepared by reaction of $(R)(HC{\equiv}CCH_2)P{=}MoCp(CO)_2$ (**1**)[2b-d] with the azides $R'N_3$ (R′ = C_6H_5 (**2a**), $2,4,6\text{-}Me_3C_6H_2$ (**2b**)) in toluene at 25 °C (pathway a, Scheme I). The five-membered-ring species **3** were isolated, depending on the nature of R′, in excellent yields (**3a**, 75%; **3b**, 93%). Minor amounts of **4** were also formed in the reaction of **1** with **2a** (pathway c, Scheme I); **4** can be separated from **3a** by column chromatography.

The formation of **4** by the reaction of **1** with **2a** (Scheme I) can be explained by at least two different mechanisms: one possibility is the conversion of $R'N_3$ to the nitrene $:\ddot{N}R'$ via elimination of dinitrogen. The electron-sextet species $:\ddot{N}R'$ then adds, by means of a cheletropic reaction,[3] to the phosphorus–molybdenum π-bond system to yield the three-membered cycle **4** (pathway b, Scheme I). Another possibility is via a 1,3-dipolar cycloaddition reaction[4] of the azide $R'N_3$ (**2**) to the formal P=Mo double bond to yield **3**; extrusion of dinitrogen then affords **4** (pathways a and c, Scheme I).

The evidence that the reaction of **1** with **2** goes via a 1,3-dipolar cycloaddition (pathway a, Scheme I) is given by the isolation of intermediate **3**. The reaction of **1** with $C_6H_5N_3$ (**2a**) yields **3a** as the major product (75%) as well as **4** (15%). Complex **1** can be converted to **4** without isolating **3a** when the reaction is conducted at higher temperatures. However, the reaction of **1** with $2,4,6\text{-}Me_3C_6H_2N_3$ (**2b**) affords only **3b**; a compound similar to **4** could not be detected, even when higher temperatures are used for the reaction (Scheme I).

In a further experiment we confirmed that the three-membered cycle of **4** can be obtained by thermal treatment of **3a** via elimination of dinitrogen in toluene at 90 °C (pathway c, Scheme I). A color change from yellow (**3a**)

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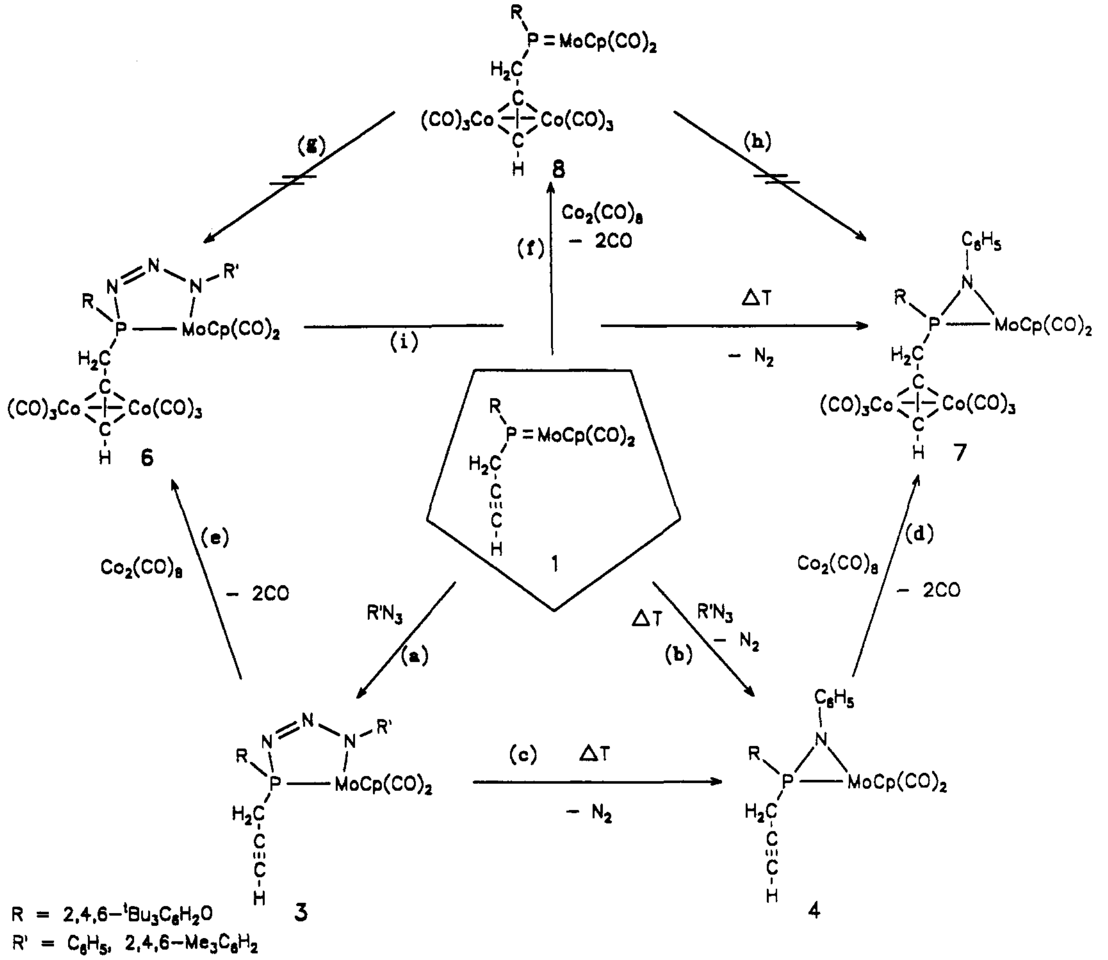
Scheme I. Reaction of 1 with R'N$_3$: Reactivity of 3 and 4



to orange (4) indicates the progress of the reaction. Compound 4 is best purified by filtration of the reaction mixture through silica gel, evaporation of the solvents under vacuum, and recrystallization of the residue from ether/*n*-pentane at −30 °C. Compounds of type 4, RR'P—E—ML$_n$ (R, R' = singly bonded organic ligand; ML$_n$ = 15-electron complex fragment; E = RN, RP, RR'C, ...), have already been synthesized using different synthetic routes.[2,8]

The π-bond polarity in "neutral phosphenium ion compounds" was determined by theoretical calculations,[5,6] as well as by experimental results.[1,2] It was found that the phosphorus atom is positively charged. With this in mind, and on the basis of theoretical studies of 1,3-dipoles[4,7] the stereoselective cycloaddition of 2 to 1 by formation of just one isomer of 3 can be best explained by a steric interaction between R in $[(R)(HC{\equiv}CCH_2)]P{=}MoCp(CO)_2$ (1) (R = 2,4,6-^{t}Bu$_3$C$_6$H$_2$O) and R' in R'N$_3$ (2) (R' = Ph, 2,4,6-Me$_3$C$_6$H$_2$) (Scheme I).

Complex 1 reacts, even with an excess of 2, to afford selectively 3 or 4 (Scheme I). As with reactions of acetylenes with aryl azides to form triazoline derivatives,[9] no reaction was observed between the carbon–carbon triple bond of the 2-propynyl ligand of compounds 1, 3, and 4 with the appropriate azides. However, with $Co_2(CO)_8$ (5) the propargyl substituent in 1, 3, and 4 reacts at ambient temperature to yield the complexes $(R)[(\eta^2\text{-}CH_2C{\equiv}CH)Co_2(CO)_6]P{=}MoCp(CO)_2$ (8) (reaction of 1 with 5; pathway f, Scheme I), $(R)[(\eta^2\text{-}CH_2C{\equiv}CH)Co_2(CO)_6]P{-}N{=}N{-}NR'{-}MoCp(CO)_2$ (6) (reaction of 3 with 5; pathway e, Scheme I), and $(R)[(\eta^2\text{-}CH_2C{\equiv}CH)Co_2(CO)_6]P{-}NR'{-}MoCp(CO)_2$ (7) (reaction of 4 with 5; pathway d, Scheme I), respectively.[10] In these compounds the propargyl ligand is converted into a sterically hindered dicobaltatetrahedrane unit.[11] The steric demand of this organometallic group shows significant influence on the phosphorus–molybdenum π bond in 8, compared to 1: when the same conditions are used as described for the reaction of 1 with 2 (see above), no reaction occurs between 8 and 2, even with a wide variety of different reaction conditions (temperature, solvent, ...), no addition of R'N$_3$ or R'N has ever been observed. The same observations were made in the reaction of 8 with CH$_2$N$_2$[2a] or even organometallic building blocks isolobal with carbene or nitrene.[10] That it is presumably not an electronic effect is given by comparison of spectroscopic data of 1 with 8 (Experimental Section). From our point of view it seems to be only a steric effect that prevents the 1,3-dipolar cycloaddition reaction of 2 to 8, and this is in addition confirmed by the fact that, for example, dicobaltatetra-

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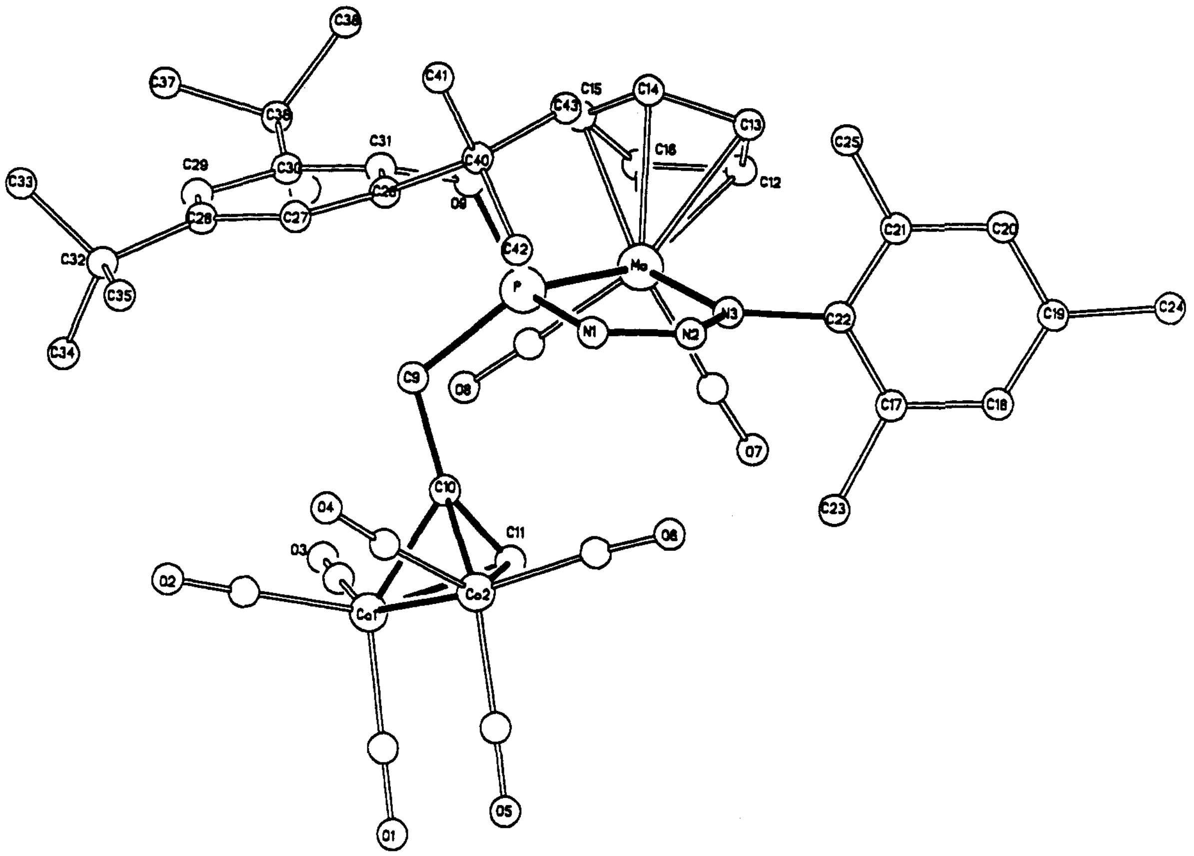

Figure 1. Molecular geometry and atom-labeling scheme for **6b**.[14] Important interatomic distances (Å) and angles (deg) are as follows: P–Mo = 2.413(4), P–O(9) = 1.649(7), P–C(9) = 1.85(1), P–N(1) = 1.686(8), N(1)–N(2) = 1.30(1), N(2)–N(3) = 1.32(1), N(3)–Mo = 2.221(8), N(3)–C(22) = 1.45(1), C(9)–C(10) = 1.52(1), C(10)–C(11) = 1.35(2), Co(1)–Co(2) = 2.467(3); P–Mo–N(3) = 71.3(2), Mo–P–O(9) = 111.1(3), N(1)–P–O(9) = 108.1(4), Mo–P–N(1) = 106.8(3), Mo–P–C(9) = 127.2, N(1)–P–C(9) = 101.4(4), O(9)–P–C(9) = 100.9(4), P–N(1)–N(2) = 116.6(6), N(1)–N(2)–N(3) = 118.5(8), N(2)–N(3)–Mo = 126.4(6), Mo–N(3)–C(22) = 124.5(5), N(2)–N(3)–C(22) = 109.1(7).

hedrane cluster fragments can be used in general to stabilize otherwise reactive metal–phosphorus multiple bonds.[2,10,11]

The proposed structures of compounds 3, 4, and 6–8 are based on analytical and spectroscopic (IR, MS, and ^{1}H, ^{31}P, and ^{13}C NMR) data. Compounds of types 1, 3, and 4 can be easily distinguished by their ^{31}P{^{1}H} NMR spectra. The ^{31}P{^{1}H} NMR resonance signal of 1 is observed at δ 309.0, the characteristic region for σ^3,λ^4-phosphanediyl complexes.[2c,12] The ^{31}P{^{1}H} NMR spectra of 3 and 6 each show a singlet in the region δ 225–240. In contrast to this, there is an extreme high-field shift observed from 3 to 4 (δ 54.6) and from 6 to 7 (δ 56.0). This effect has already been observed for phosphorus- and nitrogen-containing three-membered cycles.[8,13]

The ^{1}H and ^{13}C NMR spectra were completely assigned. While for 1 only a single resonance signal is observed for the *o-tert*-butyl groups in 2,4,6-^{t}Bu$_3$C$_6$H$_2$O,[2c] the compounds 3, 4, 6, and 7 show two signals indicating a hindered rotation around the oxygen–carbon axis of the tri-*tert*-butyl-substituted phenoxy group. Conspicuous is the fact that the shift of the *p*-^{t}Bu group in all compounds is nearly independent of the steric influence of the other ligands. However, the separation of the *o*-^{t}Bu signals is dependent on the steric influence of the substituents at the phosphorus center and the resonance signals are always slightly broadened compared to the signals of the p-^{t}Bu groups and are, thus easily assigned.

To establish the solid-state molecular structure of compound 6, an X-ray structure determination was carried out on a single crystal of **6b**, the results of which are illustrated in Figure 1.[14]

Compound **6b** consists of a nearly planar five-membered MoPN$_3$ cycle (average deviation 0.036 Å). A notable feature of **6b** is that the N–N bond lengths are almost equal (N(1)–N(2) = 1.30 Å; N(2)–N(3) = 1.32 Å). The sum of angles around N(3) (360°) points to a trigonal-planar environment. This indicates that the three nitrogen atoms form a three-center–four-electron π system. The phosphorus–molybdenum distance (2.413 Å) is lengthened, compared to that in 1 (2.197 Å),[2c] and is in the range of usual P–Mo distances (2.35–2.60 Å)[15] found in many organomolybdenum–phosphine complexes involving P→Mo dative bonds.

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[14] (14) Crystal data for **6b**: C$_{43}$H$_{48}$Co$_2$MoN$_3$O$_9$P; M_r = 995.65; triclinic; a = 10.204(9) Å, b = 14.56(1) Å, c = 17.50(2) Å; α = 92.82(9)°, β = 94.62(8)°, γ = 94.72(8)°; V = 2578(4) Å^3; space group $P\bar{1}$ (No. 2); Z = 2; D_{calcd} = 1.28 g cm^{-3}; orange crystals (0.3 × 0.3 × 0.6 mm) sealed on a glass fiber; μ(Mo Kα) = 11.7 cm^{-1} (T = 213 K). Data collection and processing: diffraction data were collected on a Siemens (Nicolet Syntex) R3m/V diffractometer using the ω-scan technique (2θ limits 2.0–42.0, scan range 0.75°, scan speed $3.4 \leq \dot{\omega} \leq 29.3°$ min^{-1} (in 2θ)) and Mo Kα radiation (λ = 0.710 69 Å). The structure was solved by direct methods (SHELXS-86)[19] on 4331 unique reflections with $F \geq 4\sigma(F)$: no. of variables 5546, no. of unique data 388, F(000) = 1054. An empirical absorption correction was applied. The atoms Mo, Co, P, N, C(1)–C(11), C(23)–C(25), C(32), C(36), and C(40) were refined isotropically; all other atoms were refined anisotropically. The functional discrepancy indices were R_F = 0.059, R_w = 0.055.

The Co(1)–Co(2) distance of 2.467 Å in the tetrahedrane fragment and the acetylene bond length (C(10)–C(11)) of 1.35 Å are comparable with distances in other cobalt-containing tetrahedrane fragments of the type (η^2-$RC{\equiv}CR'$)$Co_2(CO)_6$.[16]

Experimental Section

General Comments. All reactions were carried out under an atmosphere of nitrogen by using standard Schlenk techniques. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were purified by distillation from sodium/benzophenone, while *n*-pentane, toluene, and dichloromethane were purified by distillation from CaH_2.

Infrared spectra were obtained from a Perkin-Elmer 983G double-beam grating spectrometer. Proton nuclear magnetic resonance spectra, as well as carbon-13 and phosphorus-31 NMR spectra, were recorded on a Bruker AC 200 spectrometer operating at 200.13 MHz (^1H), 50.323 MHz (^{13}C), and 81.015 MHz (^{31}P) in the Fourier transform mode. EI mass spectra were recorded on a Finnigan MAT 8230 mass spectrometer operating at 70 eV. Melting points were determined with use of analytically pure samples, which were sealed in nitrogen-purged capillaries, on a Gallenkamp melting point apparatus. Microanalyses were performed by the analytical laboratories at the University of Heidelberg.

Synthesis of (R)(HC≡CCH₂)P—N=N—N(Ph)-MoCp(CO)₂ (3a) and (R)(HC≡CCH₂)P—N(Ph)—MoCp(CO)₂ (4). Compound 1[2c] (1.1 g, 2.0 mmol) was treated with 2a[17] (300 mg, 2.5 mmol) in toluene (200 mL) for 18 h at 20 °C. The reaction mixture slowly turned yellow. All volatiles were removed under high vacuum, and the resulting residue was purified by column chromatography at −25 °C (column size 1.5 × 20 cm; *n*-pentane, silica gel). Two fractions could be collected: an orange one (4) with *n*-pentane/CH_2Cl_2 (2:1) and a yellow one (3a) with THF. After removal of the solvents under reduced pressure and recrystallization from Et_2O/*n*-pentane (4) or CH_2Cl_2/Et_2O (3a) at −30 °C orange crystals of 4 and pale yellow crystals of 3a were obtained.

3a: yield 1.0 g (1.5 mmol, 75%); mp 183 °C dec; IR (*n*-pentane) 3311 m $\nu({\equiv}C{-}H)$, 2117 vw $\nu(C{\equiv}C)$, 1977 vs, 1918 s $\nu(CO)$ cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.29 (s, 9H, *o*-^{t}Bu), 1.35 (s, 9H, *p*-^{t}Bu), 1.54 (s, 9H, *o*-^{t}Bu), 1.93 (dt, *J*(P–H) = 8.0 Hz, *J*(H–H) = 2.7 Hz, 1H, $CH_2C{\equiv}C\mathit{H}$), 3.59 (ddd, *J*(P–H) = 16.3 Hz, *J*(H–H) = 16.6 Hz, *J*(H–H) = 2.7 Hz, 1H, $C\mathit{H}_2C{\equiv}CH$), 3.82 (ddd, *J*(P–H) = 6,5 Hz, *J*(H–H) = 16.6 Hz, *J*(H–H) = 2.7 Hz, 1H, $C\mathit{H}_2C{\equiv}CH$), 4.81 (s, 5H, Cp), 7.36 (s, 2H, C_6H_2), 7.1–7.4 (m, 5H, C_6H_5); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 233.7 (s); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 31.5 (s, 3C, *p*-^{t}Bu), 32.3 (s, 3C, *o*-^{t}Bu), 32.7 (s, 3C, *o*-^{t}Bu), 34.4 (s, 1C, ^{i}C/*p*-^{t}Bu), 36.1 (s, 1C, ^{i}C/*o*-^{t}Bu), 36.4 (s, 1C, ^{i}C/*o*-^{t}Bu), 27.2 (d, *J*(P–C) = 58 Hz, 1C, $\mathit{C}H_2C{\equiv}CH$), 72.4 (d, *J*(P–C) = 11 Hz, 1C, $CH_2C{\equiv}\mathit{C}H$), 76.0 (d, *J*(P–C) = 1 Hz, 1C, $CH_2\mathit{C}{\equiv}CH$), 92.8 (s, 5C, Cp), 122.6 (s, 1C, C_6H_5), 124.0 (s, 2C, C_6H_5), 124.3 (s, 1C, C_6H_2), 125.1 (s, 1C, C_6H_2), 128.4 (s, 2C, C_6H_5), 141.9 (d, *J*(P–C) = 4 Hz, 1C, C_6H_2), 143.4 (d, *J*(P–C) = 3 Hz, 1C, C_6H_2), 146.0 (s, 1C, C_6H_2), 148.3 (d, *J*(P–C) = 10 Hz, 1C, C_6H_2), 155.9 (s, 1C, C_6H_5), 232.6 (s, 1C, *C*O), 245.7 (d, *J*(P–C) = 32 Hz, 1C, *C*O); FD mass spectrum molecular ion at *m/e* (relative intensity) 669 (4), 641 (14) ($M^+ - N_2$), 613 (100) ($M^+ - 2CO$). Anal. Calcd for $C_{34}H_{42}MoN_3O_3P$: C, 61.17; H, 6.34; N, 6.29. Found: C, 61.52; H, 6.83; N, 5.76.

4: yield 200 mg (0.3 mmol, 15%); mp 162 °C dec; IR (CH_2Cl_2) 3311 m $\nu({\equiv}C{-}H)$, 2120 vw $\nu(C{\equiv}C)$, 1960 vs, 1885 s $\nu(CO)$ cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.30 (s, 9H, *o*-^{t}Bu), 1.35 (s, 9H, *p*-^{t}Bu), 1.56 (s, 9H, *o*-^{t}Bu), 2.18 (dt, *J*(P–H) = 6.4 Hz, *J*(H–H) = 2.8 Hz, 1H, $CH_2C{\equiv}C\mathit{H}$), 3.16 (ddd, *J*(P–H) = 7.7 Hz, *J*(H–H) = 17.6 Hz, *J*(H–H) = 2.8 Hz, 1H, $C\mathit{H}_2C{\equiv}CH$), 3.88 (ddd, *J*(P–H) = 13.3 Hz, *J*(H–H) = 17.6 Hz, *J*(H–H) = 2.8 Hz, 1 H, $C\mathit{H}_2{\equiv}CH$), 5.01 (s, 5H, Cp), 7.32 (s, 2H, C_6H_2), 6.7–7.2 (m, 5H, C_6H_5); $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 54.6 (s); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 31.6 (s, 3C, *p*-^{t}Bu), 32.5 (s, 3C, *o*-^{t}Bu), 33.0 (s, 3C, *o*-^{t}Bu), 34.6 (s, 1C, ^{i}C/*p*-^{t}Bu), 36.1 (s, 1C, ^{i}C/*o*-^{t}Bu), 36.8 (s, 1C, ^{i}C/*o*-^{t}Bu), 20.1 (d, *J*(P–C) = 38 Hz, 1C, $\mathit{C}H_2C{\equiv}CH$), 73.4 (d, *J*(P–C) = 9 Hz, 1C, $CH_2C{\equiv}\mathit{C}H$), 75.4 (d, *J*(P–C) = 8 Hz, 1C, $CH_2\mathit{C}{\equiv}CH$), 93.4 (s, 5C, Cp), 119.8 (s, 1C, C_6H_5), 123.3 (s, 1C, C_6H_2), 123.7 (d, *J*(P–C) = 9 Hz, 2C, C_6H_5), 124.7 (s, 1C, C_6H_2), 128.2 (s, 2C, C_6H_5), 142.4 (d, *J*(P–C) = 5 Hz, 1C, C_6H_2), 143.7 (d, *J*(P–C) = 4 Hz, 1C, C_6H_2), 146.2 (d, *J*(P–C) = 3 Hz, 1C, C_6H_2), 148.2 (d, *J*(P–C) = 6 Hz, 1C, C_6H_2), 150.7 (d, *J*(P–C) = 22 Hz, 1C, C_6H_5), 241.6 (s, 1C, *C*O), 251.7 (d, *J*(P–C) = 34 Hz, 1C, *C*O); EI mass spectrum molecular ion at *m/e* (relative intensity) 641 (10), 585 (12) ($M^+ - 2CO$), 546 (2) ($M^+ - 2CO - C_3H_3$), 528 (2) ($M^+ - 2CO - {}^tBu$), 489 (1) ($M^+ - 2CO - {}^tBu - C_3H_3$), 324 (100) ($M^+ - {}^tBu_3C_6H_2O - 2CO$). Anal. Calcd for $C_{34}H_{42}MoNO_3P$: C, 63.85; H, 6.62; N, 2.19. Found: C, 63.88; H, 6.85; N, 2.40.

Synthesis of (R)(HC≡CCH₂)P—N=N—N(2,4,6-Me₃-C₆H₂)—MoCp(CO)₂ (3b). Compound 1[2c] (1.67 g, 3.0 mmol) was treated with 2b[18] (560 mg, 3.5 mmol) in toluene (200 mL) for 24 h at 25 °C. Workup similar to that described earlier yielded pale yellow 3b: 93% yield (2.0 g, 2.8 mmol); mp 150 °C dec. No compound of type 4 could be detected. IR (*n*-pentane): 3311 m $\nu({\equiv}C{-}H)$, 2123 vw $\nu(C{\equiv}C)$, 1978 vs, 1908 s $\nu(CO)$ cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.33 (s, 9H, *o*-^{t}Bu), 1.37 (s, 9H, *p*-^{t}Bu), 1.54 (s, 9H, *o*-^{t}Bu), 1.77 (s, 3H, Mes CH_3), 1.87 (dt, *J*(P–H) = 6.6 Hz, *J*(H–H) = 3.0 Hz, 1H, $CH_2C{\equiv}CH$), 2.02 (s, 3H, Mes CH_3), 2.30 (s, 3H, Mes CH_3), 3.32 (ddd, *J*(P–H) = 16.3 Hz, *J*(H–H) = 16.3 Hz, *J*(H–H) = 3.0 Hz, 1H, $CH_2C{\equiv}CH$), 3.69 (ddd, *J*(P–H) = 6.3 Hz, *J*(H–H) = 16.3 Hz, *J*(H–H) = 3.0 Hz, 1H, $CH_2C{\equiv}CH$), 5.11 (s, 5H, Cp), 6.85 (s, 1H, C_6H_2), 6.87 (s, 1H, C_6H_2), 7.24 (s, 1H, C_6H_2O), 7.34 (s, 1H, C_6H_2O). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 238.2 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 18.7 (s, 1C, Mes CH_3), 19.7 (s, 1C, Mes CH_3), 20.9 (s, 1C, Mes CH_3), 27.4 (d, *J*(P–C) = 55 Hz, 1C, $\mathit{C}H_2C{\equiv}CH$), 31.6 (s, 3C, *p*-^{t}Bu), 32.5 (s, 3C, *o*-^{t}Bu), 33.1 (s, 3C, *o*-^{t}Bu), 34.5 (s, 1C, ^{i}C/*p*-^{t}Bu), 36.3 (s, 1C, ^{i}C/*o*-^{t}Bu), 36.9 (s, 1C, ^{i}C/*o*-^{t}Bu), 72.4 (d, *J*(P–C) = 10 Hz, 1C, $CH_2\mathit{C}{\equiv}CH$), 76.8 (s, 1C, $CH_2C{\equiv}\mathit{C}H$), 92.2 (s, 5C, Cp), 122.5 (s, 1C, C_6H_2O), 125.0 (s, 1C, C_6H_2O), 129.0 (s, 1C, C_6H_2), 129.4 (s, 1C, C_6H_2), 130.8 (s, 1C, C_6H_2), 135.2 (s, 1C, C_6H_2), 138.8 (s, 1C, C_6H_2), 141.2 (s, 1C, C_6H_2O), 143.4 (s, 1C, C_6H_2O), 146.0 (s, 1C, C_6H_2O), 147.8 (d, *J*(P–C) = 13 Hz, 1C, C_6H_2O), 152.3 (s, 1C, C_6H_2), 235.7 (s, 1C, CO), 243.7 (d, *J*(P–C) = 34 Hz, 1C, CO). FD mass spectrum: molecular ion at *m/e* 711 M^+. Anal. Calcd for $C_{37}H_{48}MoN_3O_3P$: C, 62.62; H, 6.82; N, 5.92. Found: C, 62.45; H, 7.11; N, 5.91.

Synthesis of (R)(HC≡CCH₂)P—N(Ph)—MoCp(CO)₂ (4) via Thermal Treatment of 3a. Compound 3a (400 mg, 0.60 mmol) was stirred in toluene (100 mL) for 3 h at 90 °C. The reaction mixture slowly turned from yellow to orange, and dinitrogen evolution was observed. Workup similar to that described earlier, followed by column chromatography at −25 °C (column size 1.5 × 20 cm; *n*-pentane, silica gel) yielded with *n*-pentane/CH_2Cl_2 (2:1) an orange fraction. Evaporation of the solvents and recrystallization from Et_2O/*n*-pentane at −30 °C gave pure 4 (280 mg, 0.44 mmol, 73% yield) as an orange crystalline product. For analytical and spectroscopic data, see above.

Synthesis of (R)[(η^2-CH₂C≡CH)Co₂(CO)₆]P—N=N—N(R')—MoCp(CO)₂ (6) (6a, R' = C₆H₅; 6b, R' = 2,4,6-Me₃C₆H₂). Compound 3 (3a, 70 mg, 0.1 mmol; 3b, 70 mg, 0.1 mmol) in toluene (30 mL) at 25 °C was added to $Co_2(CO)_8$ (5, 36 mg, 0.1 mmol)

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in toluene/*n*-pentane (1:1) (40 mL). After 3 h all volatiles were removed under reduced pressure and the resulting dark residue was extracted with *n*-pentane and filtered through a pad of silica gel. Evaporation of the solvent gave **6a** (60 mg, 0.063 mmol, 63% yield) or **6b** (65 mg, 0.065 mmol, 66% yield). Recrystallization from *n*-pentane at −30 °C affords dark orange crystals (**6a**, mp 128 °C dec; **6b**, 149 °C dec).

6a: IR (*n*-pentane) 2091 m, 2054 vs, 2022 vs, 2006 s, 1968 s, 1905 m ν(CO) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.31 (S, 9H, *o*-^{t}Bu), 1.39 (s, 9H, *p*-^{t}Bu), 1.54 (s, 9H, *o*-^{t}Bu), 3.89 (dd, *J*(P–H) = 18 Hz, *J*(H–H) = 16 Hz, 1H, $\mathrm{C}\mathit{H}_2\mathrm{C{\equiv}CH}$), 4.30 (dd, *J*(P–H) = 2 Hz, *J*(H–H) = 16 Hz, 1H, $\mathrm{C}\mathit{H}_2\mathrm{C{\equiv}CH}$), 5.86 (d, *J*(P–H) = 2 Hz, 1H, $\mathrm{CH_2C{\equiv}C}\mathit{H}$), 5.01 (s, 5H, Cp), 7.1–7.4 (m, 7H, C_6H_2/C_6H_5); ^{31}P{^{1}H} NMR ($CDCl_3$) δ 228.1 (s); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 31.2 (s, 3C, *p*-^{t}Bu), 32.6 (s, 3C, *o*-^{t}Bu), 32.8 (s, 3C, *o*-^{t}Bu), 34.3 (s, 1C, ^{i}C/*p*-^{t}Bu), 35.9 (s, 1C, ^{i}C/*o*-^{t}Bu), 36.1 (s, 1C, ^{i}C/*o*-^{t}Bu), 38.7 (d, *J*(P–C) = 38 Hz, 1C, $\mathit{C}\mathrm{H_2C{\equiv}CH}$), 72.5 (s, 1C, $\mathrm{CH_2C{\equiv}}\mathit{C}\mathrm{H}$), 85.2 (s, 1C, $\mathrm{CH_2}\mathit{C}\mathrm{{\equiv}CH}$), 93.3 (s, 5C, Cp), 121.7 (s, 1C, C_6H_2), 122.1 (s, 1C, C_6H_2), 123.8 (s, 2C, C_6H_5), 125.3 (s, 1C, C_6H_5), 128.5 (s, 2C, C_6H_5), 141.4 (s, 1C, C_6H_2), 143.1 (s, 1C, C_6H_2), 145.6 (s, 1C, C_6H_2), 147.5 (br s, 1C, C_6H_2), 155.9 (s, 1C, C_6H_5), 199.5 (br s, 6C, Co–*C*O), 228.2 (s, 1C, Mo–*C*O), 245.5 (s, 1C, Mo–*C*O); FD mass spectrum *m*/*e* 731 (M$^+$ − 8CO). Anal. Calcd for $C_{40}H_{42}Co_2MoN_3O_9P$: C, 50.38; H, 4.44; N, 4.41. Found: C, 50.04; H, 4.69; N, 4.26.

6b: IR (*n*-pentane) 2090 m, 2055 vs, 2022 s, 2009 w, 1978 m, 1898 m ν(CO) cm^{-1}; ^{1}H NMR ($CDCl_3$) 1.35 (s, 9H, *o*-^{t}Bu), 1.42 (s, 9H, *p*-^{t}Bu), 1.56 (s, 9H, *o*-^{t}Bu), 1.89 (s, 3H, Mes CH_3), 1.99 (s, 3H, Mes CH_3), 2.31 (s, 3H, Mes CH_3), 3.97 (br s, 2H, $\mathrm{CH_2C{\equiv}CH}$), 5.87 (br s, 1H $\mathrm{CH_2C{\equiv}CH}$), 5.23 (s, 5H, Cp), 6.88 (s, 2H, C_6H_2), 7.27 (s, 1H, C_6H_2O), 7.40 (s, 1H, C_6H_2O); ^{31}P{^{1}H} NMR ($CDCl_3$) 227.3 (s); ^{13}C{^{1}H} NMR ($CDCl_3$) 18.7 (s, 1C, Mes CH_3), 19.2 (s, 1C, Mes CH_3), 20.5 (s, 1C, Mes CH_3), 31.2 (s, 3C, *p*-^{t}Bu), 32.2 (s, 3C, *o*-^{t}Bu), 32.8 (s, 3C, *o*-^{t}Bu), 34.2 (s, 1C, ^{i}C/*p*-^{t}Bu), 35.9 (s, 1C, ^{i}C/*o*-^{t}Bu), 36.8 (s, 1C, ^{i}C/*o*-^{t}Bu), 39.5 (br s, 1C, $\mathit{C}\mathrm{H_2C{\equiv}CH}$), 71.9 (s, 1C, $\mathrm{CH_2}\mathit{C}\mathrm{{\equiv}CH}$), 85.5 (s, 1C, $\mathrm{CH_2C{\equiv}}\mathit{C}\mathrm{H}$), 92.5 (s, 5C, Cp), 121.9 (s, 1C, C_6H_2O), 125.0 (s, 1C, C_6H_2O), 128.9 (s, 1C, C_6H_2), 129.3 (s, 1C, C_6H_2), 131.3 (s, 1C, C_6H_2), 133.6 (s, 1C, C_6H_2), 135.7 (s, 1C, C_6H_2), 141.1 (s, 1C, C_6H_2O), 143.2 (s, 1C, C_6H_2O), 145.5 (s, 1C, C_6H_2O), 148.3 (br s, 1C, C_6H_2O), 151.8 (s, 1C, C_6H_2), 199.5 (br s, 6C, Co–CO), 234.6 (s, 1C, Mo–CO), 245.3 (br s, 1C, Mo–CO); DCI mass spectrum molecular ion at *m*/*e* (relative intensity) 829 (M$^+$ − 6CO). Anal. Calcd for $C_{43}H_{48}Co_2MoN_3O_9P$: C, 51.87; H, 4.86; N, 4.22. Found: C, 51.42; H, 4.99; N, 4.26.

Synthesis of (R)[(η^2-$\mathrm{CH_2C{\equiv}CH}$)$Co_2(CO)_6$]P—N-(Ph)—MoCp$(CO)_2$ (7) via Reaction of 4 with 5. Similar to the method described for the preparation of **6**, compound **4**, (250 mg, 0.4 mmol) was treated with $Co_2(CO)_8$ (**5**) (140 mg, 0.4 mmol). The reaction mixture gradually turned deep red. After 3 h of stirring at 25 °C all volatiles were removed under reduced pressure and column chromatography (column size 1.5 × 20 cm; *n*-pentane, silica gel) of the dark residue afforded with Et_2O/*n*-pentane (1:10) a red-brown fraction. Removing the solvents under reduced pressure and recrystallization of the resulting residue from *n*-pentane at −30 °C gave dark red **7** (240 mg, 0.26 mmol, 65% yield): mp 162 °C dec; IR (*n*-pentane) 2091 m, 2057 s, 2025 vs, 1954 s, 1882 m, 1874 m ν(CO) cm^{-1}; ^{1}H NMR ($CDCl_3$) 1.31 (s, 9H, *o*-^{t}Bu), 1.34 (s, 9H, *p*-^{t}Bu), 1.59 (s, 9H, *o*-^{t}Bu), 4.07 (dd, *J*(P–H) = 5.6 Hz, *J*(H–H) = 17.7 Hz, 1H, $\mathrm{C}\mathit{H}_2\mathrm{C{\equiv}CH}$), 4.90 (dd, *J*(P–H) = 13.4 Hz, *J*(H–H) = 17.7 Hz, 1H, $\mathrm{C}\mathit{H}_2\mathrm{C{\equiv}CH}$), 6.13 (br s, 1H, $\mathrm{CH_2C{\equiv}C}\mathit{H}$), 5.00 (s, 5H, Cp), 7.30 (s, 1H, C_6H_2O), 7.34 (s, 1H, C_6H_2O), 6.7–7.2 (m, 5H, C_6H_5); ^{31}P{^{1}H} NMR ($CDCl_3$) 56.0 (s); ^{13}C{^{1}H} NMR ($CDCl_3$) 31.5 (s, 3C, *p*-^{t}Bu), 32.6 (s, 3C, *o*-^{t}Bu), 33.4 (s, 3C, *o*-^{t}Bu), 34.6 (s, 1C, ^{i}C/*p*-^{t}Bu), 36.4 (s, 1C, ^{i}C/*o*-^{t}Bu), 36.8 (s, 1C, ^{i}C/*o*-^{t}Bu), 34.6 (d, *J*(P–C) = 21 Hz, 1C, $\mathit{C}\mathrm{H_2C{\equiv}CH}$), 74.0 (s, 1C, $\mathrm{CH_2C{\equiv}}\mathit{C}\mathrm{H}$), 83.7 (d, *J*(P–C) = 6 Hz, 1C, $\mathrm{CH_2}\mathit{C}\mathrm{{\equiv}CH}$), 93.6 (s, 5C, Cp), 120.0 (s, 1C, C_6H_5), 123.5 (d, *J*(P–C) = 9 Hz, 2C, C_6H_5), 124.2 (s, 1C, C_6H_2), 124.8 (s, 1C, C_6H_2), 128.4 (s, 2C, C_6H_5), 142.0 (d, *J*(P–C) = 5 Hz, 1C, C_6H_2), 143.6 (d, *J*(P–C) = 4 Hz, 1C, C_6H_2), 146.2 (d, *J*(P–C) = 3 Hz, 1C, C_6H_2), 147.8 (d, *J*(P–C) = 7 Hz, 1C, C_6H_2), 150.3 (d, *J*(P–C) = 22 Hz, 1C, C_6H_5), 199.5 (d, *J*(P–C) = 27 Hz, 6C, Co–*C*O), 242.5 (s, 1C, Mo–*C*O), 252.2 (d, *J*(P–C) = 33 Hz, 1C, Mo–*C*O); FD mass spectrum molecular ion at *m*/*e* 927. Anal. Calcd for $C_{40}H_{42}Co_2MoNO_9P$: C, 51.91; H, 4.63; N, 1.51. Found: C, 52.44; H, 4.90; N, 1.75.

Synthesis of (R)[(η^2-$\mathrm{CH_2C{\equiv}CH}$)$Co_2(CO)_6$]P═MoCp$(CO)_2$ (8) via Reaction of 1 with 5. Compound **1**[2c] (530 mg, 0.97 mmol) was dissolved in toluene/*n*-pentane (1:1) (100 mL). At 0 °C an equimolar amount of $Co_2(CO)_8$ (**5**; 330 mg, 0.97 mmol) dissolved in toluene/*n*-pentane (1:1) (100 mL) was added. After 3 h of stirring at 25 °C all the volatiles were removed under high vacuum and the resulting residue was purified by column chromatography at −25 °C (column size 1.5 × 25 cm; *n*-pentane, silica gel). One deep red fraction could be collected with *n*-pentane/CH_2Cl_2 (10:1). After removal of the solvents under reduced pressure and recrystallization of the residue from *n*-pentane at −30 °C, deep red crystals of **8** (470 mg, 0.56 mmol, 58% yield) were afforded: mp 156 °C dec; IR (*n*-pentane) 2092 s, 2055 vs, 2028 vs, 2025 vs, 1952 s, 1883 m ν(CO) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.40 (s, 9H, *p*-^{t}Bu), 1.44 (s, 18H, *o*-^{t}Bu), 4.33 (d, *J*(P–H) = 11.2 Hz, 2H, "$\mathrm{C}\mathit{H}_2\mathrm{C{\equiv}CH}$"), 6.58 (s, 1H, "$\mathrm{CH_2C{\equiv}C}\mathit{H}$"), 4.88 (s, 5H, Cp), 7.39 (s, 2H, C_6H_2); ^{31}P{^{1}H} NMR ($CDCl_3$) δ 324.6 (s); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 31.7 (s, 3C, *p*-^{t}Bu), 33.3 (s, 6C, *o*-^{t}Bu), 34.8 (s, 1C, ^{i}C/*p*-^{t}Bu), 36.3 (s, 2C, ^{i}C/*o*-^{t}Bu), 52.8 (s, 1C, "$\mathit{C}\mathrm{H_2C{\equiv}CH}$"), 74.7 (s, 1C, "$\mathrm{CH_2}\mathit{C}\mathrm{{\equiv}CH}$"), 85.5 (s, 1C, "$\mathrm{CH_2C{\equiv}}\mathit{C}\mathrm{H}$"), 91.7 (s, 5C, Cp), 124.2 (s, 2C, C_6H_2), 142.0 (s, 2C, C_6H_2), 146.8 (s, 1C, C_6H_2), 149.1 (s, 1C, C_6H_2), 199.6 (br s, 6C, Co–CO), 236.4 (d, *J*(P–C) = 20 Hz, 2C, Mo–CO); FD mass spectrum molecular ion at *m*/*e* 836. Anal. Calcd for $C_{34}H_{37}Co_2MoO_9P$: C, 48.94; H, 4.47. Found: C, 49.00; H, 4.60.

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Supplementary Material Available: Tables of positional and isotropic thermal parameters, bond distances and angles, and X-ray data collection and refinement details for **6b** (6 pages). Ordering information is given on any current masthead page.

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