

Chelate Complexes of Functionalized Cycloheptatrienyl Ligands: 17- and 18-Electron Molybdenum Complexes with Linked Cycloheptatrienyl–Phosphane Ligands and Their Use in Transition Metal Catalysis

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The synthesis of *P*-functionalized molybdenum chelate complexes incorporating the linked cycloheptatrienyl–phosphane ligand [2-(diphenylphosphanyl)phenyl]cycloheptatrienyl, *o*-Ph₂P–C₆H₄–C₇H₆, is described. The air-stable ligand precursor [2-(cyclohepta-2,4,6-trienyl)phenyl]diphenylphosphane (**2**) can be obtained in large quantities by addition of lithiated 2-BrC₆H₄PPh₂ (**1**) to the tropylium cation C₇H₇⁺. Hydride abstraction employing the trityl cation, Ph₃C⁺, results in the formation of the tricyclic phosphonium salt **3**. The *P*-functionalized cycloheptatriene **2** acts as an eight-electron ligand on reaction with Mo(CO)₆ to afford the cycloheptatriene–phosphane complex [(*o*-Ph₂PC₆H₄-η⁶-C₇H₇)Mo(CO)₂(*P*-Mo)] (**4**) as a single, chiral regioisomer, which undergoes clean hydride abstraction on treatment

with (Ph₃C)BF₄. The resulting cationic cycloheptatrienyl–phosphane complex **5** reacts with sodium bromide to yield the uncharged “chiral-at-metal” complex [(*o*-Ph₂PC₆H₄-η⁷-C₇H₆)Mo(CO)Br(*P*-Mo)] (**6**). This 18-electron complex can be oxidized with 0.5 equiv. of Br₂ to give the paramagnetic dibromo complex **7**, which is a versatile starting material for the preparation of the 17-electron mono- and dialkyl complexes [(*o*-Ph₂PC₆H₄-η⁷-C₇H₆)Mo(CH₂SiMe₃)X(*P*-Mo)] (X = Br, **8**; X = CH₂SiMe₃, **9**). In combination with Me₃SiCH₂MgCl, complexes **7** and **9** prove to be active catalysts for the ring-opening metathesis polymerization of norbornene. In addition, the X-ray crystal structures of **2**, **4**, 5·CH₂Cl₂, 7·CHCl₃, **8**, and 9·C₆H₁₄ are reported.

Introduction

η-Cyclopentadienyl complexes, (η-C₅R₅)M, as well as η-arene complexes, (η-C₆R₆)M, are among the most important classes of compounds in organotransition metal chemistry.^[1] In particular, the widespread use of cyclopentadienes as organometallic ligands is due to the large number of ring-substituted derivatives, which have been synthesized since the serendipitous synthesis and discovery of ferrocene. Successive replacement of hydrogen atoms by alkyl or aryl substituents alters the steric and electronic properties of the Cp ring and gives rise to increased steric bulk, solubility and stability of the resulting complexes.^[2] Numerous routes to ring-substituted Cp derivatives are known to date, and stable cyclopentadienyl complexes of almost any element have been synthesized. It has recently been estimated that about 80% of all organometallic compounds of the trans-

ition metals are cyclopentadienyl complexes.^[2a] Consequently, cyclopentadienyl complexes are now ubiquitous and indispensable in research areas such as homogeneous catalysis,^[3] organic synthesis^[4] and materials science.^[5] In contrast, η-cycloheptatrienyl transition metal complexes, (η-C₇R₇)M, have been much less thoroughly studied, and with a few exceptions, the use of cycloheptatrienyl ligands had been confined to the parent C₇H₇ system.^[6] Only recently have we been able to report on the syntheses and properties of the first heptamethylcycloheptatrienyl (CHT*) complexes^[7] and of complexes derived from sterically demanding tropylium salts of the type (1,3,5-C₇H₄R₃)BF₄ (R = *tert*-butyl, SiMe₃).^[8]

Another concept, which has been extremely successful, in particular in cyclopentadienyl chemistry, is ligand functionalization, whereby an additional coordinating site is linked to the periphery of the five-membered ring via a suitable bridging moiety. This prospering area has produced a large number of novel cyclopentadienyl ligands bearing pendant *N*-,^[9,10] *O*-,^[11] *P*-, *As*-, and *S*-donor groups.^[12] If properly designed, these ligands can coordinate to a transition metal center in a chelating η⁵:η¹-fashion, and several of these complexes have played a key role in homogeneous catalysis as so-called constraint-geometry catalyst sys-

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tems.^[13] In cycloheptatrienyl transition metal chemistry on the other hand, ligand functionalization is an almost unknown concept, and we have recently started to apply this concept to the preparation of cycloheptatrienyl complexes bearing pendant phenolate,^[13] amine, and phosphane donor groups (Figure 1). The reasons for our interest in the development of such ligand systems are twofold. Firstly, donor-functionalization can in general lead to the formation of chelate complexes of significantly enhanced stability, which can allow the preparation and isolation of complexes of previously unknown structural types and reactivities. For instance, since the coordination of the cycloheptatrienyl ring to a transition metal center is often much more difficult than the introduction of a cyclopentadienyl group, the donor group can serve as a *Trojan horse*, which binds to a metal ion first followed by the formation of the metal–carbon bonds. Secondly, some of the donor groups might only coordinate in a labile fashion or could be converted into hemilabile groups, which offers the possibility of reversibly providing free coordination sites for other molecules or substrates.

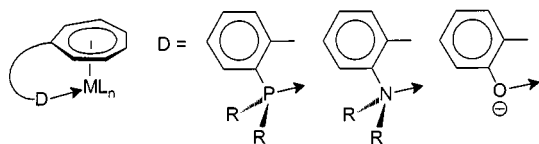


Figure 1. Cycloheptatrienyl complexes bearing pendant *P*-, *N*-, and *O*-donors

To the best of our knowledge, no complexes with donor-functionalized cycloheptatrienyl ligands coordinating in a chelating $\eta^7:\eta^1$ -fashion have been reported prior to our work,^[13] whereas a few examples are known, in which the functional group is directly attached to the seven-membered ring allowing the cycloheptatrienyl ligand to only bridge two different metal centers.^[14–16] For instance, lithiation of $[(\eta\text{-C}_7\text{H}_7)\text{Ti}(\eta\text{-C}_5\text{H}_5)]$ with *n*BuLi occurs preferentially at the seven-membered ring,^[14] and the consecutive reaction with chlorodiphenylphosphane allows the selective functionalization of the cycloheptatrienyl ring to yield $[(\eta^7\text{-C}_7\text{H}_6\text{PPh}_2)\text{Ti}(\eta\text{-C}_5\text{H}_5)]$, which has been used as a monodentate phosphane ligand forming bimetallic complexes.^[15] Dimetalation of $[(\eta\text{-C}_7\text{H}_7)\text{Ti}(\eta\text{-C}_5\text{H}_5)]$ can also be achieved, and the reaction with ClPR_2 (*R* = Me, Ph) produces $[(\eta^7\text{-C}_7\text{H}_6\text{PR}_2)\text{Ti}(\eta^5\text{-C}_5\text{H}_4\text{PR}_2)]$, which can react with various carbonylmetal complexes to produce a series of complexes with the bifunctionalized sandwich unit acting as a chelating or bridging diphosphane ligand.^[16] In this respect, bimetallic sesquifulvalene derivatives can also be regarded as complexes containing cyclopentadienyl-functionalized cycloheptatrienyl ligands, and various complexes have been reported, in which the five- and seven-membered rings are coordinated in a bridging $\mu\text{-}\eta^7:\eta^5$ -mode.^[17,18]

With this contribution, we introduce, for the first time, phosphorus-functionalized cycloheptatrienyl ligands, which are capable of binding the metal center in a chelating $\eta^7:\eta^1$ -fashion (Figure 1), and we wish to report on the syntheses

of a series of molybdenum complexes of the type $[(o\text{-Ph}_2\text{PC}_6\text{H}_4\text{-}\eta^7\text{-C}_7\text{H}_6)\text{MoLL}'(P\text{-}Mo)]$ containing a cycloheptatrienyl ligand with a linked 2-(diphenylphosphanyl)-phenyl substituent. The *ortho*-phenylene moiety had been chosen as the bridging unit between the seven-membered ring and the *P*-donor group, as it will lead to the formation of complexes with a very rigid, C_s -symmetric ligand backbone and will additionally allow the alteration of their steric and electronic properties by modification of the aryl fragment. Furthermore, the synthesis and use of 17-electron complexes of the type $[(o\text{-Ph}_2\text{PC}_6\text{H}_4\text{-}\eta^7\text{-C}_7\text{H}_6)\text{MoX}_2(P\text{-}Mo)]$ (*X* = Br, CH_2SiMe_3) for the ring-opening metathesis polymerization of norbornene will be described, which is among the first reports on the application of cycloheptatrienyl complexes to homogeneous transition metal catalysis.

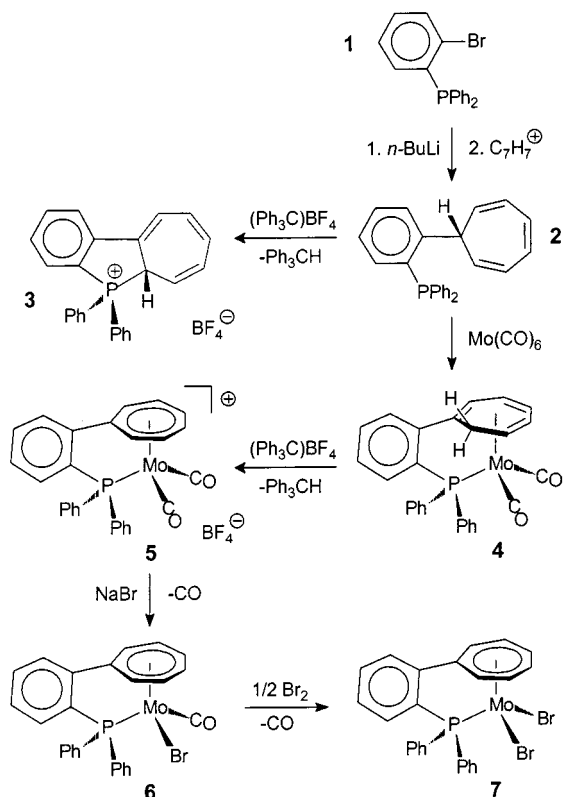
Results and Discussion

Ligand Synthesis

Although a large number of phosphorus-functionalized cyclopentadienyl systems are known,^[12] we are only aware of a few related cyclopentadienyl complexes, in which the phosphane group is attached to the five-membered ring via a bridging *ortho*-phenylene moiety.^[19–21] For instance, Trost and co-workers have obtained the ligand precursor [2-(diphenylphosphanyl)phenyl]cyclopentadiene by the reaction of (2-bromophenyl)diphenylphosphane (**1**) with 1 equiv. of *n*-butyllithium followed by addition of 2-cyclopentenone.^[19] Similarly, one should be able to obtain the related cycloheptatriene–phosphane ligand precursor **2** (Scheme 1) by addition of 2-(diphenylphosphanyl)phenyllithium^[22] to the tropylium cation C_7H_7^+ .^[23] In fact, careful monolithiation of 1,2-dibromobenzene and reaction with ClPPh_2 led to 2- $\text{BrC}_6\text{H}_4\text{PPh}_2$ (**1**),^[22,24] which was successively treated with *n*BuLi and $(\text{C}_7\text{H}_7)\text{BF}_4$ to afford the air-stable ligand precursor [2-(cyclohepta-2,4,6-trienyl)phenyl]diphenylphosphane (**2**) in large quantities.

The ^{31}P NMR spectrum of **2** exhibits one single resonance at $\delta = -15.9$, which is about 10 ppm up-field from the resonance observed for triphenylphosphane under identical conditions.^[25] The molecular structure of **2** could be established by X-ray diffraction (Figure 2, top) confirming the *ortho* linkage between the phosphorus atom and the cycloheptatriene moiety, which bears the PPh_2 residue in the allylic 1-position. As anticipated,^[26] the seven-membered ring adopts a boat conformation, and all bond lengths and angles fall in the expected ranges.

As we have recently developed a method for the quantitative complexation of tropylium salts by an arene exchange reaction employing $[(\eta\text{-}p\text{-xylene})\text{Mo}(\text{CO})_3]$,^[8,18a] we sought for the synthesis of a phosphanyl-functionalized tropylium salt by hydride abstraction using triphenylcarbenium tetrafluoroborate, $(\text{Ph}_3\text{C})\text{BF}_4$. The direct reaction of **2** with $(\text{Ph}_3\text{C})\text{BF}_4$, however, did not result in a clean reaction, presumably due to steric hindrance at the allylic position of the seven-membered ring created by the 2-(diphenylphos-



Scheme 1

phenyl)phenyl substituent. Therefore, **2** was heated in DMF at 150 °C to undergo a thermal rearrangement through consecutive 1,5-sigmatropic hydrogen migrations.^[18b,27] The resulting isomeric mixture was treated with $(\text{Ph}_3\text{C})\text{BF}_4$ to afford Ph_3CH and a colorless tetrafluoroborate salt, which turned out to be the tricyclic phosphonium salt **3**, formed by intramolecular nucleophilic attack of the tethered phosphane group at the seven-membered ring in the intermediate [2-(diphenylphosphanyl)phenyl]cycloheptatrienylum tetrafluoroborate (Scheme 1). A similar ring-closure has been observed for a linked cycloheptatrienyl–phenolate system.^[13] As expected for asymmetric **3**, the ^1H NMR spectrum exhibits six different resonances for the allylic and vinylic cycloheptatrienyl protons, and the ^{31}P NMR spectrum displays a resonance at $\delta = 43.8$ indicative of a deshielded phosphonium center.^[25]

Synthesis of 18-Electron Cycloheptatrienyl–Phosphane Complexes

Attempts to use **3** for the direct synthesis of the linked cycloheptatrienyl–phosphane complex **5** were unsuccessful, and the reaction with various $\text{Mo}(\text{CO})_3$ transfer reagents such as $[(\text{CH}_3\text{CN})_3\text{Mo}(\text{CO})_3]$ or $[(\eta\text{-}p\text{-xylene})\text{Mo}(\text{CO})_3]$ did not result in ring-opening of the phosphonium salt and insertion of the molybdenum complex fragment into the $\text{P}-\text{CH}$ bond. More conveniently, the cycloheptatriene–phosphane ligand can be used as a multidentate ligand, and the reaction with $\text{Mo}(\text{CO})_6$ in refluxing methylcyclohexane leads to the substitution of four

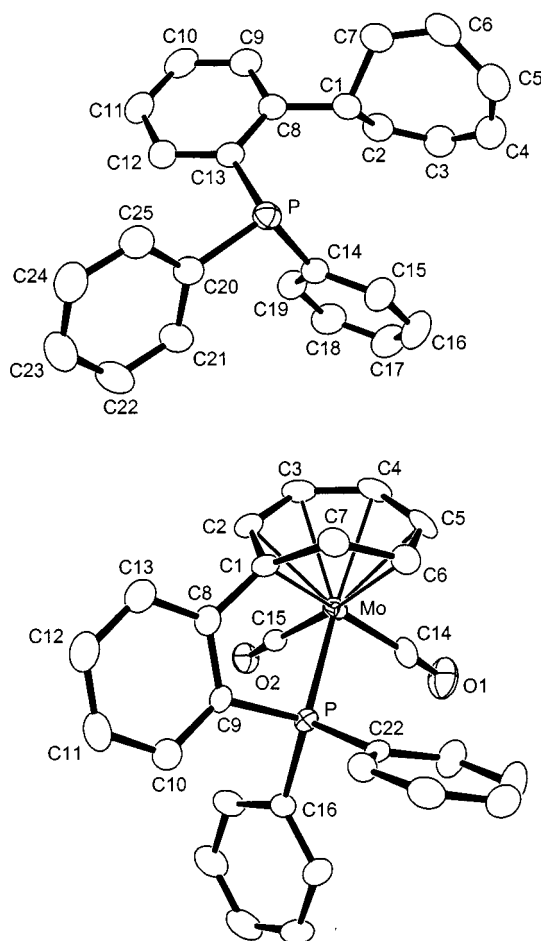


Figure 2. ORTEP drawings of **2** (top) and **4** (bottom) with thermal ellipsoids drawn at 50% probability

carbonyl groups and the formation of cycloheptatriene–phosphane complexes of the type $[(o\text{-Ph}_2\text{PC}_6\text{H}_4\text{-}\eta^6\text{-C}_7\text{H}_7)\text{Mo}(\text{CO})_2(\text{P}-\text{Mo})]$. In comparison to the reaction of cycloheptatriene, C_7H_8 , with $\text{Mo}(\text{CO})_6$, the reaction described here proceeds much faster and no sublimation of hexacarbonylmolybdenum out of the flask into the reflux condenser was observed indicating that the phosphane group adds rapidly to the molybdenum center to form an involatile material followed by coordination of the cycloheptatriene moiety. If the reaction mixture is kept at 100 °C overnight, complex **4** crystallizes from the solution, upon cooling with dry ice, as the only detectable regioisomer (Scheme 1). The formation of **4** must have resulted from thermal rearrangement of the coordinated cycloheptatriene ring involving, in principle, two consecutive 1,5-hydrogen shifts.^[28] In its ^1H NMR spectrum **4** exhibits five resonances due to the vinylic protons and two resonances due to the allylic *exo* and *endo* protons (Figure 3). The ^{31}P NMR resonance is observed at $\delta = 64.5$ revealing that the phosphorous atom is coordinated to the metal center. As **4** is obtained as a racemic mixture of two enantiomers, two different sets of resonances are observed for the diastereotopic phenyl groups in the ^{13}C NMR spectrum. Accordingly, two doublets are found for the ^{13}CO

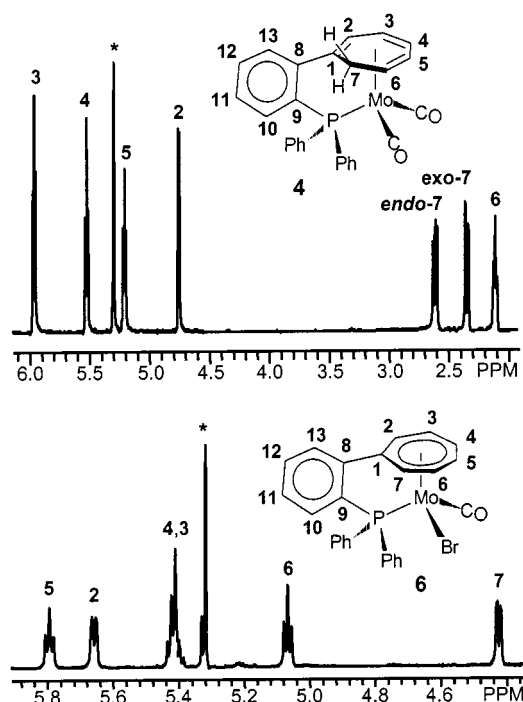


Figure 3. Selected parts of the ^1H NMR spectra (600 MHz, CD_2Cl_2) of **4** (top) and **6** (bottom)

carbonyl resonances at $\delta = 227.2$ ($^2J_{\text{C,P}} = 10$ Hz) and 223.9 ($^2J_{\text{C,P}} = 12$ Hz), respectively.

In order to confirm the spectroscopic results, the molecular structure of **4** was established by X-ray diffraction analysis, and Figure 2 (bottom) shows an ORTEP diagram of one enantiomer. The 2-(diphenylphosphanyl)phenyl substituent is indeed attached to the vinylic carbon atom C1, which is next to the CH_2 group, and the cycloheptatriene–phosphane ligand binds to the metal center in a chelating $\eta^6:\eta^1$ fashion. If compared to the molecular structures of related (cycloheptatriene)molybdenum complexes, e.g. $[(\eta^6\text{-C}_7\text{H}_8)\text{Mo}(\text{CO})_3]^{[29]}$ and $[(\eta^6\text{-C}_7\text{H}_8)\text{Mo}(\text{CRR}')(\text{CO})_2]$ ($\text{R} = \text{OEt}$, $\text{R}' = o\text{-tolyl}$), $^{[30]}$ the bond lengths and angles within the seven-membered ring fall in the expected ranges (Table 1). The distances between the molybdenum atom and the cycloheptatriene carbon atoms, however, differ significantly with the shortest bond to C3 [2.296(3) Å] and the longest bond to C6 [2.468(3) Å], which is probably due to the asymmetry of the linked cycloheptatriene–phosphane ligand as well as the mixed set of co-ligands (one phosphane and two carbonyl ligands) about the molybdenum center. $^{[30]}$

In **4** the *exo* hydrogen atom is accessible to the trityl cation for hydride abstraction, and the cycloheptatrienyl–phosphane complex $[(o\text{-Ph}_2\text{PC}_6\text{H}_4\text{-}\eta^7\text{-C}_7\text{H}_6)\text{Mo}(\text{CO})_2(\text{P-Mo})]\text{BF}_4$ (**5**) is formed almost quantitatively upon treatment with $(\text{Ph}_3\text{C})\text{BF}_4$ (Scheme 1). With removal of the hydrogen atom from the CH_2 group, **5** becomes C_s -symmetric and exhibits three cycloheptatrienyl resonances in its ^1H NMR spectrum at $\delta = 6.06$, 6.00 , and 5.59 in a 2:2:2 ratio. Accordingly, the ^{13}C NMR spectrum

displays four resonances for the C_7H_6 carbon atoms together with ten resonances for the phenyl and phenylene carbon atoms. The ^{13}CO resonance for the magnetically equivalent carbonyl groups is observed as a doublet at $\delta = 212.7$ ($^2J_{\text{P,C}} = 25$ Hz), and the ^{31}P resonance at 59.9 is slightly shifted to higher field in comparison with **4**. To unambiguously confirm the formation of the first cycloheptatrienyl–phosphane chelate complex, a single-crystal of **5**· CH_2Cl_2 was subjected to X-ray diffraction analysis, and the molecular structure of the cation in **5** is depicted in Figure 4 (top). One recognizes that the ligand does indeed act as a chelate ligand in an $\eta^7:\eta^1$ fashion with almost perfectly perpendicularly oriented six- and seven-membered rings (interplanar angle of 85.8°). The molybdenum atom is symmetrically η^7 -coordinated with the shortest bond to C1 [2.262(2) Å] and the longest bond to C6 [2.323(2) Å] (Table 1). On average, these distances are similar to those found for $[(\eta\text{-C}_7\text{H}_7)\text{Mo}(\text{CO})_3]\text{BF}_4$ (mean 2.31 Å), $^{[31]}$ $[(\eta\text{-C}_7\text{H}_7)\text{Mo}(\text{CO})_2\text{X}]$ ($\text{X} = \text{Cl}$, mean 2.31 Å; $\text{X} = \text{Br}$, mean = 2.32 Å) $^{[32]}$ and $[(\eta\text{-C}_7\text{H}_7)\text{Mo}(\text{CO})_2(\text{C}_6\text{F}_5)]$ (mean = 2.32 Å). $^{[33]}$ No significant deviation from planarity can be observed for the seven-membered ring in **5**, and the mean and maximum deviations from the least-squares plane (C1–C7) are 0.028 and -0.058 Å (for C1), respectively. In order to allow chelate formation, the six-membered ring bends slightly down towards the metal center, and the angle between the centroid of the seven-membered ring, C1 and C8 deviates by 10.3° from a perfectly linear orientation. On the other hand, this out-of-plane displacement observed for C8 could also be attributed to a reorientation of the large seven-membered ring favoring a better metal overlap (vide infra). In addition, the phenylene bridge also leads to a somewhat distorted tetrahedral environment about the phosphorous atom with the angle Mo-P-C13 [$105.95(8)^\circ$] being smaller than the adjacent angles Mo-P-C16 [$116.53(7)^\circ$] and Mo-P-C22 [$119.12(7)^\circ$].

It has previously been demonstrated that monophosphane complexes of the type $[(\eta\text{-C}_7\text{H}_7)\text{M}(\text{CO})\text{X}(\text{PR}_3)]$ ($\text{M} = \text{Mo}$, W ; $\text{X} = \text{halide}$) allow the introduction of various nucleophiles by halide substitution reactions and are suitable precursors for studying organometallic transformations supported by the (cycloheptatrienyl)molybdenum and -tungsten fragments. $^{[34]}$ Therefore, **5** was treated with an excess of NaBr in THF at elevated temperature leading to the direct, high-yield formation of $[(o\text{-Ph}_2\text{PC}_6\text{H}_4\text{-}\eta^7\text{-C}_7\text{H}_6)\text{Mo}(\text{CO})\text{Br}(\text{P-Mo})]$ (**6**). Due to chelation by the linked cycloheptatrienyl–phosphane ligand, complex **6** seems to be significantly more stable than related unbridged phosphane halide complexes, and chromatographic purification is possible under ambient conditions using alumina (4% H_2O). In **6**, the pseudotetrahedrally coordinated molybdenum center has four different ligands, and the complex is thus obtained as a racemic mixture of two enantiomers. Since this new representative of so-called “chiral-at-metal” half-sandwich compounds $^{[35,36]}$ is configurationally stable, the diastereotopic cycloheptatrienyl hydrogen atoms give rise to six different ^1H NMR resonances. This portion of

Table 1. Selected bond lengths [Å] and angles [°] for **2**, **4**, **5**·CH₂Cl₂, **7**·CHCl₃, **8**, and **9**·C₆H₁₄

	2	4	5 ·CH ₂ Cl ₂	7 ·CHCl ₃	8	9 ·C ₆ H ₁₄
C1–C2	1.509(2)	1.395(4)	1.423(3)	1.415(5)	1.417(4)	1.429(3)
C2–C3	1.334(2)	1.418(4)	1.406(3)	1.390(5)	1.409(5)	1.401(4)
C3–C4	1.436(3)	1.419(4)	1.413(4)	1.418(5)	1.407(5)	1.418(4)
C4–C5	1.346(3)	1.419(4)	1.399(3)	1.395(5)	1.402(5)	1.387(4)
C5–C6	1.437(3)	1.381(4)	1.418(4)	1.409(5)	1.415(4)	1.418(4)
C6–C7	1.338(2)	1.505(4)	1.398(4)	1.396(4)	1.399(4)	1.387(4)
C1–C7	1.5083(19)	1.526(4)	1.427(3)	1.429(4)	1.431(4)	1.422(4)
C1–C8	1.516(2)	1.490(4)	1.497(3)	1.500(4)	1.494(4)	1.495(4)
Mo–C1		2.365(3)	2.262(2)	2.239(3)	2.234(3)	2.261(2)
Mo–C2		2.314(3)	2.321(2)	2.273(3)	2.261(3)	2.319(2)
Mo–C3		2.296(3)	2.320(2)	2.257(3)	2.266(3)	2.294(2)
Mo–C4		2.322(3)	2.320(2)	2.310(3)	2.306(3)	2.289(3)
Mo–C5		2.350(3)	2.319(2)	2.292(3)	2.300(3)	2.302(3)
Mo–C6		2.468(3)	2.323(2)	2.281(3)	2.361(3)	2.312(2)
Mo–C7			2.321(2)	2.271(3)	2.303(3)	2.324(2)
Mo–C14/C26		1.985(3)	2.033(2)		2.211(3)	2.225(2)
Mo–C15/C18		1.951(3)	2.044(3)			2.228(2)
Mo–P		2.4343(8)	2.4813(6)	2.5763(9)	2.5484(8)	2.5427(7)
Mo–Br1				2.5834(5)	2.5865(4)	
Mo–Br2				2.5806(6)		
C14–O1		1.155(4)	1.137(3)			
C15–O2		1.167(3)	1.132(3)			
mean/max. dev. ^[a]			0.028/–0.058 (at C1)	0.012/–0.020 (at C2)	0.030/–0.045 (at C1)	0.027/0.054 (at C1)
Mo–C14–O1		177.2(3)	177.9(2)			
Mo–C15–O2		175.4(2)	179.4(2)			
centroid (C1–C7)–C1–C8 (C1–C7)–(C8–C13) ^[b]			169.7 85.5	169.4 78.2	169.1 71.5	170.4 85.4

^[a] Minimum and maximum deviations from the least-squares plane containing C1–C7. ^[b] Interplanar angles.

the 600-MHz NMR spectrum is shown in Figure 3. Accordingly, seven ¹³C NMR resonances are observed for the C₇H₆ carbon atoms together with six resonances for the phenylene bridge and eight resonances for the diastereotopic phenyl groups. The assignment of all ¹H and ¹³C NMR resonances in **6** is supported by two-dimensional NMR spectroscopy (COSY and NOE experiments). The ¹³CO carbonyl resonance in **6** is observed as a doublet at $\delta = 232.3$ (²J_{C,P} = 15.6 Hz), and one single ³¹P NMR resonance is found at $\delta = 49.1$. As expected, the IR spectrum of **6** exhibits one CO absorption at 1946 cm^{–1}, which is in good agreement with the stretching frequency of 1944 cm^{–1} reported for the closely related, unbridged analogue [(η -C₇H₇)Mo(CO)Br(PPh₃)].^[34a] Single crystals of **6**·CHCl₃ could be obtained by recrystallization from a CHCl₃ solution allowing the molecular structure of **6** to be established by X-ray crystal structure determination.^[37]

Synthesis of 17-Electron Cycloheptatrienyl–Phosphane Complexes

Ng et al. have recently reported on the ring-opening metathesis polymerization of norbornene promoted by (η -cycloheptatrienyl)molybdenum and -tungsten complexes of the type [(η -C₇H₇)MLI₂] (M = Mo, W; L = CH₃CN, PPh₃).^[38] This is one of the first reports on the application of cycloheptatrienyl complexes to homogeneous transition

metal catalysis.^[6] Activated by Me₃SiCH₂MgCl, these 17-electron complexes give high molecular weight poly(1,3-cyclopentadienevinylene). The synthesis of such complexes has been developed by Green and co-workers, during the last decade, employing the sandwich compound [(η -C₇H₇)M(η ⁵-C₇H₉)] (M = Mo, W), which can be obtained in a one-pot reaction from cycloheptatriene, sodium amalgam and MoCl₅ or WCl₆, respectively. Treatment of these complexes with chlorine, bromine or iodine in the presence of Lewis bases provides a convenient route to half-sandwich derivatives such as [(η -C₇H₇)MLX₂] (M = Mo, W; L = CH₃CN, THF, PPh₃, PMe₃; X = Cl, Br, I).^[39,40] Moreover, the magnetic properties of several of these paramagnetic compounds have been studied in detail.^[41]

Herein, we present a new route to analogous 17-electron complexes containing linked cycloheptatrienyl–phosphane ligands. If [(η -Ph₂PC₆H₄- η ⁷-C₇H₆)Mo(CO)Br(*P-Mo*)] (**6**) is treated with 0.5 equiv. of bromine in CH₂Cl₂ a rapid color change from green to brown-red is observed together with the evolution of gas. After stirring for 1 h at ambient temperature, paramagnetic [(η -Ph₂PC₆H₄- η ⁷-C₇H₆)MoBr₂(*P-Mo*)] (**7**) can be isolated as an air-stable brown dichloromethane adduct after precipitation with hexane (Scheme 1). The formation of **7** is obtained by oxidation of **6** with 0.5 equiv. of bromine to give the labile odd-electron intermediate [(η -Ph₂PC₆H₄- η ⁷-C₇H₆)Mo(CO)Br(*P-Mo*)]-

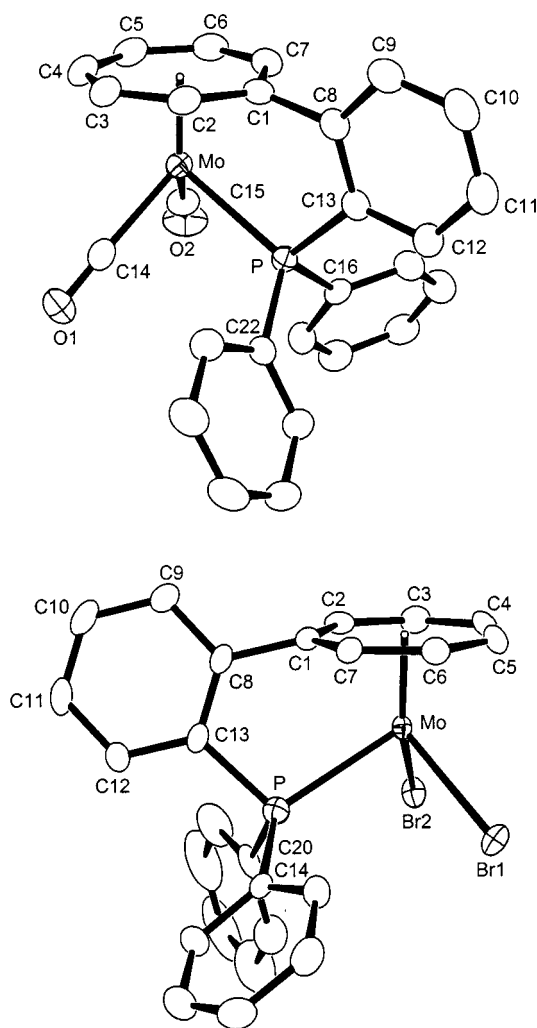


Figure 4. ORTEP drawings of the cation in **5**·CH₂Cl₂ (top) and of **7** in **7**·CH₂Cl₂ (bottom) with thermal ellipsoids drawn at 50% probability

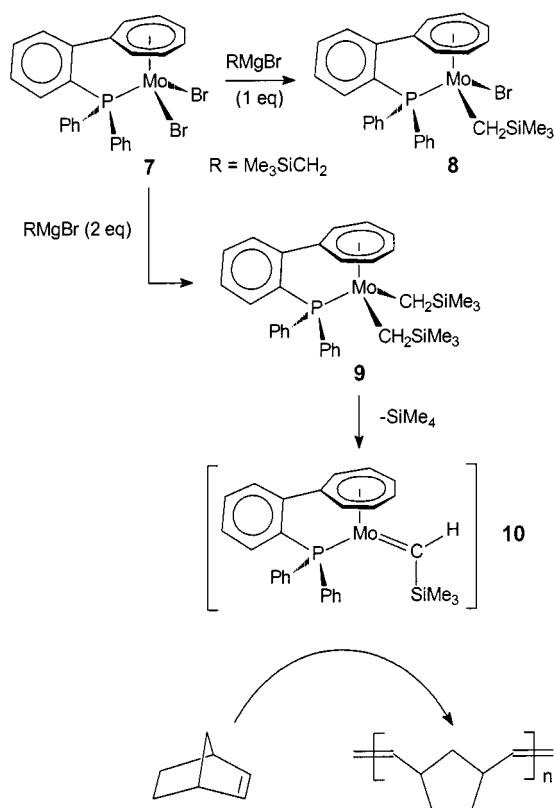
Br, which rapidly undergoes carbonyl substitution by bromide to give complex **7** in high yield. Due to the unpaired electron in **7**, the compound was only characterized by mass spectrometry and by ³¹P NMR spectroscopy revealing a resonance at $\delta = 38.5$, and the purity was additionally checked by elemental analysis.

Recrystallization from chloroform afforded single crystals of **7**·CHCl₃, which were suitable for structure determination by X-ray diffraction. The molecular structure is shown in Figure 4 (bottom). The Mo–C distances range from 2.239(3) to 2.310(3) Å (mean 2.27 Å, Table 1), which are similar to those in the 17-electron complexes [(η -C₇H₇)Mo(CH₃CN)I₂] [2.258(5)–2.280(5), mean 2.27 Å]^[41] and [(η -C₇H₇)Mo(THF)I₂] [2.23(2)–2.29(2), mean 2.25 Å]^[42] and they are, on average, shorter than the corresponding values observed in 18-electron complexes such as **5** [2.262(2)–2.323(2), mean 2.31 Å] (vide supra). In contrast, the Mo–P bond length of 2.5763(9) Å is significantly longer than that in **5** [2.4183(6) Å]. Again, the cycloheptatrienyl ring in **7** is almost perfectly planar, and the mean

and maximum deviations from the least-squares plane (C1–C7) are 0.012 and –0.020 Å (for C2), respectively. The structural features of the ligand backbone are quite similar to those found for the molecular structure of **5**, with an interplanar angle between the least-squares planes containing C1–C7 and C8–C13 of 78.2° and an angle between the centroid of the seven-membered ring, C1 and C8 of 169.4°.

As indicated above, it has been observed that, on activation with Me₃SiCH₂MgCl, molybdenum complexes such as [(η -C₇H₇)MoLI₂] (M = Mo, W; L = CH₃CN, PPh₃) catalyze the ring-opening metathesis polymerization of norbornene. It was concluded that these reactions presumably involve the intermediate carbene complexes [(η -C₇H₇)Mo(=CHSiMe₃)L], which could have been generated by α -deprotonation of the initially formed dialkyl complexes [(η -C₇H₇)Mo(CH₂SiMe₃)₂L].^[38] Although precedents for similar reaction sequences can be found in the literature,^[43] the formation of 17-electron dialkyl(cycloheptatrienyl) complexes has not yet been confirmed. As the formation of metal–alkyl bonds is essential for most industrially important catalytic processes^[3,4] and since cycloheptatrienyl complexes bearing alkyl ligands are generally a rare class of compounds,^[6,44] we sought to isolate the first 17-electron alkyl(cycloheptatrienyl) complexes by the reaction of the dibromide [(*o*-Ph₂PC₆H₄- η ⁷-C₇H₆)MoBr₂(*P-Mo*)] (**7**) with Me₃SiCH₂MgCl (1.0 M solution in diethyl ether). Treatment of **7** with 2 equiv. of the Grignard reagent resulted, after extraction with hexane, in a mixture of two compounds as indicated by the observation of two ³¹P NMR resonances. Recrystallization from hexane afforded orange crystals of [(*o*-Ph₂PC₆H₄- η ⁷-C₇H₆)Mo(CH₂SiMe₃)Br(*P-Mo*)] (**8**), which contains only one trimethylsilylmethyl group, in moderate yield (Scheme 2). Transfer of the mother liquor to a chromatography column (SiO₂) and elution with diethyl ether/petroleum ether (1:1) led to the collection of an orange-yellow fraction, from which the dialkyl complex [(*o*-Ph₂PC₆H₄- η ⁷-C₇H₆)Mo(CH₂SiMe₃)₂(*P-Mo*)] could be isolated in low yield. Presumably, the introduction of the second alkyl substituent to form **9** is obstructed by steric hindrance produced by the first neosilyl (CH₂SiMe₃) group in **8**. In order to selectively prepare the monoalkyl derivative, the dibromide **7** can be treated with just 1 equiv. of the Grignard reagent to obtain **8** in about 60% yield. Complete dialkylation can be achieved by employing a large excess (about tenfold based on **7**) of the Grignard solution to afford excellent yields of the dialkyl complex **9**. The purity of the two paramagnetic compounds was only checked by elemental analysis and by ³¹P NMR spectroscopy to reveal one resonance each at $\delta = 51.9$ for **8** and at $\delta = 54.6$ for **9**. Both compounds are air-stable and highly soluble in non-polar solvents such as hexane or toluene as well as in THF and diethyl ether. As indicated above, **9** can even be purified by chromatography on silica without any significant loss of material by decomposition.

The molecular structures of both complexes could additionally be established by means of X-ray diffraction. **9** crystallizes with one molecule of hexane per formula unit,



Scheme 2

and Figure 5 shows ORTEP presentations of **8** (top) and of **9** in $9 \cdot C_6H_{14}$ (bottom). Successive substitution of the two bromine atoms in **7** by the sterically more demanding Me_3SiCH_2 group does not seem to have great consequences on the structural parameters of the cycloheptatrienyl–phosphane scaffold in **8** and **9**. Thus, the Mo–C distances range from 2.234(3) to 2.361(3) Å (mean 2.29 Å) in **8** and from 2.261(2) to 2.324(4) Å (mean 2.30 Å) in **9** and are only slightly elongated in comparison to those in **7** [2.239(3)–2.310(3) Å (mean 2.27 Å) (Table 1). In contrast, the Mo–P bond length slightly decreases on going from **7** [2.5763(9) Å] to **8** [2.5484(8) Å] and **9** [2.5427(7) Å]. The cycloheptatrienyl rings in **8** and **9** remain planar, and the mean and maximum deviations from the least-squares plane (C1–C7) together with the dihedral angle between the best planes containing C1–C7 and C8–C13 are summarized in Table 1. The metal-to-alkyl carbon distances observed for compounds **8** [2.211(3) Å] and **9** [2.225(2), 2.228(2) Å] are rather large but still comparable to those found in other alkylmolybdenum complexes, which lie in the range 2.08–2.20 Å.^[45] The bond angles Mo–C–Si of 121.71(16)° in **8** and 124.62(13) and 129.34(12)° in **9** are significantly larger than expected for sp^3 -hybridized carbon atoms, although similar bond angles have also been found in neosilylmolybdenum(VI) and -tungsten(VI) complexes.^[43,45] It should be noted that the positions of all hydrogen atoms could be refined for **8**. Therefore, it is possible to establish the angles between the centroid of the cycloheptatrienyl ring, the C_7 carbon atoms and the adjacent hydro-

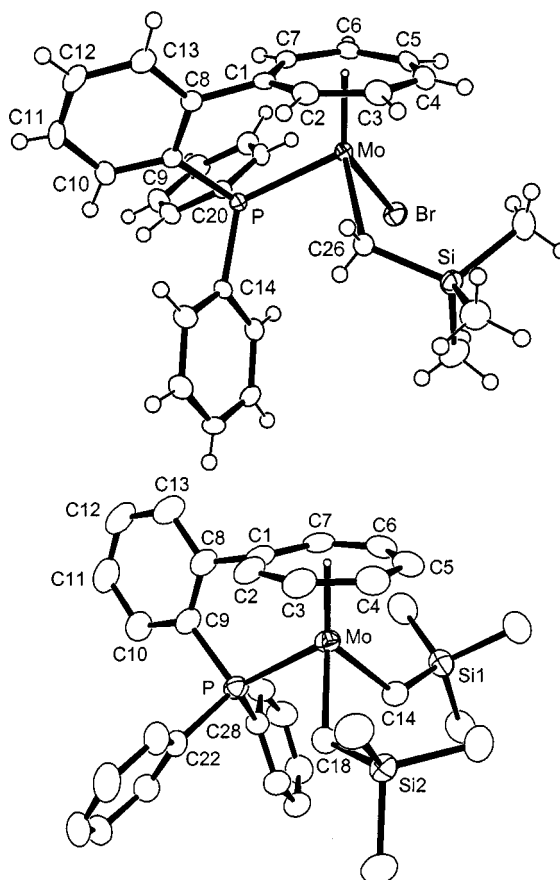


Figure 5. ORTEP drawings of the cation in **8** (top) and of **9** in $9 \cdot C_6H_{14}$ (bottom) with thermal ellipsoids drawn at 50% probability

gen atoms revealing a significant out-of-plane displacement for the C_7 hydrogen atoms. The average bending is about 9° toward the molybdenum center, and such a deviation has been attributed to a reorientation of the large seven-membered ring for a better metal overlap.^[6,46]

Ring-Opening Metathesis Polymerization (ROMP) of Norbornene

Homogeneous metathesis polymerization is dominated by well-defined alkylidene complexes of group-VI and group-VIII transition metals,^[47,48] some of which have been neosilyl ($M-CH_2SiMe_3$) or neosilylidene complexes ($M=CHSiMe_3$), respectively.^[43,45] Encouraged by the report on the ability of complexes of the type $[\eta-C_7H_7]MLI_2$ ($M = Mo, W$; $L = CH_3CN, PPh_3$) to promote the ring-opening metathesis polymerization of norbornene,^[38] we were prompted to test the ROMP activity of our 17-electron cycloheptatrienyl–phosphane complexes. Hence, the dibromo complex **7** was treated with 300 equiv. of norbornene in toluene. After addition of an excess amount of Me_3SiCH_2MgCl (6 equiv. of a 1.0 M solution in diethyl ether), the reaction mixture, which gradually became viscous, was heated for 12 h at 40 °C to ensure completion of the polymerization. The formed poly(1,3-cyclopentylenevinylene) was obtained as a colorless, fibrous material after

quenching with a few drops of benzaldehyde and dropwise addition of the hot solution to vigorously stirred methanol. Initial ^{13}C NMR and IR spectroscopic studies show in comparison with the literature data,^[49,50] that about 80% of the double bonds in the polymer are in the *trans* configuration.

As we have demonstrated, that $[(o\text{-Ph}_2\text{PC}_6\text{H}_4\text{-}\eta^7\text{-C}_7\text{H}_6)\text{Mo}(\text{CH}_2\text{SiMe}_3)_2(P\text{-Mo})]$ (**9**) is actually formed by the reaction of $\text{Me}_3\text{SiCH}_2\text{MgCl}$ with **7**, we anticipated that **9** might be an active single-source catalyst, from which the active species $[(o\text{-Ph}_2\text{PC}_6\text{H}_4\text{-}\eta^7\text{-C}_7\text{H}_7)\text{Mo}=\text{CHSiMe}_3(P\text{-Mo})]$ (**10**) could be generated by intramolecular α -deprotonation and elimination of Me_4Si (Scheme 2). The formation of this alkylidene complex would then allow the course of the metathesis polymerization to be described by the Chauvin mechanism.^[51] Treatment of **9** with norbornene in different solvents at various temperatures, however, did not give detectable amounts of polymer. On the other hand, addition of 1 equiv. of $\text{Me}_3\text{SiCH}_2\text{MgCl}$ to such a reaction mixture resulted in a rapid and quantitative formation of medium molecular weight polynorbornene ($M_n = 2.6 \cdot 10^4$ g/mol, $\text{PDI} = M_w/M_n = 6.7$, approx. 80% *trans* double bonds). A standard procedure is described in the Exp. Sect. It should be noted, that we have ruled out the possibility of the Grignard reagent alone reacting as a ROMP catalyst by independent control experiments, and at this stage, the mechanism as well as the active catalyst in our system remains unclear. Further work will be directed toward the synthesis and isolation of paramagnetic alkylidene complexes such as **10**, which might then dimerize to form interesting bis(μ -alkylidene) species containing metal–metal bonds. Substitution of the neosilyl by other alkyl groups, e.g. by neopentyl groups, as well as modification of the residues of the R_2P donor moiety will allow fine tuning of the activity of this catalyst system and adjustment of the electronic and steric requirements of the resulting complexes according to future challenges.

Conclusion

With this contribution, chelate complexes of functionalized cycloheptatrienyl ligands bearing a pendant phosphane donor group have been reported for the first time, and we have presented a high-yielding protocol for the synthesis of a series of 17- and 18-electron molybdenum complexes containing linked cycloheptatrienyl–phosphane ligands. These complexes are archetypal for the new class of donor-functionalized cycloheptatrienyl complexes,^[13] that will emerge from our laboratory in the near future. Although the preliminary results on the use of the 17-electron complexes presented herein as catalyst systems for olefin metathesis polymerization are by no means spectacular, these findings indicate that cycloheptatrienyl complexes can be potentially useful for applications in homogeneous transition metal catalysis. Hence, we are currently pursuing a general study on the utilization of these systems in various areas of application in view of our general objectives in or-

der to extend the chemistry of cycloheptatrienyl complexes and to raise their level of significance in comparison with that of cyclopentadienyl and benzene complexes.

Experimental Section

General: All operations were performed in dry argon by using Schlenk and vacuum techniques. Solvents were dried by standard methods and distilled prior to use. (2-bromophenyl)diphenylphosphane (**1**),^[24] tropylium tetrafluoroborate,^[52] and triphenylcarbenium tetrafluoroborate,^[53] were prepared according to published procedures. Elemental analyses (C, H, N) were performed with a Heraeus CHNO-Rapid elemental analyzer. EI and ESI mass spectra were recorded with a Varian MAT 212 or with a Micromass Quattro LCZ mass spectrometer, respectively. ^1H and ^{13}C NMR spectra were measured with Bruker AC 200, Bruker AMX 400 or Varian U 600 spectrometers using the solvent as internal standard, whereas ^{31}P NMR spectroscopic measurements were run with a Bruker AC 200 spectrometer using aqueous H_3PO_4 (85%) as an external reference. IR spectra were recorded with a Bruker Vector 22 instrument. The assignment of all ^1H and ^{13}C NMR resonances has been supported by two-dimensional NMR spectroscopy (COSY and NOE experiments). For the atomic numbering schemes used in the Exp. Sect., see Figure 3.

[2-(Cyclohepta-2,4,6-trienyl)phenyl]diphenylphosphane (2): A solution of **1** (9.62 g, 28.20 mmol) in THF (140 mL) was treated with *n*-butyllithium (12.2 mL of a 2.5 M solution in hexane, 30.5 mmol). After stirring for 45 min, solid $(\text{C}_7\text{H}_7)\text{BF}_4$ (5.01 g, 28.16 mmol) was added at -78°C , and the resulting reaction mixture was slowly warmed to room temperature (3 h). It was then diluted with a saturated aqueous NH_4Cl solution (100 mL) and extracted with diethyl ether (100 mL) and dichloromethane (2×50 mL). The combined organic extracts were dried with MgSO_4 . Evaporation of the solvents and purification by column chromatography on silica using petroleum ether/dichloromethane (1:1) as eluent afforded **2** as a colorless, crystalline solid. Yield: 7.41 g (75%). ^1H NMR (CDCl_3 , 400 MHz): $\delta = 7.66$ (dd, 1 H, 13-H), 7.49 (t, 1 H, 12-H), 7.40–7.28 (m, 10 H, C_6H_5), 7.24 (t, 1 H, 11-H), 6.98 (dd, 1 H, 10-H), 6.65 (t, 2 H, 4,5-H), 6.11 (m, 2 H, 3,6-H), 5.26 (dd, 2 H, 2,7-H), 3.66 (m, 1 H, 1-H). ^{31}P NMR (CDCl_3 , 81 MHz): $\delta = -15.9$. MS (EI): m/z (%) = 352 (100) $[\text{M}^+]$, 351 (94) $[\text{M} - \text{H}]^+$, 262 (25) $[\text{PPh}_3]^+$. $\text{C}_{25}\text{H}_{21}\text{P}$ (352.42): calcd. C 85.20, H 6.01; found C 84.93, H 6.27.

Phosphonium Salt 3: Prior to hydride abstraction, the phosphane **2** was thermally rearranged by heating in *N,N*-dimethylformamide at 150°C overnight. After evaporation of the solvent, the mixture was purified by chromatography as described above. A solution of this isomeric mixture (0.82 g, 2.33 mmol) in acetonitrile (35 mL) was treated with $(\text{Ph}_3\text{C})\text{BF}_4$ (0.69 g, 2.09 mmol) at 0°C . After it was warmed to room temperature, the reaction mixture was warmed to reflux for 2 h. The solvent was removed by evaporation, and the residue was washed with diethyl ether to remove Ph_3CH and recrystallized from dichloromethane/petroleum ether at 0°C to afford **3** as a yellow, crystalline solid. Yield: 0.64 g (70%). ^1H NMR (CD_2Cl_2 , 400 MHz): $\delta = 8.02$ –7.66 (m, 14 H, $\text{C}_6\text{H}_5 + 10,11,12,13\text{-H}$), 7.28 (m, 1 H, C_7 ring: CH), 6.98 (dd, 1 H, C_7 ring: CH), 6.85 (dd, 1 H, C_7 ring: CH), 6.43 (m, 1 H, C_7 ring: CH), 4.89 (m, 1 H, C_7 ring: CH), 3.89 (m, 1 H, C_7 ring: CHP). ^{31}P NMR (CD_3CN , 81 MHz): $\delta = 43.8$. MS (ESI): m/z (%) = 351 (100) $[\text{M} - \text{BF}_4]^+$. $\text{C}_{25}\text{H}_{20}\text{BF}_4\text{P}$ (438.21): calcd. C 68.52, H 4.60; found C 68.24, H 4.70.

[(*o*-Ph₂PC₆H₄-η⁶-C₇H₇)Mo(CO)₂(*P*-Mo)] (4): The phosphane **2** (9.72 g, 28.58 mmol) and Mo(CO)₆ (7.65 g, 28.98 mmol) were dissolved in methylcyclohexane (250 mL) and slowly heated to 120 °C within 2 h. Heating was continued at this temperature while stirring for 10 h. The solvent and unchanged Mo(CO)₆ were removed in vacuo, and the residue was recrystallized from dichloromethane/hexane at 0 °C. After 12 h, **4** was isolated as a red crystalline solid by filtration. Yield: 8.84 g (64%) – ¹H NMR (CD₂Cl₂, 600 MHz): δ = 7.66 (m, 2 H, *o*-C₆H₅), 7.47 (dd, 1 H, 13-H), 7.42 (m, 6 H, C₆H₅), 7.38 (m, 3 H, C₆H₅ + 12-H), 7.31 (t, 1 H, 11-H), 7.27 (t, 1 H, 10-H), 5.97 (t, 1 H, 3-H), 5.53 (t, 1 H, 4-H), 5.22 (t, 1 H, 5-H), 4.77 (d, 1 H, 2-H), 2.62 (dd, 1 H, 7-*endo*-CH₂), 2.35 (dd, 1 H, 7-*exo*-CH₂), 2.12 (tt, 1 H, 6-H). ¹³C NMR (CD₂Cl₂, 150.7 MHz): δ = 227.2 (d, ²J_{C,P} = 10.2 Hz, CO), 223.9 (d, ²J_{C,P} = 12.1 Hz, CO), 153.6 (d, ²J_{C,P} = 27.5 Hz, C-8), 151.3 (d, ¹J_{C,P} = 40.9 Hz, C-9), 142.0 (d, ¹J_{C,P} = 36.4 Hz, *i*-C₆H₅), 138.1 (d, ¹J_{C,P} = 40.2 Hz, *i*-C), 133.4 (s, C-10), 133.1 (d, ²J_{C,P} = 12.8 Hz, *o*-C), 132.8 (d, ²J_{C,P} = 11.5 Hz, *o*-C), 130.3 (s, C-12), 129.8 (s, *p*-C), 129.6 (s, *p*-C), 128.7 (d, ³J = 9.6 Hz, *m*-C), 128.4 (d, ³J = 10.1 Hz, *m*-C), 127.4 (d, ³J = 12.8 Hz, C-13), 127.3 (d, ³J = 5.8 Hz, C-11), 104.7 (s, C-5), 98.8 (s, C-2), 90.9 (s, C-3), 86.3 (s, C-4), 86.0 (s, C-1), 54.8 (s, C-6), 33.6 (s, CH₂-7). ³¹P NMR (CDCl₃, 81 MHz): δ = 64.5. MS (EI): *m/z* (%) = 504 (12) [M⁺], 476 (4) [M – CO]⁺, 448 (100) [M – 2 CO]⁺. IR (KBr): ν(CO) = 1905 (shoulder), 1889, 1873, 1816 cm^{–1}. C₂₇H₂₁MoO₂P (504.38): calcd. C 64.30, H 4.20; found C 64.90, H 4.30.

[(*o*-Ph₂PC₆H₄-η⁷-C₇H₆)Mo(CO)₂(*P*-Mo)]BF₄ (5): A solution of **4** (8.84 g, 17.53 mmol) in dichloromethane (200 mL) was treated with (Ph₃C)BF₄ (5.20 g, 15.75 mmol) at 0 °C, and the resulting mixture was subsequently heated to reflux for 30 min. The solution was reduced in volume to about 50 mL and added dropwise to rapidly stirred diethyl ether at 0 °C to precipitate **5**, which was isolated as an orange crystalline solid by filtration, washing with diethyl ether and drying in vacuo. Yield: 8.34 g (90%). ¹H NMR (CD₂Cl₂, 600 MHz): δ = 7.88 (dd, 1 H, 13-H), 7.71 (t, 1 H, 12-H), 7.59 (t, 1 H, 11-H), 7.55–7.59 (m, 6 H, *p*- + *m*-C₆H₅), 7.43–7.39 (m, 4 H, *o*-C₆H₅), 7.38 (t, 1 H, 10-H), 6.06 (m, 2 H, 3,6-H), 6.00 (m, 2 H, 4,5-H), 5.59 (dd, 2 H, 2,7-H). ¹³C NMR (CD₂Cl₂, 150.7 MHz): δ = 212.6 (d, ²J_{C,P} = 25.3 Hz, CO), 146.7 (d, ²J_{C,P} = 25.5 Hz, C-8), 141.5 (d, ¹J_{C,P} = 47.3 Hz, C-9), 133.3 (s, C-10), 132.8 (d, ⁴J_{C,P} = 2.6 Hz, C-12), 132.3 (d, ²J_{C,P} = 12.1 Hz, *o*-C), 132.1 (d, ¹J_{C,P} = 47.2 Hz, *i*-C), 132.0 (d, ⁴J_{C,P} = 2.6 Hz, *p*-C), 131.0 (d, ³J_{C,P} = 6.4 Hz, C-11), 129.9 (d, ³J_{C,P} = 10.9 Hz, *m*-C), 127.3 (d, ³J_{C,P} = 11.5 Hz, C-13), 126.7 (d, ³J_{C,P} = 3.2 Hz, C-1), 98.2 (s, C-3,6), 96.0 (s, C-4,5), 94.7 (d, ⁴J_{C,P} = 3.6 Hz, C-2,7). ³¹P NMR (CDCl₃, 81 MHz): δ = 59.9. MS (ESI): *m/z* (%) = 503 (100) [M – BF₄]⁺. IR (KBr): ν(CO) = 2032, 1988 cm^{–1}. IR (CH₂Cl₂): ν(CO) = 2035, 1994 cm^{–1}. C₂₇H₂₀BF₄MoO₂P (590.17): calcd. C 54.95, H 3.42; found C 54.16, H 3.48.

[(*o*-Ph₂PC₆H₄-η⁷-C₇H₆)Mo(CO)Br(*P*-Mo)] (6): A solution of **5** (2.40 g, 4.07 mmol) in acetone (160 mL) was treated with NaBr (3.04 g, 29.55 mmol), and the resulting mixture was subsequently heated to reflux for 14 h. After evaporation of the solvent, the residue was transferred to a silica chromatography column. Elution with dichloromethane produced a green band that was collected to give **6** as a green, crystalline solid. Yield: 0.72 g (35%). ¹H NMR (CD₂Cl₂, 600 MHz): δ = 7.79 (dd, 1 H, 13-H), 7.71 (dd, 2 H, *o*-C₆H₅), 7.53 (t, 1 H, 12-H), 7.47 (t, 1 H, 11-H), 7.44 (t, 1 H, 10-H), 7.43–7.33 (m, 6 H, *p*- + *m*-C₆H₅), 7.20 (dd, 2 H, *o*-C₆H₅), 5.80 (t, 1 H, 5-H), 5.66 (d, 1 H, 2-H), 5.42 (t, 1 H, 4-H), 5.40 (t, 1 H, 3-H), 5.07 (t, 1 H, 6-H), 4.42 (d, 1 H, 7-H). ¹³C NMR (CD₂Cl₂, 150.7 MHz): δ = 232.3 (d, ²J_{C,P} = 15.6 Hz, CO), 150.4 (d, ²J_{C,P} =

29.4 Hz, C-8), 141.5 (d, ¹J_{C,P} = 45.3 Hz, C-9), 134.5 (d, ¹J_{C,P} = 42.1 Hz, *i*-C), 134.2 (d, ²J_{C,P} = 12.1 Hz, *o*-C), 132.7 (d, ¹J_{C,P} = 37.7 Hz, *i*-C), 132.2 (s, C-10), 131.6 (d, ²J_{C,P} = 12.1 Hz, *o*-C), 130.6 (d, ⁴J_{C,P} = 1.9 Hz, C-12), 130.5 (d, ⁴J_{C,P} = 2.6 Hz, *p*-C), 129.8 (d, ⁴J_{C,P} = 1.9 Hz, *p*-C), 129.1 (d, ³J_{C,P} = 5.8 Hz, C-11), 128.5 (d, ³J_{C,P} = 9.6 Hz, *m*-C), 128.3 (d, ³J_{C,P} = 10.2 Hz, *m*-C), 127.5 (d, ³J_{C,P} = 9.6 Hz, C-13), 107.3 (d, ³J_{C,P} = 2.2 Hz, C-1), 99.4 (d, ⁴J_{C,P} = 1.3 Hz, C-3), 99.2 (s, C-2), 98.5 (d, ⁴J_{C,P} = 5.3 Hz, C-4), 93.6 (d, ⁴J_{C,P} = 5.1 Hz, C-5), 89.5 (s, C-7), 80.9 (s, C-6). ³¹P NMR (CDCl₃, 81 MHz): δ = 49.1. MS (EI): *m/z* (%) = 527 (11) [M – CO]⁺, 447 (9) [M – CO – Br]⁺. IR (KBr): ν(CO) = 1946 cm^{–1}. IR (CH₂Cl₂): ν(CO) = 1956 cm^{–1}. C₂₆H₂₀BrMoOP (555.26): calcd. C 56.24, H 3.63; found C 55.30, H 3.64.

[(*o*-Ph₂PC₆H₄-η⁷-C₇H₆)MoBr₂(*P*-Mo)] (7): A solution of **6** (4.92 g, 8.86 mmol) in dichloromethane (120 mL) was treated with a solution of bromine (0.24 mL, 4.68 mmol) in dichloromethane (10 mL) at 0 °C, and the resulting mixture was subsequently stirred for 1 h at ambient temperature. The solution was reduced in volume to about 50 mL and added dropwise to rapidly stirred hexane to precipitate **7**, which was isolated as a brown, crystalline solid by filtration, washing with hexane and drying in vacuo. Purification was possible by recrystallization from dichloromethane to afford crystals of **7**·CH₂Cl₂. Yield: 5.30 g (86%). ³¹P NMR (CDCl₃, 81 MHz): δ = 38.5. MS (EI): *m/z* (%) = 607 (16) [M⁺], 527 (68) [M – Br]⁺, 448 (21) [M – 2 Br]⁺. C₂₆H₂₂Br₂Cl₂MoP (692.09): calcd. C 45.12, H 3.20; found C 45.72, H 3.13.

[(*o*-Ph₂PC₆H₄-η⁷-C₇H₆)Mo(CH₂SiMe₃)Br(*P*-Mo)] (8): A solution of **7**·CH₂Cl₂ (200 mg, 0.29 mmol) in THF (20 mL) was treated with Me₃SiCH₂MgCl (0.3 mL of a 1.0 M solution in diethyl ether, 0.3 mmol) at –78 °C, and the resulting mixture was allowed to warm to room temperature and was subsequently stirred for 12 h at ambient temperature. The solvent was evaporated, and the residue was extracted with hexane (20 mL). Keeping the filtrate in the refrigerator for 24 h at 0 °C afforded orange crystals of **8**. Yield: 110 mg (62%). ³¹P NMR (CDCl₃, 81 MHz): δ = 51.9. C₂₉H₃₁BrMoPSi (614.47): calcd. C 56.69, H 5.09; found C 56.97, H 5.11.

[(*o*-Ph₂PC₆H₄-η⁷-C₇H₆)Mo(CH₂SiMe₃)₂(*P*-Mo)] (9): A solution of **7**·CH₂Cl₂ (500 mg, 0.72 mmol) in THF (20 mL) was treated with a large excess of Me₃SiCH₂MgCl (7.2 mL of a 1.0 M solution in diethyl ether, 7.2 mmol) at –78 °C, and the resulting mixture was allowed to warm to room temperature and was subsequently stirred for 12 h at ambient temperature. The solvent was evaporated, and the residue was extracted with hexane (20 mL). Purification was possible by column chromatography on silica using diethyl ether/petroleum ether (1:1) as eluent to isolate **8** as an orange-yellow, crystalline solid. Yield: 420 mg (93%). ³¹P NMR (CDCl₃, 81 MHz): δ = 54.6. C₃₃H₄₂MoPSi₂ (621.78): calcd. C 63.75, H 6.81; found C 63.35, H 6.74.

X-ray Crystallography:^[37,54] Data sets were collected at –75 °C (for **2**, **4**, and **5**) with an Enraf–Nonius KappaCCD or at –120 °C (for **6**–**9**) with a Bruker AXS APEX diffractometer both equipped with a rotating anode using Mo-K_α radiation (λ = 0.71073 Å). Empirical absorption correction with SORTAV^[55] (for **2**, **4**, and **5**) or SADABS^[56] (for **6**–**9**) was applied to the raw data. Structure solution was performed in all cases with SHELXS^[57] and refinement with SHELXL^[58] with anisotropic thermal parameters for all atoms. Hydrogen atoms were added to the structure models on calculated positions and were refined as riding atoms (**2**, **4**, and **5**) or are unrefined for **6**, **7**, and **9**. Hydrogen atoms for **8** were located in the difference Fourier map and were refined with isotropic ther-

Table 2. Crystallographic Data for **2**, **4**, **5**·CH₂Cl₂, **7**·CHCl₃, **8**, and **9**·C₆H₁₄

	2	4	5 ·CH ₂ Cl ₂	7 ·CHCl ₃	8	9 ·C ₆ H ₁₄
Empirical formula	C ₂₅ H ₂₁ P	C ₂₇ H ₂₁ MoO ₂ P	C ₂₈ H ₂₂ BrCl ₂ F ₄ MoO ₂ P	C ₂₆ H ₂₁ Br ₂ Cl ₃ MoP	C ₂₉ H ₃₁ BrMoPSi	C ₃₉ H ₅₆ MoPSi ₂
Formula mass	352.39	504.35	675.08	726.51	614.45	707.93
<i>a</i> [Å]	7.0168(1)	13.933(1)	10.3457(2)	8.364(1)	14.6027(13)	15.3044(7)
<i>b</i> [Å]	11.1396(2)	12.979(1)	10.8398(2)	27.749(5)	18.5103(17)	16.0758(7)
<i>c</i> [Å]	25.0062(4)	24.305(1)	12.8623(2)	11.225(2)	19.3375(18)	15.5570(7)
α [°]	90	90	90.474(1)	90	90	90
β [°]	91.689(1)	90.14(1)	105.434(1)	92.643(4)	90	97.925(1)
γ [°]	90	90	92.154(1)	90	90	90
<i>V</i> [Å ³]	1953.74(5)	4395.2(5)	1389.20(5)	2602.3(7)	5226.9(8)	3790.9(3)
<i>d</i> _{calcd.} [g cm ⁻³]	1.198	1.524	1.614	1.854	1.562	1.240
Crystal system	monoclinic	monoclinic	triclinic	monoclinic	orthorhombic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i> (no. 14)	<i>C</i> 2/ <i>c</i> (no. 15)	<i>P</i> 1̄ (no. 2)	<i>P</i> 2 ₁ / <i>c</i> (no. 14)	<i>Pbca</i> (no. 61)	<i>P</i> 2 ₁ / <i>n</i> (no. 14)
<i>Z</i>	4	8	2	4	8	4
μ [mm ⁻¹]	1.45	6.91	7.74	3.959	2.15	0.476
Unique data	4586	5052	6341	5978	8307	11750
Observed data [<i>I</i> > 2σ(<i>I</i>)]	3555	3539	5438	4538	6307	7265
<i>R</i> 1 (obs. data) [%]	3.93, <i>wR</i> 1 = 9.01	4.01, <i>wR</i> 1 = 7.02	3.28, <i>wR</i> 1 = 7.29	3.59, <i>wR</i> 1 = 6.86	5.44, <i>wR</i> 1 = 8.95	4.76, <i>wR</i> 1 = 8.86
<i>R</i> 2 (all data) [%]	5.80, <i>wR</i> 2 = 9.93	7.68, <i>wR</i> 2 = 8.48	4.30, <i>wR</i> 2 = 7.76	5.35, <i>wR</i> 2 = 7.17	7.95, <i>wR</i> 2 = 9.55	9.21, <i>wR</i> 2 = 9.84
GoF	1.030	1.011	1.043	0.939	1.076	0.917
No. of variables	235	280	352	298	422	381
Res. electr. dens. [e/Å ³]	0.22/−0.24	0.42/−0.48	0.51/−0.51	0.94/−0.55	1.10/−0.88	0.81/−0.44

mal parameters. ORTEP^[59] was used for all drawings. Additional crystallographic data are listed in Table 2 and in ref.^[37]

Metathesis Studies: A solution of norbornene (750 mg, 7.97 mmol) and the bis(neosilyl) complex **9** (16.5 mg, 26.5 μmol) in chlorobenzene (60 mL) was treated with Me₃SiCH₂MgCl (30 μL of a 1.0 M solution in diethyl ether, 30 μmol), and the resulting mixture was heated at 40 °C for 12 h. After quenching with a few drops of benzaldehyde, the viscous mixture was heated to 80 °C and then added dropwise to rapidly stirred methanol (400 mL) to precipitate a white, fibrous material, which was collected by filtration and dried in vacuo. Yield: 650 mg (87%). The molecular weights of the poly(1,3-cyclopentylenevinylene) samples thus obtained were determined by GPC with THF as eluent using refraction index detection and polystyrene as standard (*M*_n = 2.6·10⁴ g/mol, PDI = *M*_w/*M*_n = 6.7, approx. 80% *trans* double bonds as indicated by ¹³C NMR^[49] and IR^[50] measurements).

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