

Bifunctional neutral phosphonium ion complexes: synthesis of phenylethynyl- and styryl-substituted $(R)(R')P=Mo(\eta^5-C_5Me_5)(CO)_2$ compounds. Crystal structure of $[2,6-{}^tBu_2-4-MeC_6H_2O)(PhC\equiv C)]P=Mo(\eta^5-C_5Me_5)(CO)_2$

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Abstract

The reactions of the phenylethynylchlorophosphine $(2,6-{}^tBu_2-4-MeC_6H_2O)P(Cl)-C\equiv CPh$ (I) or the styrylchlorophosphine $(2,4,6-{}^tBu_3C_6H_2O)P(Cl)[(Ph)(H)C=C(H)]$ (IV) with $Li[Mo(\eta^5-C_5Me_5)(CO)_3]$ (II) in THF give bifunctionalized terminal phosphonium ion complexes of the type $(R)(R')P=Mo(\eta^5-C_5Me_5)(CO)_2$ (III: $R = 2,6-{}^tBu_2-4-MeC_6H_2O$, $R' = C\equiv CPh$; V: $R = 2,4,6-{}^tBu_3C_6H_2O$, $R' = (Ph)(H)C=C(H)$), which contain a trigonally planar coordinated phosphorus atom. Compounds III and V have been identified from analytical and spectroscopic (IR, 1H , ${}^{13}C$, ${}^{31}P$ NMR) data. The molecular structure of $[(2,6-{}^tBu_2-4-MeC_6H_2O)(PhC\equiv C)]P=Mo(\eta^5-C_5Me_5)(CO)_2$ (III) has been determined by an X-Ray diffraction study.

Introduction

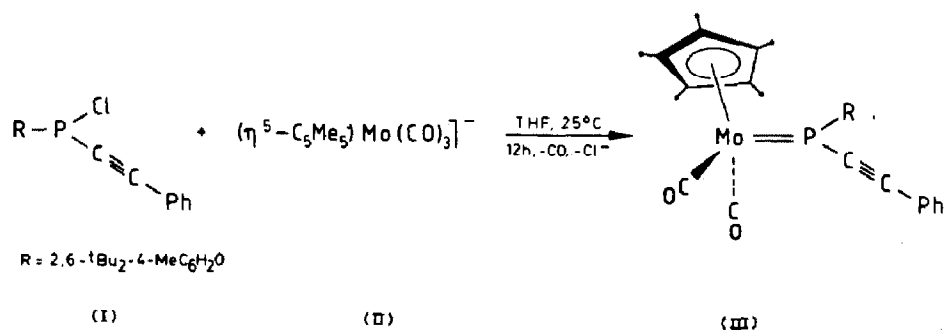
The metal phosphorus multiple bond in neutral phosphonium ion complexes [1–3] of the type $R_2P=ML_n$ ($ML_n = CpMo(CO)_2$, $CpW(CO)_2$; $R =$ alkyl, aryl) shows an interesting reactivity pattern. The formal analogy between these complexes and metal carbene compounds [4], and the well known reactivity of Fischer type carbene complexes with alkynyl building blocks [4,5], suggested to us that a study of alkynyl-substituted phosphonium ion compounds of the type $[(R)(PhC\equiv C)]P=Mo(\eta^5-C_5Me_5)(CO)_2$ ($R =$ singly-bonding organic ligand) would be of particular interest. The bifunctional reactivity of these complexes (metal–phosphorus and carbon–carbon multiple bonds) should give rise to a wide range of reactions.

A different type of bifunctionality is shown by the phosphonium ion complex $\{(R)[(Ph)(H)C=C(H)]\}P=Mo(\eta^5-C_5Me_5)(CO)_2$, which can be regarded as a heterobutadiene system.

We describe here the reactions of $\text{Li}[\text{Mo}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_3]$ with $(\text{R})(\text{R}')\text{PCl}$ ($\text{R} = 2,6\text{-}^t\text{Bu}_2\text{-4-MeC}_6\text{H}_2\text{O}$, $2,4,6\text{-}^t\text{Bu}_3\text{C}_6\text{H}_2\text{O}$; $\text{R}' = \text{PhC}\equiv\text{C}$, $(\text{Ph})(\text{H})\text{C}=\text{C}(\text{H})$), which yield the phosphonium ion compounds $(\text{R})(\text{R}')\text{P}=\text{Mo}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2$ ($\text{R}, \text{R}' = \text{see above}$).

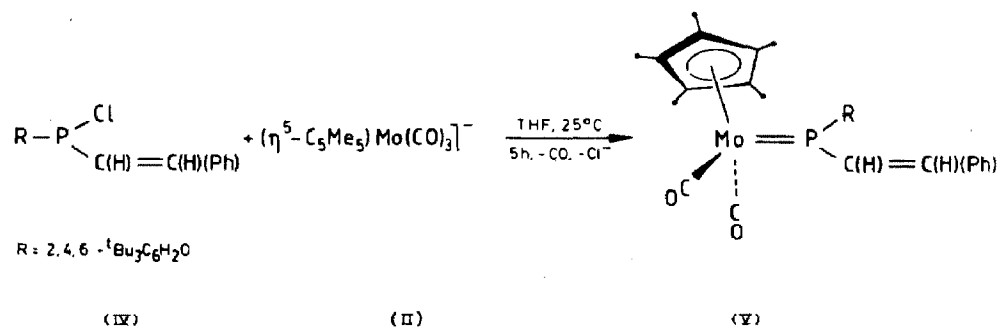
Results and discussion

The reaction between equimolar amounts of $\text{Li}[\text{Mo}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_3]$ (II) [6], and $(2,6\text{-}^t\text{Bu}_2\text{-4-MeC}_6\text{H}_2\text{O})\text{P}(\text{Cl})(\text{C}\equiv\text{CPh})$ (I) [7], in tetrahydrofuran at 25°C (12 h) resulted in slow elimination of CO, and the solution became dark red-purple. After the solvent had been removed in vacuo, the dark residue was extracted with *n*-pentane/ CH_2Cl_2 , and the extract filtered through silica gel and the red-purple filtrate evaporated to dryness. Recrystallization of the residue from *n*-pentane/toluene gave analytically pure III in 80% yield.



In a similar experiment $\text{Li}[\text{Mo}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_3]$ [6] was treated with $(2,4,6\text{-}^t\text{Bu}_3\text{C}_6\text{H}_2\text{O})\text{P}(\text{Cl})[(\text{Ph})(\text{H})\text{C}=\text{C}(\text{H})]$ (IV) itself prepared in 86% yield by the reaction of $(2,4,6\text{-}^t\text{Bu}_3\text{C}_6\text{H}_2\text{O})\text{PCl}_2$ with an equimolar amount of $\text{BrMg}[(\text{Ph})(\text{H})\text{C}=\text{C}(\text{H})]$ at -70°C in a *n*-pentane/THF mixture. The chloro-substituted compound IV obtained, always contained, in varying proportions, the corresponding bromophosphine $(2,4,6\text{-}^t\text{Bu}_3\text{C}_6\text{H}_2\text{O})[(\text{Ph})(\text{H})\text{C}=\text{C}(\text{H})]\text{PBr}$, formed by metathetical exchange with MgBr_2 , as revealed by ^1H and ^{31}P NMR spectroscopy as well as by EI mass spectrometry.

After 5 h stirring of a solution of II and IV in THF at room temperature and work up as before, the phosphonium complex V, which in terms of the isolobal analogy proposed by Hoffmann et al. [8] may be considered as a hetero-substituted butadiene, was isolated in 25% yield as dark red-purple crystals.



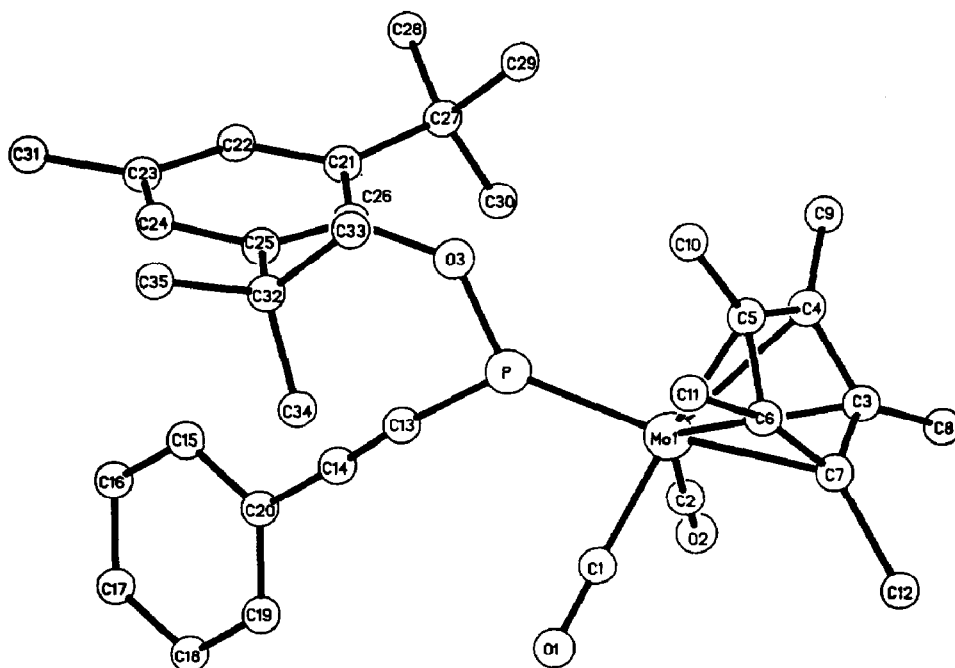


Fig. 1. Molecular geometry and atom labelling scheme for $[(2,6\text{-}t\text{Bu}_2\text{-}4\text{-MeC}_6\text{H}_2\text{O})(\text{PhC}\equiv\text{C})]\text{P}=\text{Mo}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2$ [9]. Selected bond distances (pm) and angles (deg): P–Mo 219.7(4), P–O(3) 163.3(9), P–C(13) 175(1), C(13)–C(14) 119(2); O(3)–P–Mo 129.2(3), O(3)–P–C(13) 100.7(5), Mo–P–C(13) 130.2(4).

The infrared spectra of III and V in *n*-pentane solution each show two strong carbonyl bands, at 1955 and 1889 cm^{-1} (III) and at 1937 and 1871 cm^{-1} (V), consistent with the presence of two terminal carbonyl ligands. The band pattern is that expected for complexes containing a $\text{MoCp}'(\text{CO})_2$ ($\text{Cp}' = \eta^5\text{-C}_5\text{H}_5$, $\eta^5\text{-C}_5\text{Me}_5$) fragment, and the frequencies are similar to those reported for several $\text{R}_2\text{P}=\text{Mo}(\text{Cp}')(\text{CO})_2$ ($\text{Cp}' = \eta^5\text{-C}_5\text{H}_5$, $\eta^5\text{-C}_5\text{Me}_5$) compounds [1,2]. The phenylethynyl ligand in III shows a weak band at 2145 cm^{-1} in the $\nu(\text{C}\equiv\text{C})$ region, consistent with an uncoordinated alkynyl ligand. In the case of V, two very weak infrared absorptions are observed in the C=C stretching region, at 1592 and 1564 cm^{-1} , respectively.

The ^1H , $^{31}\text{P}\{-^1\text{H}\}$ and ^{13}C NMR spectra were completely assigned, and the data are consistent with the proposed formulation of III and V as neutral phosphonium ion complexes.

The $^{31}\text{P}\{-^1\text{H}\}$ NMR spectra each show a singlet, centred at 207.2 ppm for III and 271.6 ppm for V (see Experimental). The large downfield shifts for III and V compared to those for the starting compounds I (139.4 ppm) and IV (180.1 ppm) are characteristic of those observed formation of most metallophosphonium ion complexes [1–3].

In the ^{13}C NMR the acetylenic carbon atoms of III appear as two singlets at 94.6 and 104.3 ppm. The carbon resonances of the C=C unit in V are centred at 135.2 and 142.2 ppm, with $J(\text{PC})$ coupling constants of 27 and 34 Hz respectively. The corresponding resonances for the carbonyl ligands appear at 238.5 (III) and 239.8 (V) ppm as doublets with a $J(\text{PC})$ coupling constant of 20 Hz in each case.

The X-ray diffraction study of III confirmed the proposed formulation for $[(2,6\text{-}^1\text{Bu}_2\text{-4-MeC}_6\text{H}_2\text{O})(\text{PhC}\equiv\text{C})]\text{P}=\text{Mo}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2$ [9*]. A view of the molecule is shown in Fig. 1. Selected bond distances and angles are given in the footnote to Fig. 1.

The structure of III is related to that of other phosphonium ion complexes of the type $\text{R}_2\text{P}=\text{MoCp}'(\text{CO})_2$ ($\text{Cp}' = \eta^5\text{-C}_5\text{H}_5, \eta^5\text{-C}_5\text{Me}_5$; $\text{R} = \text{alkyl, aryl}$) [1,2]. The molybdenum atom geometry is pseudooctahedral. The most notable feature of III is that the atoms Mo, O(3), C(13) and P form a plane almost perpendicular to the $\text{Mo}(\text{CO})_2$ plane (interplanar angle 89.4°); the sum of the angles around phosphorus (360.2°) also point to a trigonal planar environment around the central phosphorus atom [9]. The Mo–P distance, 219.7(4) pm, is in the range observed for other phosphonium ion complexes (distances: 220–223 pm [1,2]), but is considerably shorter than the usual range of distances, 235–260 pm [10], found in many organomolybdenum-phosphine complexes involving $\text{P} \rightarrow \text{Mo}$ dative bonds. Such bond shortening can be taken to imply P–Mo multiple bonding in III [1,2]. The acetylene bond distance, C(13)–C(14), of 119(2) pm is comparable with corresponding distances in other alkyne derivatives [11]. The P–C(13) length is slightly shorter than that for a normal P–C single bond, and this may be due to the sp -hybridization of the $\text{C}\equiv\text{C}$ bonding system.

Experimental

All reactions were carried out under nitrogen by Schlenk techniques. Tetrahydrofuran was purified by distillation from sodium/benzophenone ketyl, *n*-pentane and toluene by distillation from sodium, and dichloromethane by distillation from phosphorus pentoxide.

Infrared spectra were recorded on a Perkin Elmer spectrometer (model 983 G). ^1H , ^{13}C and ^{31}P NMR spectra on a Bruker AC 200 spectrometer operating in the Fourier transform mode: ^1H NMR: 200.13 MHz; ^{13}C NMR: 50.323 MHz; ^{31}P - $\{^1\text{H}\}$ NMR: 80.015 MHz; Chemical shifts are reported in δ units, downfield from tetramethylsilane, the solvents being used for reference signals. EI mass spectra were recorded on a Finnigan (Varian) MAT 8230 spectrometer operating at 70 eV (the m/e values given correspond to isotopes of highest natural abundance). Melting points were determined with analytically pure samples, which were sealed in nitrogen-filled capillaries on a Gallenkamp melting point apparatus, and are uncorrected.

Starting materials $(2,4,6\text{-}^1\text{Bu}_3\text{C}_6\text{H}_2\text{O})\text{PCl}_2$ [7,12], $(2,6\text{-}^1\text{Bu}_2\text{-4-MeC}_6\text{H}_2\text{O})(\text{PhC}\equiv\text{C})\text{PCl}$ [7] and $(\eta^5\text{-C}_5\text{Me}_5)\text{Mo}(\text{CO})_3^-$ [6] were prepared by published procedures.

(A) Synthesis of $(2,4,6\text{-}^1\text{Bu}_3\text{C}_6\text{H}_2\text{O})[(\text{Ph})(\text{H})\text{C}=\text{C}(\text{H})]\text{PCl}$ (IV)

A solution of 16.4 g (45 mmol) of $(2,4,6\text{-}^1\text{Bu}_3\text{C}_6\text{H}_2\text{O})\text{PCl}_2$ [7,12] in 200 ml of *n*-pentane was cooled to -70°C and treated dropwise with a solution of styryl-magnesium-bromide in THF, prepared from 9.15 g (50 mmol) of β -bromostyrene and 3.65 g (150 mmol) of magnesium turnings. The mixture was allowed to warm to room temperature and then stirred for 1 h at 25°C . After evaporation of the volatile

* Reference number with asterisk indicates a note in the list of references.

Table 1

Atomic coordinates and equivalent isotropic displacement parameters for III

Atom	x	y	z	U_{eq}^a
Mo1	0.1127(1)	0.20773(6)	0.15957(3)	0.0536(3)
P	0.0161(4)	0.2947(2)	0.13466(8)	0.055(1)
C1	-0.080(2)	0.1753(9)	0.1655(6)	0.104(8)
C2	0.099(2)	0.1607(7)	0.1154(4)	0.087(7)
O1	-0.201(2)	0.1543(7)	0.1697(5)	0.150(8)
O2	0.093(2)	0.1322(7)	0.0886(3)	0.172(8)
O3	0.0576(9)	0.3711(4)	0.1409(2)	0.060(3)
C3	0.336(1)	0.1513(6)	0.1712(3)	0.070(6)
C4	0.365(1)	0.2191(6)	0.1729(3)	0.071(6)
C5	0.279(1)	0.2456(6)	0.2012(3)	0.14(1)
C6	0.197(1)	0.1941(6)	0.2170(3)	0.15(1)
C7	0.232(1)	0.1359(6)	0.1984(3)	0.111(9)
C8	0.413(2)	0.1026(8)	0.1477(4)	0.119(6)
C9	0.478(2)	0.2497(9)	0.1477(5)	0.118(6)
C10	0.275(4)	0.308(2)	0.2204(9)	1.000(6)
C11	0.124(4)	0.243(1)	0.250(1)	1.000(6)
C12	0.197(4)	0.054(2)	0.1948(9)	1.000(6)
C10X	0.324(4)	0.332(2)	0.2016(8)	1.000(6)
C11X	0.087(3)	0.184(1)	0.2509(9)	1.000(6)
C12X	0.159(4)	0.084(2)	0.2225(8)	1.000(6)
C13	-0.125(2)	0.3018(6)	0.1029(3)	0.061(5)
C14	-0.216(1)	0.3019(7)	0.0797(3)	0.064(5)
C15	-0.325(1)	0.3592(4)	0.0292(3)	0.077(6)
C16	-0.419(1)	0.3610(4)	-0.0006(3)	0.100(8)
C17	-0.508(1)	0.3076(4)	-0.0084(3)	0.104(9)
C18	-0.503(1)	0.2525(4)	0.0134(3)	0.101(8)
C19	-0.409(1)	0.2508(4)	0.0431(3)	0.082(7)
C20	-0.320(1)	0.3041(4)	0.0510(3)	0.059(5)
C21	0.053(2)	0.4471(7)	0.0914(4)	0.065(5)
C22	-0.029(2)	0.4937(7)	0.0738(4)	0.075(6)
C23	-0.162(2)	0.5183(7)	0.0862(4)	0.077(7)
C24	-0.207(2)	0.4991(7)	0.1187(4)	0.076(6)
C25	-0.131(2)	0.4518(6)	0.1395(3)	0.058(5)
C26	-0.007(2)	0.4243(6)	0.1237(3)	0.055(5)
C27	0.206(2)	0.4261(8)	0.0773(5)	0.084(7)
C28	0.260(2)	0.4738(8)	0.0482(5)	0.14(1)
C29	0.320(2)	0.430(1)	0.1063(5)	0.16(1)
C30	0.199(2)	0.3607(8)	0.0601(5)	0.17(1)
C31	-0.250(2)	0.5666(7)	0.0645(4)	0.14(6)
C32	-0.188(2)	0.4375(7)	0.1782(4)	0.067(6)
C33	-0.058(2)	0.4414(9)	0.2044(4)	0.129(9)
C34	-0.261(2)	0.3699(7)	0.1805(4)	0.119(8)
C35	-0.300(2)	0.4899(8)	0.1907(4)	0.14(1)

^a Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

materials in high vacuo, the residue was extracted three times with a 100 ml portions of n-pentane, and the extract was filtered through a pad of Celite. Removal of the solvent on recrystallization of the residue from n-pentane at -30°C gave colorless crystals of IV in 86% yield (17.2 g).

The compound $(2,4,6\text{-}^t\text{Bu}_3\text{C}_6\text{H}_2\text{O})[(\text{Ph})(\text{H})\text{C}=\text{C}(\text{H})]\text{PCl}$ (IV) was always obtained as a mixture with varying proportions of the corresponding bromophosphine

(2,4,6-¹Bu₃C₆H₂O)(Ph(H)C=C(H))PBr, formed by metathetical exchange with MgBr₂, as revealed by ³¹P-¹H} NMR (186.6(s) ppm) and EI mass spectroscopy (*m/e* (rel. intensity): 474 (8)).

Found: C, 70.51; H, 8.20. C₂₆H₃₆ClOP (431.00) calc.: C, 70.38; H, 8.12% (The analysis is calculated for a 5/2 mixture of chloro/bromo derivative; see above). IR (n-pentane, CaF₂ cells): $\nu(\text{C}=\text{C})$: 1595w, 1572w cm⁻¹. ¹H NMR (CDCl₃): 1.37(s, 9H, *p*-¹Bu), 1.55(s, 18H, *o*-¹Bu), 7.1–7.7(m, 9H, C₆H₂/C₆H₅/(H)C=C(H)). ³¹P-¹H} NMR (CDCl₃): 180.1(s, 1P). ¹³C NMR (CDCl₃): 31.6(q, *J*(CH) 125 Hz, 3C, *p*-¹Bu), 33.4(q, *J*(CH) 123 Hz, 6C, *o*-¹Bu), 34.6(s, 1C, ¹C *p*-¹Bu), 36.4(s, 2C, ¹C *o*-¹Bu), 131.5(dd, *J*(PC) 37 Hz, *J*(CH) 125 Hz, 1C, HC=), 143.1(dd, *J*(PC) 46 Hz, *J*(CH) 111 Hz, 1C, HC=), 124.4(d, *J*(CH) 162 Hz, 2C, C₆H₂/C₆H₅), 127.8(d, *J*(CH) 169 Hz, 2C, C₆H₂/C₆H₅), 128.9(d, *J*(CH) 163 Hz, 2C, C₆H₅/C₆H₂), 129.9(d, *J*(CH) 168 Hz, 1C, C₆H₂/C₆H₅), 135.4(s, 1C, C₆H₂/C₆H₅), 141.4(s, 2C, C₆H₂/C₆H₅), 145.2(s, 1C, C₆H₂/C₆H₅), 148.3(s, 1C, C₆H₂/C₆H₅). EI MS (*m/e* (rel. intensity)): *M*⁺ 430(30), *M*⁺ – Cl 395(86), *M*⁺ – [(Ph)(H)C=C(H)] 373(60), *M*⁺ – Cl – ¹Bu 338(45), ¹Bu₃C₆H₂OH⁺ 262(28), ¹Bu₃C₆H₂OH⁺ – Me 247(26), (H)PCCPh⁺ 133(100).

(B) Synthesis of III

To a solution of 1.20 g (3.73 mmol) of Li[Mo(η^3 -C₅Me₅)(CO)₃] [6] in 80 ml of THF a solution of the stoichiometric amount of (2,6-¹Bu₂-4-MeC₆H₂O)(PhC≡C)P(Cl) (I) [7] in 20 ml of THF was added dropwise at 25 °C. The mixture gradually turned dark red. After 12 h stirring at room temperature the THF was removed on a high vacuum line and the residue extracted with n-pentane/CH₂Cl₂. The extract was filtered through a pad of silica gel, the solvent was removed, and the residue recrystallized from n-pentane/toluene at –20 °C to give dark red-purple needles of III (1.91 g, 80%).

Found: C, 65.73; H, 6.84. C₃₅H₄₃MoO₃P (638.65) calc.: C, 65.83; H, 6.79%. M.p. 162 °C (decomp.). IR (CH₂Cl₂; CaF₂ cells): $\nu(\text{C}\equiv\text{C})$: 2141m cm⁻¹, $\nu(\text{CO})$: 1932vs, 1868vs cm⁻¹; (n-pentane; CaF₂ cells): $\nu(\text{C}\equiv\text{C})$: 2145m, $\nu(\text{CO})$: 1955vs, 1889vs cm⁻¹. ¹H NMR (CDCl₃): 1.55(s, 18H, ¹C₄H₉), 2.14(d, *J*(PH) 1.8 Hz, 15H, C₅Me₅), 2.34(s, 3H, CH₃), 7.13(s, 2H, C₆H₂), 7.0–7.5(m, 5H, C₆H₅). ³¹P-¹H} NMR (CDCl₃): 207.2(s, 1P). ¹³C-¹H} NMR (CDCl₃): 11.6(s, 5C, C₅Me₅), 21.4(s, 1C, CH₃), 32.0(s, 6C, ¹C₄H₉), 35.6(s, 2C, ¹C ¹C₄H₉), 94.6(s, 1C, C≡C), 104.3(s, 1C, C≡C), 105.9(s, 5C, C₅Me₅), 121.3, 126.6, 128.4, 129.5, 132.0, 132.6, 142.2, 152.5(each s, [12C], C₆H₂/C₆H₅), 238.5(d, *J*(PC) 20 Hz, 2C, CO). EI MS (*m/e* (rel. intensity); *m/e*-values refer to ⁹⁸Mo): *M*⁺ 640(19), *M*⁺ – 2CO 584(9), *M*⁺ – 2CO – ¹Bu 527(28), (C₅Me₅)MoPC₂Ph⁺ 365(100), (C₅Me₅)MoP(C₂)(MeC₆H₂O)⁺ 393(83), ¹Bu₂MeC₆H₂OH⁺ 220(19), ¹Bu₂C₆H₂OH⁺ 205(59), P¹BuC₆H₂O⁺ 178(11), ¹Bu⁺ 57(92).

(C) Synthesis of V

In a procedure analogous to that used for the reaction of I with II, 1.0 g (2.32 mmol) IV was treated with 750 mg (2.33 mmol) of II [6] in 80 ml of THF at 25 °C (5 h) to give a red mixture. Work up as before and recrystallization from n-pentane at –20 °C gave analytically pure V (400 mg, 25%).

Found: C, 66.55; H, 7.35; C₃₈H₅₁MoO₃P (682.74) calc.: C, 66.85; H, 7.53%. M.p.: 110 °C (decomp.). IR (n-pentane; CaF₂ cells): $\nu(\text{CO})$: 1937vs, 1871vs cm⁻¹, $\nu(\text{C}=\text{C})$:

1592w, 1564w cm^{-1} ; (KBr pellets): $\nu(\text{CO})$: 1925vs, 1857vs cm^{-1} , $\nu(\text{C}=\text{C})$: 1591w, 1557w cm^{-1} . ^1H NMR (CDCl_3): 1.37(s, 9H, $^1\text{C}_4\text{H}_9$), 1.49(s, 18H, $^1\text{C}_4\text{H}_9$), 1.92(d, $J(\text{PH})$ 1.0 Hz, 15H, C_5Me_5), 6.51(dd, $J(\text{HCCH})$ 17 Hz, $J(\text{PH})$ 20 Hz, 1H, $\text{HC}=\text{C}$), 7.2–7.5(m, 8H, $\text{C}_6\text{H}_2/\text{C}_6\text{H}_5/\text{HC}=\text{C}$). $^{31}\text{P}\{-^1\text{H}\}$ NMR (CDCl_3): 271.6(s, 1P). ^{13}C NMR (CDCl_3): 11.6(q, $J(\text{CH})$ 127 Hz, 5C, C_5Me_5), 30.5(q, $J(\text{CH})$ 125 Hz, 3C, $^1\text{C}_4\text{H}_9$), 32.4(q, $J(\text{CH})$ 125 Hz, 6C, $^1\text{C}_4\text{H}_9$), 34.8(s, 1C, ^1C $^1\text{C}_4\text{H}_9$), 35.9(s, 2C, ^1C $^1\text{C}_4\text{H}_9$), 105.9(s, 5C, C_5Me_5), 123.4(d, $J(\text{CH})$ 158 Hz, 2C, $\text{C}_6\text{H}_5/\text{C}_6\text{H}_5$), 127.6(d, $J(\text{CH})$ 158 Hz, 2C, $\text{C}_6\text{H}_2/\text{C}_6\text{H}_5$), 128.8(d, $J(\text{CH})$ 158 Hz, 2C, $\text{C}_6\text{H}_2/\text{C}_6\text{H}_5$), 129.3(d, $J(\text{CH})$ 157 Hz, 1C, $\text{C}_6\text{H}_2/\text{C}_6\text{H}_5$), 135.2(dd, $J(\text{CH})$ 182 Hz, $J(\text{PC})$ 27 Hz, 1C, $\text{C}=\text{C}$), 136.4(d, $J(\text{PC})$ 18 Hz, 1C, $\text{C}_6\text{H}_2/\text{C}_6\text{H}_5$), 141.5(s, 2C, $\text{C}_6\text{H}_2/\text{C}_6\text{H}_5$), 142.2(dd, $J(\text{CH})$ 158 Hz, $J(\text{PC})$ 34 Hz, 1C, $\text{C}=\text{C}$), 145.5(s, 1C, $\text{C}_6\text{H}_2/\text{C}_6\text{H}_5$), 150.3(d, $J(\text{PC})$ 12 Hz, 1C, $\text{C}_6\text{H}_2/\text{C}_6\text{H}_5$), 239.8(d, $J(\text{PC})$ 20 Hz, 2C, CO). EI MS (m/e (rel. intensity); m/e -values refer to ^{98}Mo): M^+ 684(1), $M^+ - 2\text{CO}$ 628(1), $M^+ - ^1\text{Bu}$ 627(1), $M^+ - 2\text{CO} - ^1\text{Bu}$ 571(1), $M^+ - \text{C}_5\text{Me}_5$ 549(1), $M^+ - 2\text{CO} - 2^1\text{Bu}$ 514(2), $\text{Mo}(\text{C}_5\text{Me}_5)(\text{CO})_2\text{P}(\text{C}_2\text{Ph})^+$ 423(2), $\text{Mo}(\text{C}_5\text{Me}_5)\text{P}(\text{C}_2\text{Ph})^+$ 367(2), $\text{P}(^1\text{Bu}_3\text{C}_6\text{H}_2\text{O})^+$ 292(8), $^1\text{Bu}_3\text{C}_6\text{H}_2\text{OH}^+$ 262(48), $^1\text{Bu}_3\text{C}_6\text{H}_2\text{OH}^+ - \text{CH}_3$ 247(100), $^1\text{Bu}^+$ 57(24).

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- Single crystals of III were grown from a saturated toluene/n-pentane solution at -20°C . A crystal of dimensions $0.30 \times 0.25 \times 0.10$ mm was lodged in a glass capillary and sealed under nitrogen. Compound III crystallizes in the orthorhombic space group *Pbca* with lattice constants a 907.3(3) pm, b 2057.2(9) pm, c 3716.3(1) pm, V 6943(4) $\times 10^6$ pm³, $Z = 8$, $\mu(\text{Mo}-\text{K}_\alpha = 4.4 \text{ cm}^{-1})$ and ρ_{calcd}

1.22 g cm⁻³. Diffraction data were collected on a Nicolet (Siemens) R3 diffractometer by using the θ - 2θ technique (2θ limits 2–48°, scan range 0.8°, scan speed $1.8 \leq \dot{\omega} \leq 29.3$ deg min⁻¹ (in 2θ) and Mo- K_{α} radiation (λ 71.069 pm) at 293 K. The structure was solved by direct methods (SHELXTL-PLUS [13]) on 2962 unique reflections with $F \geq 4\sigma(F)$. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were fixed at calculated positions. An empirical absorption correction was applied. The final discrepancy indices were $R_F = 0.084$ and $R_{wF} = 0.072$. Atomic coordinates for non-hydrogen atoms are listed in Table 1. A complete list of bond lengths and angles, a table of thermal parameters, and a list of observed and calculated structure factors are available from the authors.

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