Chelate Complexes of Functionalized Cycloheptatrienyl Ligands: Molybdenum Complexes with Linked Cycloheptatrienyl-Phosphane Ligands and Their Use in Catalytic Carbon−Carbon Bond Formation

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The synthesis of *P*-functionalized molybdenum chelate complexes incorporating the linked cycloheptatrienyl-phosphane ligand [2-(diisopropylphosphanyl)phenyl]cycloheptatrienyl (*o*-*i*Pr_2P–C_6H_4–C_7H_6) is described. From the ligand precursor [2-(cyclohepta-2,4,6-trienyl)phenyl]diisopropylphosphane (**1**) the paramagnetic 17-electron dibromide [(*o*-*i*$Pr_2PC_6H_4$-η^7-C_7H_6)$MoBr_2$(*P–Mo*)] (**2**) can readily be obtained. This is a versatile starting material for the preparation of cycloheptatrienyl molybdenum hydrides [(*o*-*i*$Pr_2PC_6H_4$-η^7-C_7H_6)Mo(η^2-BH_4)(*P–Mo*)] (**3**) and [(*o*-*i*$Pr_2PC_6H_4$-η^7-C_7H_6)Mo(PPh_3)-H(*P–Mo*)] (**4**). Treatment of **3** with dimethylanilinium tetraphenylborate ([$PhNMe_2H$][BPh_4]) allows the production of the cationic 14-electron complex fragment [(*o*-*i*$Pr_2PC_6H_4$-η^7-C_7H_6)Mo(*P–Mo*)]$^+$ (**13**), which can be stabilized in the presence of suitable ligands L. The complexes [(*o*-*i*$Pr_2PC_6H_4$-η^7-C_7H_6)MoL_2(*P–Mo*)]BPh_4 [L = dimethylphenyl isocyanide, (**5**)BPh_4; L_2 = η^4-2,5-norbornadiene, (**6**)BPh_4; L_2 = η^2-phenylacetylene, (**7**)BPh_4; L_2 = η^2-*tert*-butylacetylene, (**8**)BPh_4] can thus be isolated in good yields. The alkyne complex (**7**)BPh_4 can be used as a single-source catalyst for the oligomerization of phenylacetylene, affording a mixture of triphenylbenzenes and linear oligomers. Quantum chemical calculations reveal an intimate relationship between the catalytically active 14-electron complex fragment [(*o*-*i*$Pr_2PC_6H_4$-η^7-C_7H_6)Mo(*P–Mo*)]$^+$ (**13**) and *hypothetical* isoelectronic and isolobal complexes of the type [(*o*-*i*$Pr_2PC_6H_4$-η^5-C_5H_4)M(*P–M*)]$^+$ (M = Ru, **14**; M = Os, **15**), indicating that cycloheptatrienyl molybdenum systems might in general be a suitable replacement for cyclopentadienyl ruthenium and osmium catalysts.
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Introduction

Ruthenium half-sandwich complexes of the type [(η-C_5R_5)Ru(PR'_3)$_2$Cl] (R = H, Me; R′ = alkyl, aryl) are among the most important starting materials in organotransition metal chemistry and have played key roles in the stabilization of highly reactive species such as vinylidenes and allenylidenes by metal coordination.[1] In addition, extensive studies have shown that these complexes are particularly useful for effective ruthenium-catalyzed C−C bond formation.[2] The actual active catalyst system in this process is generated by splitting off of the halide and one phosphane ligand, resulting in the formation of the doubly coordinatively unsaturated complex fragment [(η-C_5R_5)Ru(PR'_3)]$^+$ (**I**), which allows various organic substrates to be brought together and coupled in its coordination sphere.[2,3] The similarity between the isoelectronic and isolobal fragments [(η-C_5R_5)Ru] and [(η-C_7H_7)Mo] prompted us to pursue a general study on the possibility of replacing the frequently used ruthenium catalysts by the analogous but much cheaper molybdenum systems. Consequently, similar chemical and physical properties may be expected in complexes possessing an identical set of co-ligands upon substitution of the [(η-C_5R_5)Ru] unit by [(η-C_7H_7)Mo] unit.[4,5]

Our goal of introducing cycloheptatrienyl molybdenum complexes into homogeneous catalysis is based on the concept of donor functionalization, extremely successful in cyclopentadienyl chemistry in particular,[6−9] and we have already been able to synthesize complexes with novel cycloheptatrienyl ligands bearing pendant O-, N-, S- and P-donor groups capable of coordinating to a transition metal center in a chelating η^7:η^1-fashion.[10,11] Complexes with linked cycloheptatrienyl-phosphane ligands seemed to be particularly well suited for applications in catalytic C−C coupling reactions, and so we have started to prepare precursor complexes that should allow us to obtain coordin-

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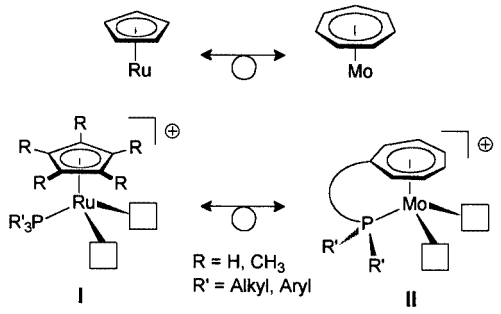
atively unsaturated molybdenum complex fragments of type **II** (Scheme 1).[12] In this contribution we present the syntheses of tetrahydroborate complexes of type [(*o*-$R_2PC_6H_4$-η^7-C_7H_6)Mo(η^2-BH_4)(*P*-*Mo*)] (R = *i*Pr, Ph), from which the cationic 14-electron complex fragments [(*o*-$R_2PC_6H_4$-η^7-C_7H_6)Mo(*P*-*Mo*)]$^+$ can be generated and stabilized in the presence of suitable co-ligands.



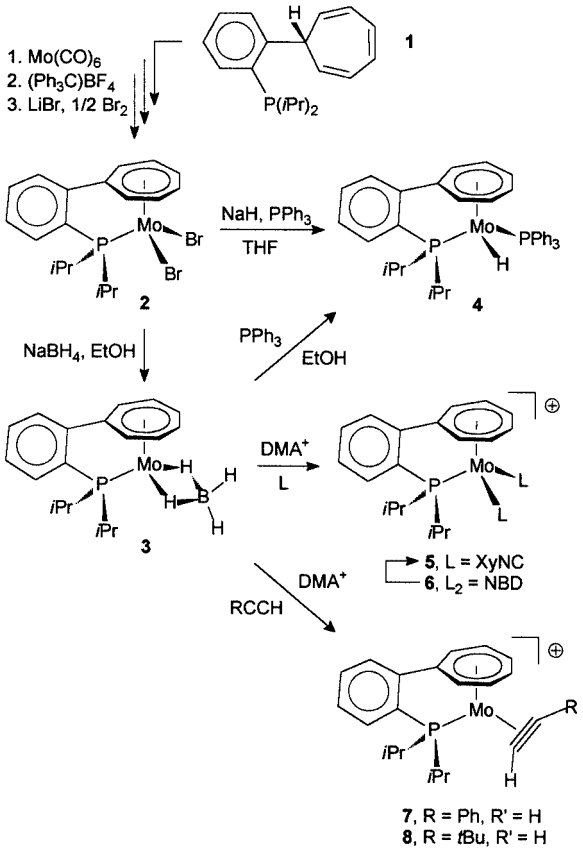
Scheme 1. Isolobal relationship between cyclopentadienyl ruthenium and cycloheptatrienyl molybdenum complex fragments

Results and Discussion

Preparation and Reactions of Molybdenum Hydride Complexes

We have recently reported on the preparation of a cycloheptatriene with a diphenylphosphanyl donor group, and were able to demonstrate that the resulting paramagnetic 17-electron complexes of the type [(*o*-$Ph_2PC_6H_4$-η^7-C_7H_6)MoX_2(*P*-*Mo*)] (X = Br, CH_2SiMe_3) can be used in the ring-opening metathesis polymerization of norbornene.[11] In order to render the donor moiety more sterically demanding and electron-rich, we aimed at replacement of the phenyl substituents with isopropyl groups, and the corresponding ligand precursor [2-(cyclohepta-2,4,6-trienyl)-phenyl]diisopropylphosphane (**1**) used in this contribution was prepared by addition of 2-(diisopropylphosphanyl)-phenyllithium to the tropylium cation $C_7H_7^+$. A three-step synthesis starting from the air-sensitive **1** and $Mo(CO)_6$ affords the 17-electron dibromo complex **2** (Scheme 2). Full details of the preparation of **1** and **2**, together with the spectroscopic and structural properties of all reaction intermediates, will be presented elsewhere.[13]

Reduction of paramagnetic **2** can be achieved by use of $NaBH_4$ in ethanol solution, resulting in the formation of the tetrahydroborate complex **3** (Scheme 2). In contrast, Suzuki and co-workers have shown that the corresponding treatment of isoelectronic ruthenium(III) complexes of the type [(η-C_5Me_5)Ru(PR_3)Cl_2] (R = Ph, *i*Pr, *cyclo*-C_6H_{11}) does indeed also give tetrahydroborate complexes [(η-C_5Me_5)Ru(PR_3)(η^2-BH_4)], but that these undergo immediate ethanolysis under these conditions to yield the trihydrides [(η-C_5Me_5)Ru(PR_3)H_3].[14] In our hands, **2** could not be converted into a trihydride complex and remained perfectly stable toward hydrolysis even in wet ethanol solution. The molecular structure of **3** is shown in Figure 1 (top), and selected bond lengths and angles are listed in Table 1.



Scheme 2. XyNC = 2,6-dimethylphenyl isocyanide; NBD = 2,5-norbornadiene; DMA^+ = dimethylanilinium $(PhNMe_2\ H)^+$

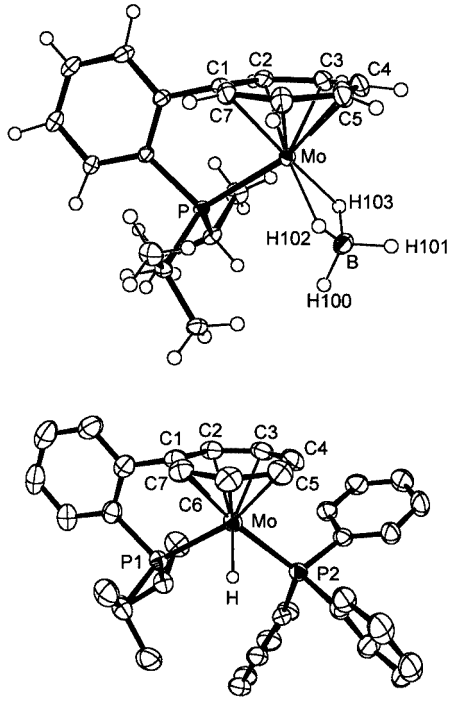


Figure 1. ORTEP drawings of **3** (top) and **4** (bottom) with thermal ellipsoids drawn at 50% probability

Table 1. Selected bond lengths (Å) and angles (°) for **3**, **4**, (**5**)$BPh_4 \cdot C_5H_{12}$, (**6**)$BPh_4 \cdot CH_2Cl_2$, (**7**)BPh_4, and (**10**)$BPh_4 \cdot 3C_4H_8O$

	3	**4**	(**5**)$BPh_4 \cdot C_5H_{12}$	(**6**)$BPh_4 \cdot CH_2Cl_2$	(**7**)BPh_4	(**10**)$BPh_4 \cdot 3C_4H_8O$
C1−C2	1.4218(19)	1.425(3)	1.417(6)	1.420(5)	1.408(4)	1.403(5)
C2−C3	1.413(2)	1.401(3)	1.376(7)	1.391(5)	1.402(4)	1.435(5)
C3−C4	1.418(2)	1.407(3)	1.404(7)	1.410(6)	1.422(5)	1.411(5)
C4−C5	1.402(2)	1.406(3)	1.401(7)	1.392(6)	1.380(5)	1.403(6)
C5−C6	1.427(2)	1.419(3)	1.401(7)	1.422(6)	1.415(5)	1.404(6)
C6−C7	1.414(2)	1.409(3)	1.403(6)	1.392(6)	1.405(4)	1.413(5)
C1−C7	1.419(2)	1.409(3)	1.416(6)	1.406(5)	1.410(4)	1.421(5)
C1−C8	1.5042(18)	1.497(3)	1.509(6)	1.502(5)	1.496(4)	1.500(5)
C14−C15/C26−C27					1.292(4)	1.279(5)
C15−C16/C27−C28					1.457(4)	1.465(5)
C20−C21				1.371(6)		
C23−C24				1.368(5)		
C20−N1			1.164(5)			
C29−N2			1.165(6)			
Mo−C1	2.2527(12)	2.286(2)	2.264(5)	2.324(3)	2.373(3)	2.366(3)
Mo−C2	2.2744(14)	2.316(2)	2.321(5)	2.294(4)	2.292(3)	2.325(3)
Mo−C3	2.2557(14)	2.319(2)	2.298(5)	2.272(4)	2.221(3)	2.226(3)
Mo−C4	2.3191(13)	2.323(2)	2.313(5)	2.343(4)	2.324(3)	2.311(3)
Mo−C5	2.3168(14)	2.310(2)	2.301(5)	2.343(4)	2.343(3)	2.351(4)
Mo−C6	2.2550(13)	2.261(2)	2.286(5)	2.270(4)	2.241(3)	2.246(3)
Mo−C7	2.2736(11)	2.294(2)	2.301(4)	2.311(4)	2.280(3)	2.268(3)
Mo−C14/C26					2.023(3)	2.035(3)
Mo−C15/C27					2.090(3)	2.090(3)
Mo−C20			2.076(5)	2.381(4)		
Mo−C21				2.401(4)		
Mo−C23				2.400(4)		
Mo−C24				2.388(4)		
Mo−C29			2.078(5)			
Mo−P/P1	2.4824(3)	2.4912(5)	2.4958(13)	2.5863(10)	2.5283(8)	2.5073(9)
Mo−P2		2.4886(6)				
C14−C15−C16/ C26−C27−C28					136.6(3)	138.4(3)

The positions of all hydrogen atoms were refinable, indicating that the BH_4 anion is coordinated to the molybdenum atom through two three-center, two-electron bonds, thereby simultaneously blocking two coordination sites. This bidentate M(μ^2-H_2BH_2) ligation represents the most common mode of bonding in tetrahydroborate transition metal complexes.[15] In addition, it is possible to establish the angles between the centroid of the cycloheptatrienyl ring, the C_7 carbon atoms, and the adjacent hydrogen atoms, to reveal a significant out-of-plane displacement for the C_7 ring hydrogen atoms. The average bending is about 9° toward the molybdenum center, such deviation having previously been attributed to a reorientation of the large seven-membered ring for a better metal overlap.[4,16]

As described above, **3** remained perfectly stable in ethanol solution. In the presence of Lewis bases such as PPh_3, however, rapid ethanolysis and cleavage of the BH_4 ligand can be achieved, and formation of the monohydride complex **4** is observed together with evolution of dihydrogen. The reaction can be followed by ^{31}P NMR spectroscopy, which reveals two doublets at 74.5 and 53.7 ppm for the two different phosphorus nuclei in **4** ($^2J_{P,P}$ = 31 Hz) together with the singlet at δ = 67.9 ppm for complex **3**. Pure hydrides such as **4** can also be efficiently prepared directly from the dibromide **2** by use of various hydride sources in the presence of Lewis bases. Consequently, treatment of **2** with sodium hydride in the presence of PPh_3 affords **4** in good yield. In **4**, the pseudotetrahedrally coordinated molybdenum center has four different ligands, and so the complex is obtained as a racemic mixture of two enantiomers. As this representative of so-called "chiral-at-metal" half-sandwich compounds[17−19] is configurationally stable, the diastereotopic cycloheptatrienyl hydrogen atoms give rise to six different ^1H NMR resonances between 3.8 and 5.5 ppm. This portion of the 600 MHz spectrum is shown in Figure 2. Correspondingly, seven ^{13}C NMR resonances are observed for the C_7H_6 carbon atoms, together with six resonances for the phenylene bridge and six resonances for the diastereotopic isopropyl groups. The hydride resonance in **4** is observed as a doublet of doublets at −2.88 ppm with 62 and 41 Hz couplings to the two different phosphorus nuclei (Figure 2). Recrystallization of **4** from hexane afforded single crystals suitable for structure determination by X-ray diffraction; the molecular structure is shown in Figure 1 (bottom). The position of the Mo−H hydrogen atom could be refined to reveal a molybdenum hydrogen

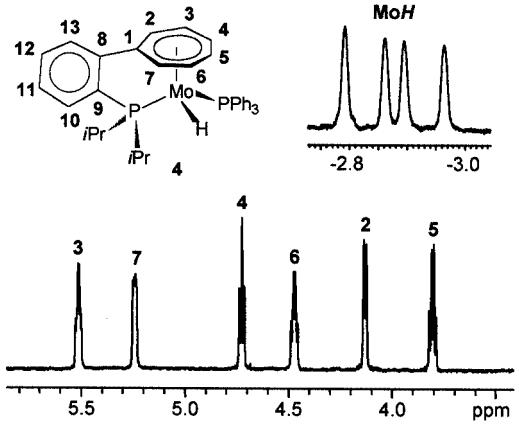


Figure 2. Selected parts of the ^{1}H NMR spectrum (600 MHz, [D_8]toluene) of **4**

bond length of 1.69(2) Å. As would be expected, this distance is slightly shorter than the Mo−H distances of 1.88(2) and 1.96(2) Å in **3**.

Compound **4** is a rare example of a cycloheptatrienyl transition metal hydride, and to the best of our knowledge, [(η^7-C_7H_7)Mo(dppe)H] represents the only previously reported closely related example,[20] apart from a series of tungsten complexes of the type [(η^7-C_7H_7)W(PR_3)(CO)H] (R = OMe, O*i*Pr, Ph).[21] Furthermore, chiral hydrides such as **4** might − in view of the extensive chemistry of related cyclopentadienyl iron, ruthenium, and osmium hydrides − be interesting starting materials for hydrometalation or hydrogenation reactions.[22] For instance, protonation of the hydride ligand in **4** might result in the formation of a cationic dihydrogen complex [(*o*-*i*$Pr_2PC_6H_4$-η^7-C_7H_6)Mo(PPh_3)(H_2)(*P*-*Mo*)]$^+$, from which the 14-electron complex fragment [(*o*-*i*$Pr_2PC_6H_4$-η^7-C_7H_6)Mo(*P*-*Mo*)]$^+$ could be generated by splitting of the phosphane and the dihydrogen ligands. To our disappointment, however, decomposition was mainly observed upon treatment of **4** with HBF_4·Et_2O.

More conveniently, the tetrahydroborate **3** proved to be an ideal starting material for the generation of our target 14-electron complex by cleavage of the boranate ligand. In fact, this unit can be made available by treatment of **3** with dimethylanilinium (DMA^+) salts, widely used as mild acids in metallocene chemistry.[23] Treatment of **3** with [$HNMe_2Ph$][BPh_4] proceeds with evolution of dihydrogen, and the formation of stable cationic adducts is observed in THF and acetonitrile solutions. The bis(acetonitrile) complex can even be isolated in crystalline form. The two available coordination sites can be blocked irreversibly by addition of more strongly coordinating ligands. If the protonolysis is carried out in the presence of 2,6-dimethylphenyl isocyanide (XyNC), for instance, the stable diisocyanide complex (**5**)BPh_4 is obtained. The CN stretching frequencies of 2099 and 2066 cm^{-1} show that the cationic [(*o*-*i*$Pr_2PC_6H_4$-η^7-C_7H_6)Mo(*P*-*Mo*)]$^+$ unit has a relatively strong electron-releasing capability, although significantly stronger metal-to-ligand backbonding is observed in, for instance, *trans*-diisocyanide molybdenum(0) complexes containing only additional phosphane ligands.[24,25] Accordingly, the molecular structure of the cation in (**5**)BPh_4·C_5H_{12} (Figure 3, top) has longer Mo-C bond lengths [2.076(5) and 2.078(5) Å] to the isocyanide carbon atoms, together with slightly shorter C≡N bond lengths [1.164(5) and 1.165(6) Å], in comparison with the values found for the centrosymmetric structure of *trans*-[$Mo(dppe)_2(CNPh)_2$] [2.031(6) and 1.171(6) Å].[25] Only slight deviation from linearity is observed for the Mo-C−N and C−N−C bond angles in **5** (168.7(5) − 174.6(5)°).

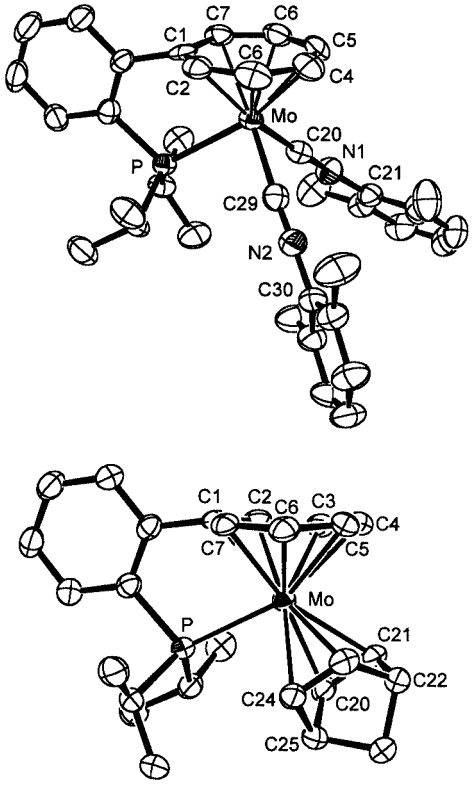


Figure 3. ORTEP drawings of the cations in (**5**)BPh_4·C_5H_{12} (top) and (**6**)BPh_4·CH_2Cl_2 (bottom) with thermal ellipsoids drawn at 50% probability

In a similar fashion, treatment of **3** with [$HNMe_2Ph$][BPh_4] in the presence of norbornadiene gives the diolefin complex (**6**)BPh_4, which is also a versatile starting material for further ligand substitution reactions. Treatment of (**6**)BPh_4 with XyNC thus results in the quantitative formation of (**5**)BPh_4. The norbornadiene complex was also characterizable by X-ray diffraction analysis, and the molecular structure of the cation in (**6**)BPh_4·CH_2Cl_2 is shown in Figure 3 (bottom). Although the structural parameters about the molybdenum centers again fall in the expected ranges (Table 1),[11] the norbornadiene ligand seems to cause some steric congestion at the metal center, and so an elongated Mo−P bond length of 2.5863(10) Å together with a slight puckering of the seven-membered ring can be observed with the longest molybdenum-carbon bonds to C4 and C5, which are adjacent to the diolefin ligand. A similar observation has been made in the related ruthenium complex [(η-C_5Me_5)Ru(PPh_3)(η^4-NBD)]ClO_4.[26]

Preparation of Molybdenum Alkyne Complexes

Cyclopentadienyl ruthenium complexes are extensively used for C−C bond formation through the employment of terminal alkynes, which can either be oligomerized or coupled with various other substrates such as allyl alcohols or alkenes.[2,3] We have consequently studied the cleavage of the tetrahydroborate ligand in the presence of phenyl- and *tert*-butylacetylene, resulting in the formation of crystalline (**7**)BPh_4 and (**8**)BPh_4. Both complexes contain η^2-coordinated alkyne ligands, which stabilize both available coordination sites with their π-electrons and must therefore act as four-electron donors. This fact is easily deduced from their ^{1}H NMR spectra, which exhibit characteristic resonances at low field for the acetylenic *H*C-hydrogen atoms.[27] These resonances appear as doublets at δ = 10.41 ppm ($^3J_{H,P}$ = 29.4 Hz) for **7** and at δ = 10.03 ppm, ($^3J_{H,P}$ = 33.0 Hz) for **8**. A similar downfield shift is observed in the ^{13}C NMR spectra for the acetylenic carbon atoms. For the phenylacetylene complex **7**, these resonances are found as doublets at δ = 178.5 ppm ($^2J_{C,P}$ = 28.4 Hz, ≡CH) and at δ = 173.2 ppm ($^2J_{C,P}$ = 4.5 Hz, ≡CPh). Surprisingly, the order of these resonances is reversed for the *tert*-butylacetylene complex **8**, its ^{13}C NMR spectrum exhibiting a broad singlet at δ = 191.2 ppm (≡C*t*Bu) and a doublet at 177.8 ppm ($^2J_{C,P}$ = 30.1 Hz, ≡CH).

In addition, the molecular structure of the cation **7** (Figure 4, top) shows the structural parameters for the alkyne ligand, with an elongated C≡C (C14−C15) bond length of 1.291(4) Å, together with a small C≡C−C(Ph) (C14−C15−C16) angle of 136.5(3)°, which are clearly indicative of a four-electron donor alkyne ligand.[27] The geometry around the molybdenum atom can be interpreted as a two-legged piano stool with the acetylenic C14−C15 carbon bond and the Mo−P axis in the same plane, and the P-Mo-C14−C15 torsion angle is 173.7°. The acetylenic phenyl and the *ortho*-phenylene rings are also almost coplanar (interplanar angle of 16.7°), so the complex can be regarded as being essentially C_s-symmetric if the two isopropyl groups are neglected. The molybdenum distances to the ring carbon atoms range from 2.221(3) Å (Mo-C3) to 2.373(3) Å (Mo-C1), indicating a fairly significant deviation from planarity (Table 1), and the mean and maximum deviations from the least-squares plane (C1−C7) are 0.075 and −0.108 Å (for C3), respectively. Nevertheless, these structural parameters are still strongly indicative of an η^7-coordinated cycloheptatrienyl ligand. We are not aware of any related ruthenium complex containing an η^2-bonded alkyne ligand. Very recently, however, the molecular structure of a related osmium complex [(η-C_5H_5)Os(η^2-HC≡CCPh_2OH)(P*i*Pr_3)]PF_6 containing a coordinated propargyl alcohol has been reported.[28] Comparison of the bond lengths and angles with those in **7** demonstrates that cycloheptatrienyl molybdenum complexes are also strongly related to cyclopentadienyl osmium systems, with which they exist in a diagonal relationship.

For purposes of comparison, we also studied the possibility of synthesizing the corresponding tetrahydroborate complex **9** containing the linked cycloheptatrienyl-phosphane ligand with a diphenylphosphanyl donor group, the synthesis and coordination chemistry of which have been reported before.[11] Treatment of [(*o*-$Ph_2PC_6H_4$-η^7-C_7H_6)$MoBr_2$-(*P*−*Mo*)] with $NaBH_4$ in EtOH does indeed result in the formation of **9**, which could be isolated in relatively low yield as a green, air-sensitive solid. The crude product was only characterized by ^{1}H and ^{31}P NMR spectroscopy and was used without further purification for the preparation of the alkyne complex (**10**)BPh_4. Thus, treatment of **9** with [$HNMe_2$Ph][BPh_4] in the presence of phenylacetylene afforded (**10**)BPh_4 as a stable, crystalline compound (Scheme 3). Single crystals of (**10**)BPh_4·3THF could be obtained by recrystallization from THF/hexane solution, and Figure 4 (bottom) shows an ORTEP presentation of the cation **10**. The alkyne ligand in **10** seems to be somewhat more weakly coordinated than in **7**, as it has a slightly shorter C≡C bond length [1.279(5) vs. 1.292(4) Å], together with a slightly larger C≡C−C(Ph) angle [138.4(3) vs. 136.5(3)°]. The overall geometry, though, is similar to that observed for **7** (Table 1), although the phenylacetylene ligand deviates more strongly from a perfectly C_s-symmetric conformation, as indicated by the torsion angle of 169.8° between the P-Mo-C26−C27 atoms and by the interplanar angle of 26.6° between the least-squares planes containing the acetylenic phenyl and phenylene carbon atoms. From the difficulties encountered in particular with the synthesis of the tetrahydroborate derivative **9**, we were able to ascertain that in our hands the more sterically demanding diisopropylphosphane donor seems to be superior to its diphenylphosphane analogue. We have generally observed increased stability upon replacement of the phenyl groups with isopropyl groups, and so both our experimental work and our catalytic studies have mainly focused on, and

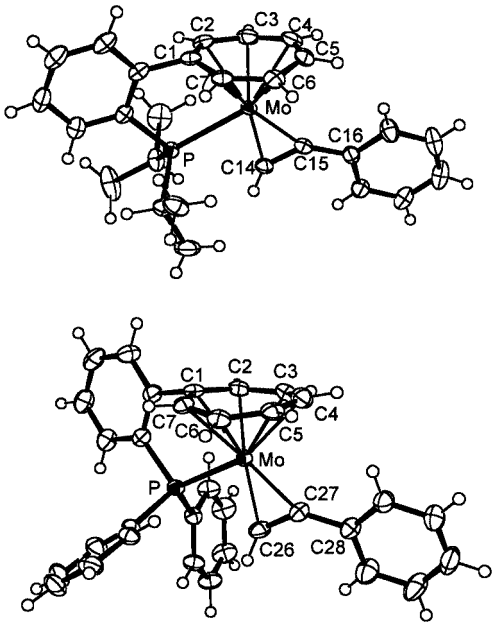
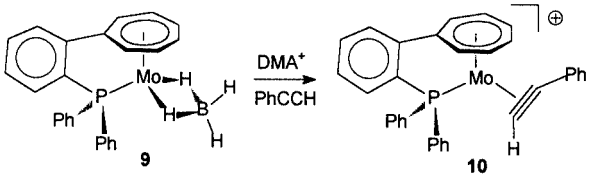


Figure 4. ORTEP drawings of the cations in (**7**)BPh_4 (top) and (**10**)BPh_4·C_6H_{14} (bottom) with thermal ellipsoids drawn at 50% probability

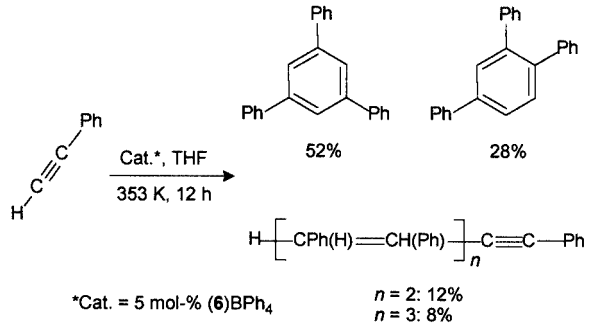
mainly will continue to focus on, the use of complexes containing the [2-(diisopropylphosphanyl)phenyl]cycloheptatrienyl ligand.



Scheme 3. DMA^+ = dimethylanilinium $(PhNMe_2\ H)^+$

Catalytic Study

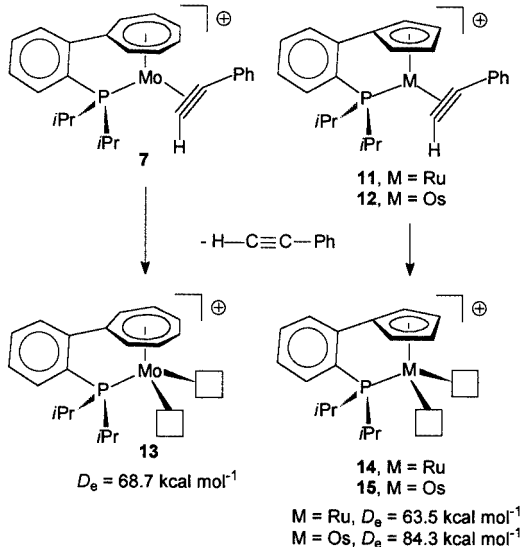
Alkyne complexes such as **7**, **8**, and **10** could be intermediates in the catalytic coupling of acetylenes at cationic molybdenum complex fragments of type II (Scheme 1).[2,3] We have therefore studied the use of (**7**)BPh_4 (5 mol %) as a catalyst for the oligomerization of phenylacetylene[29] in THF solution at 80 °C. Our preliminary results indicate that this system is indeed efficient at catalyzing the above reaction, affording a product mixture of cyclotrimers (80%) and linear oligomers (20%). Surprisingly, cyclotrimerization to give 1,3,5-triphenylbenzene (52%, unambiguously characterized by X-ray diffraction analysis)[30] and 1,2,4-triphenylbenzene (28%) is predominantly observed, in addition to the formation of a linear dimer (12%) and a linear trimer (8%) (Scheme 4). This result contrasts with the reaction involving ruthenium catalysts, in which linear dimers and trimers are formed almost exclusively.[3b,3e,3f] Further work will be directed toward the elucidation of the oligomerization mechanism[31] effective with our novel molybdenum catalyst system. Thus, (**7**)BPh_4 and our related alkyne complexes represent ideal starting materials for further controlled stoichiometric transformations, which will hopefully allow additional possible intermediates in the catalytic cycle to be identified.



Scheme 4. Catalytic oligomerization of phenylacetylene

Theoretical Study

To study the (C_7H_7)Mo-(C_5R_5)M-relationship (M = Ru, Os) by theoretical methods, we chose the molybdenum phenylacetylene complex **7** for comparison with the *hypothetical* cyclopentadienyl ruthenium and osmium complexes **11** and **12**, each containing an identical diisopropylphosphanylphenyl substituent (Scheme 5). The structures of all three cationic complexes were optimized by DFT methods employing the BP86 functional (Figure 5). The alkyne conformations in all three complexes are very similar and are in agreement with the expected nearly C_s-symmetric geometry about the metal centers. The phenylacetylene ligand in each complex exhibits the expected lengthening of the C≡C



Scheme 5. Alkyne bond dissociation energies (D_e) of phenylacetylene complexes

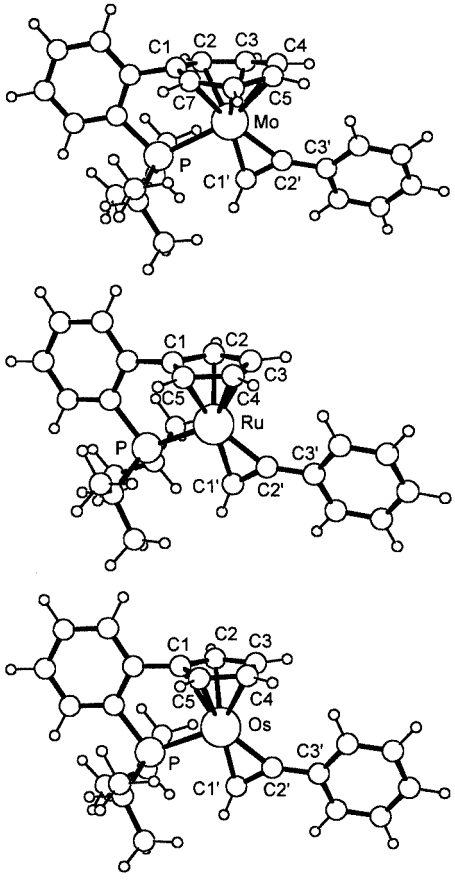


Figure 5. Calculated structures of the cations **7**, **11**, and **12**

Table 2. Experimentally measured and calculated bond lengths (Å) and angles (°) for **7**, **11**, and **12**

	(**7**)BPh_4	**7**	**11**	**12**
C1−C2	1.408(4)	1.423	1.439	1.429
C2−C3	1.402(4)	1.426	1.442	1.435
C3−C4	1.422(5)	1.426	1.427	1.420
C4−C5	1.380(5)	1.405	1.440	1.432
C5−C1			1.440	1.432
C5−C6	1.415(5)	1.428		
C6−C7	1.405(4)	1.424		
C1−C7	1.410(4)	1.421		
C1′−C2′	1.292(4)	1.318	1.309	1.306
C2′−C3′	1.457(4)	1.450	1.445	1.446
M−C1	2.373(3)	2.403	2.220	2.275
M−C2	2.292(3)	2.300	2.193	2.246
M−C3	2.221(3)	2.246	2.210	2.258
M−C4	2.324(3)	2.356	2.215	2.262
M−C5	2.343(3)	2.343	2.205	2.253
M−C6	2.241(3)	2.259		
M−C7	2.280(3)	2.338		
M−C1′	2.023(3)	2.033	2.004	2.004
M−C2′	2.090(3)	2.113	2.029	2.031
M−P	2.5283(8)	2.580	2.388	2.416
P−M−C1′	76.52(9)	76.8	81.2	82.3
P−M−C2′	112.86(8)	113.7	119.1	120.0
C1′−C2′−C3′	136.6(3)	138.8	143.8	142.7

bond length, together with a small C≡C−C(Ph) angle (Table 2). For the molybdenum complex **7**, the computed optimized geometry is in excellent agreement with the structure determined by X-ray diffraction analysis (Table 2, Figure 3), and the puckering of the seven-membered ring is also accurately reproduced. This deviation from planarity is significantly less pronounced in **11** and **12**, the structural data of which are very similar and in excellent agreement with the experimentally measured and calculated geometric parameters of unbridged cyclopentadienyl osmium alkyne complexes.[28]

Scheme 5 shows the theoretically predicted alkyne bond dissociation energies (D_e) of **7**, **11**, and **12**, calculated as the energy difference between the alkyne complex on one hand, and the *unoptimized* complex fragments **13** −**15** and the phenylacetylene ligand at its optimized geometry on the other (vertical D_e). The predicted D_e for the molybdenum complex **7** (68.7 kcal·mol^{-1}) takes an intermediate position between the values calculated for the Ru (D_e = 63.5 kcal·mol^{-1}) and Os systems (D_e = 84.3 kcal·mol^{-1}). Comparative calculations employing the popular B3LYP hybrid functional result in D_e values approximately 10 kcal·mol^{-1} lower, but the differences between the three complexes are very similar. Figure 6 shows a representation of the frontier orbitals in the unoptimized 14-electron complexes **13** −**15** formed by splitting of the phenylacetylene ligand.

In each complex, the symmetry properties of the two lowest unoccupied molecular orbitals (LUMOs), which are essentially vacant d-orbitals, match those of the occupied $\pi_{\|}$ and $\pi_{\perp}$ orbitals of an alkyne ligand. Consequently, this can act as a four-electron donor, providing 18-electron complexes.[27,28,32] Comparison of the energies and shapes of the relevant frontier orbitals reveals the close resemblance between **13**, **14**, and **15** and confirms the intimate relationship between the isoelectronic and isolobal [(η-C_7H_7)Mo] and [(η-C_5R_5)M] fragments (M = Ru, Os).

Conclusion

In summary, we present a new method for the generation and stabilization of coordinatively unsaturated cycloheptatrienyl molybdenum complexes, which can be used for catalytic alkyne-alkyne coupling reactions. These results indicate that cycloheptatrienyl complexes can indeed be potentially useful for applications in homogeneous transition metal catalysis, the goal of these studies being the develop-

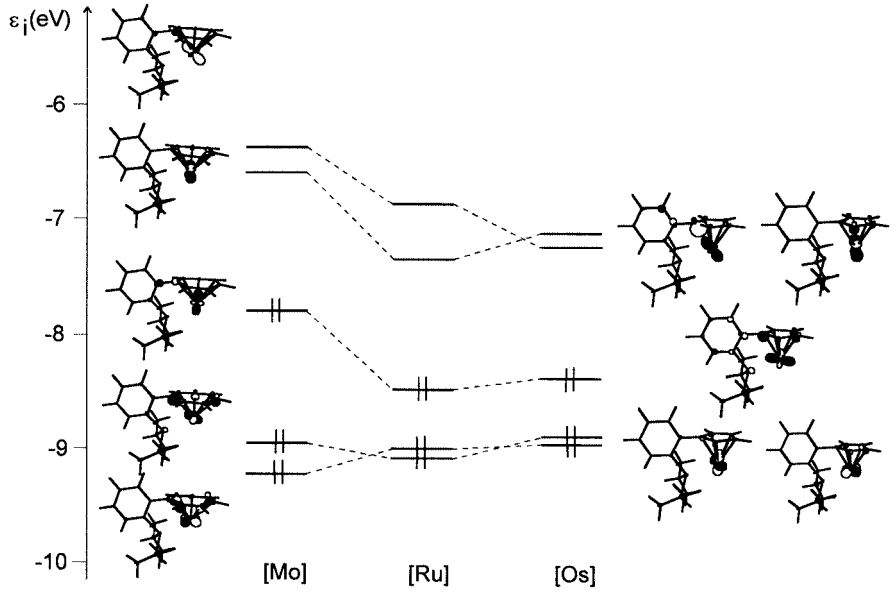


Figure 6. Frontier orbitals of the 14-electron complexes **13** [M = Mo], **14** [M = Ru], and **15** [M = Os]

ment of novel effective catalyst systems that should allow the precious metal ruthenium (and also osmium) to be substituted with the much cheaper molybdenum. This work is part of our general goal to extend the chemistry of cycloheptatrienyl complexes and to raise their level of significance in comparison with those of cyclopentadienyl and benzene complexes.

Experimental Section

General: All operations were performed under an atmosphere of dry argon by Schlenk and vacuum techniques. Solvents were dried by standard methods and distilled prior to use.

Dimethylanilinium tetrafluoroborate was prepared by published procedures.[33] Full details of the preparation of **1** and **2**, together with the spectroscopic and structural properties of all reaction intermediates, will be presented elsewhere.[13] Elemental analyses (C, H N) were performed on a Heraeus CHNS-Rapid elemental analyzer. EI and ESI mass spectra were recorded on a Varian MAT 212 or on a Micromass Quattro LCZ mass spectrometer, respectively. ^{1}H and ^{13}C NMR spectra were measured on Bruker AC 200, Bruker AMX 400, or Varian U 600 spectrometers with the solvent as internal standard, whereas ^{31}P NMR measurements were run on a Bruker AC 200 spectrometer with aqueous H_3PO_4 (85%) as an external reference. IR spectra were recorded on a Bruker Vector 22 instrument. The assignment of all ^{1}H and ^{13}C NMR resonances was supported by two-dimensional NMR spectroscopy (COSY and NOE experiments). For the atomic numbering schemes used in the Exp. Sect., see Figure 2.

[(*o*-*i*Pr$_2$PC$_6$H$_4$-η^7-C$_7$H$_6$)Mo(η^2-BH$_4$)(*Mo*−*P*)] (3): A solution of **2** (500 mg, 0.93 mmol) in ethanol was treated at 0 °C with $NaBH_4$ (250 mg, 6.52 mmol) and stirred for 3 h at ambient temperature. The solvent was removed in vacuo, and the residue was extracted with diethyl ether/hexane (1:1). After evaporation of the solvent, **3** could be isolated as a light green compound. Purification by recrystallization from diethyl ether/hexane was possible, affording green crystals of **3**. Yield: 342 mg (91%). ^{1}H NMR ([D$_8$]toluene, 600 MHz): δ = 7.56 (dm, 1 H, C_6H_4), 7.31 (tm, 1 H, C_6H_4), 7.19 (m, 2 H, C_6H_4), 5.48 (m, 2 H, C_7H_6), 4.49 (m, 4 H, C_7H_6), 1.86 (sept, 1 H, *i*Pr: CH), 1.84 (sept, 1 H, *i*Pr: CH), 0.72 (dd, 6 H, *i*Pr: CH_3), 0.64 (dd, 6 H, *i*Pr: CH_3), −5.72 (br. s, 4 H, BH_4) ppm. ^{13}C NMR ([D$_8$]toluene, 150.9 MHz): δ = 155.2 (d, $^2J_{C,P}$ = 24.8 Hz, C-8), 138.7 (d, $^1J_{C,P}$ = 33.8 Hz, C-9), 130.2 (br. s, C_6H_4), 129.6 (br. s, C_6H_4), 114.2 (d, $^3J_{C,P}$ = 2.6 Hz, C-1), 90.3 (d, $^2J_{C,P}$ = 5.4 Hz, C_7H_6), 85.8 (d, $^2J_{C,P}$ = 2.0 Hz, C_7H_6), 76.6 (s, C_7H_6), 25.0 (d, $^1J_{C,P}$ = 17.2 Hz, *i*Pr: CH), 19.1 (d, $^2J_{C,P}$ = 7.0 Hz, *i*Pr: CH_3), 19.0 (d, $^2J_{C,P}$ = 1.5 Hz, *i*Pr: CH_3) ppm. ^{31}P NMR ([D$_8$]toluene, 81 MHz): δ = 68.0 ppm. MS (EI): *m*/*z* (%) = 394 (100) [M]$^+$, 379 (80) [M$^+$ − BH_4]. $C_{19}H_{28}BMoP$ (394.1): calcd. C 57.90, H 7.16; found C 57.65, H 6.77.

[(*o*-*i*Pr$_2$PC$_6$H$_4$-η^7-C$_7$H$_6$)Mo(PPh$_3$)H(*Mo*−*P*)] (4): A solution of **2** (1.184 g, 2.20 mmol) and PPh_3 (576 mg, 2.20 mmol) in THF was treated with NaH (421 mg, 17.54 mmol) and stirred for 12 h. The reaction mixture was filtered, and the solvent was removed by evaporation. The crude product was recrystallized from hexane to afford **4** as a brown crystalline solid. Yield: 848 mg (60%). ^{1}H NMR ([D$_8$]toluene, 600 MHz): δ = 7.74 (t, 3 H, PPh_3), 7.52 (dm, 1 H, C_6H_4), 7.32 (m, 6 H, PPh_3), 7.16 (m, 1 H, C_6H_4), 7.05 (m, 1 H, C_6H_4), 7.04 (m, 6 H, PPh_3), 6.98 (t, 1 H, C_6H_4), 5.57 (m, 1 H, C_7H_6), 5.29 (m, 1 H, C_7H_6), 4.78 (t, 1 H, C_7H_6), 4.52 (q, 1 H, C_7H_6), 4.18 (d, 1 H, C_7H_6), 3.86 (q, 1 H, C_7H_6), 2.10 (m, 1 H, *i*Pr: CH), 1.09 (d sept, 1 H, *i*Pr: CH), 0.86 (m, 6 H, *i*Pr: CH_3), 0.81 (dd, 3 H, *i*Pr: CH_3), 0.68 (dd, 3 H, *i*Pr: CH_3), −2.82 (dd, 1 H, MoH) ppm. ^{13}C NMR ([D$_8$]toluene, 150.9 MHz): δ = 154.0 (d, $^2J_{C,P}$ = 25.8 Hz, C-8), 141.4 (d, $^1J_{C,P}$ = 28.7 Hz, *ipso*-C_6H_5), 140.5 (d, $^1J_{C,P}$ = 28.3 Hz, C-9), 134.2 (d, $^3J_{C,P}$ = 11.0 Hz, *o*-PPh_3), 134.0 (d, $^2J_{C,P}$ = 19.9 Hz, *m*-PPh_3), 129.1 (m, C-10), 128.3 (d, $^3J_{C,P}$ = 1.9 Hz, C-11), 127.2 (d, $J_{C,P}$ = 8.5 Hz, *p*-PPh_3), 126.9 (d, $^3J_{C,P}$ = 7.7 Hz, C-13), 126.7 (d, $J_{C,P}$ = 4.1 Hz, C-12), 105.4 (t, $^2J_{C,P}$ = 2.0 Hz, C-1), 88.3 (d, $^2J_{C,P}$ = 1.5 Hz, C-7), 87.9 (d, $^2J_{C,P}$ = 3.1 Hz, C-5), 87.9 (s, C-6), 85.9 (d, $^2J_{C,P}$ = 5.1 Hz, C-4), 84.6 (dd, $^2J_{C,P}$ = 8.3 Hz, C-2), 80.6 (s, C-3), 26.5 (d, $^1J_{C,P}$ = 21.4 Hz, *i*Pr: CH), 25.7 (dd, $^1J_{C,P}$ = 14.4 Hz, *i*Pr: CH), 19.9 (d, $^2J_{C,P}$ = 27.2 Hz, *i*Pr: CH_3), 18.9 (d, $^2J_{C,P}$ = 3.7 Hz, *i*Pr: CH_3), 18.7 (d, $^2J_{C,P}$ = 6.3 Hz, *i*Pr: CH_3), 17.4 (d, $^2J_{C,P}$ = 3.7 Hz, *i*Pr: CH_3) ppm. ^{31}P NMR ([D$_8$]toluene, 81 MHz): δ = 74.5 (d, $^2J_{P,P}$ = 31.0 Hz, P*i*Pr$_2$), 53.7 (d, $^2J_{P,P}$ = 31.0 Hz, PPh_3) ppm. MS (EI): *m*/*z* (%) = 642 (100) [M]$^+$. $C_{19}H_{28}BMoP$ (642.7): calcd. C 69.14, H 6.27; found C 70.45, H 6.51.

[(*o*-*i*Pr$_2$PC$_6$H$_4$-η^7-C$_7$H$_6$)Mo(XyNC)$_2$(*Mo*−*P*)]BPh$_4$ (5)BPh$_4$: A solution of **3** (250 mg, 0.63 mmol) in THF (50 mL) was treated at room temperature with [HNMe$_2$Ph][BPh_4] (355 mg, 0.76 mmol). After addition of an excess of 2,6-dimethylphenyl isocyanide, the reaction mixture was subsequently stirred at ambient temperature for 12 h. After evaporation of the solvent, the residue was extracted with a small amount of dichloromethane and added dropwise to rapidly stirred diethyl ether. Purification by recrystallization from dichloromethane/diethyl ether at 0 °C was possible, affording air-stable, brown crystals. Yield: 472 mg (78%). ^{1}H NMR (CD_2Cl_2, 600 MHz): δ = 7.81 (dm, 1 H, C_6H_4), 7.68 (tm, 1 H, C_6H_4), 7.64 (m, 2 H, C_6H_4), 7.41 (br. m, 8 H, *o*-BPh_4), 7.28 (t, 2 H, *p*-$C_6H_3Me_2$), 7.22 (d, 4 H, *m*-$C_6H_3Me_2$), 7.08 (t, 8 H, *m*-BPh_4), 6.93 (t, 4 H, *p*-BPh_4), 5.50 (m, 4 H, C_7H_6), 5.04 (dd, 2 H, C_7H_6), 2.55 (m, 2 H, *i*Pr: CH), 2.44 (s, 12 H, *o*-CH_3), 1.21 (dd, 6 H, *i*Pr: CH_3), 1.11 (dd, 6 H, *i*Pr: CH_3) ppm. ^{13}C NMR (CD_2Cl_2, 150.9 MHz): δ = 177.8 (d, $^2J_{C,P}$ = 16.6 Hz, CNR), 164.4 (q, $^1J_{C,B}$ = 49.4 Hz, *ipso*-BPh_4), 150.2 (d, $^2J_{C,P}$ = 25.9 Hz, C-8), 137.8 (d, $^1J_{C,P}$ = 35.9 Hz, C-9), 136.3 (s, *o*-BPh_4), 134.8 (s, *o*-$C_6H_3Me_2$), 131.6 (d, $J_{C,P}$ = 2.6 Hz, C_6H_4), 130.7 (s, C_6H_4), 129.5 (s, *p*-$C_6H_3Me_2$), 129.4 (d, $J_{C,P}$ = 5.1 Hz, C_6H_4), 128.7 (s, *m*-$C_6H_3Me_2$), 127.5 (d, $J_{C,P}$ = 9.3 Hz, C_6H_4), 127.3 (s, *ipso*-$C_6H_3Me_2$), 125.9 (q, $^3J_{C,B}$ = 2.6 Hz, *m*-BPh_4), 122.0 (s, *p*-BPh_4), 118.0 (d, $^3J_{C,P}$ = 2.5 Hz, C-1), 92.9 (s, C_7H_6), 91.1 (d, $^2J_{C,P}$ = 3.9 Hz, C_7H_6), 91.0 (s, C_7H_6), 26.2 (d, $^1J_{C,P}$ = 21.1 Hz, *i*Pr: CH), 19.2 (s, $C_6H_3\mathit{Me}_2$), 18.6 (d, $^2J_{C,P}$ = 5.1 Hz, *i*Pr: CH_3), 18.1 (s, *i*Pr: CH_3) ppm. ^{31}P NMR (CD_2Cl_2, 81 MHz): δ = 75.7 ppm. MS (ESI): *m*/*z* (%) = 641 (100) [M − BPh_4]$^+$. IR (CH_2Cl_2): ṽ = 2099 ν(CN), 2067 ν(CN) cm^{-1}. $C_{61}H_{62}BMoN_2P$ (960.9): calcd. C 76.25, H 6.50, N 2.92; found C 75.59, H 6.02, N 2.37.

[(*o*-*i*Pr$_2$PC$_6$H$_4$-η^7-C$_7$H$_6$)Mo(η^4-NBD)(*Mo*−*P*)]BPh$_4$ (6)BPh$_4$: Compound (**6**)BPh_4 could be prepared in a manner similar to that described for (**5**)BPh_4, by treatment of a solution of **3** (157 mg, 0.40 mmol) in THF with [HNMe$_2$Ph][BPh_4] (175 mg, 0.40 mmol), followed by addition of norbornadiene (44 mg, 0.48 mmol). Yield: 258 mg (82%). ^{1}H NMR (CD_2Cl_2, 600 MHz): δ = 7.80 (d, 1 H, C_6H_4), 7.74 (dd, 1 H, C_6H_4), 7.45 (t, 1 H, C_6H_4), 7.40 (dm, 1 H, C_6H_4), 7.34 (br. m, 8 H, *o*-BPh_4), 7.03 (t, 8 H, *m*-BPh_4), 6.88 (t, 4 H, *p*-BPh_4), 5.66 (m, 2 H, C_7H_6), 5.22 (m, 2 H, C=CH), 4.93 (m, 2 H, C_7H_6), 4.85 (dd, 2 H, C_7H_6), 3.52 (m, 2 H, C=CH), 3.43 (br. s, 1 H, CH), 3.27 (br. s, 1 H; CH), 2.92 (m, 2 H, *i*Pr: CH), 1.29 (dd, 6 H, *i*Pr: CH_3), 1.23 (dd, 6 H, *i*Pr: CH_3), 1.02 (s, 2 H, CH_2) ppm. ^{13}C NMR (CD_2Cl_2, 150.9 MHz): δ = 164.9 (br. s, *ipso*-BPh_4),

136.3 (q, $^2J_{C,B}$ = 1.3 Hz, *o*-BPh_4), 135.0 (s, C_6H_4), 131.6 (d, $^2J_{C,P}$ = 2.0 Hz, C-8), 131.3 (s, C-1), 129.9 (s, C_6H_4), 129.4 (d, $^1J_{C,P}$ = 4.6 Hz, C-9), 128.2 (s, C_6H_4), 126.9 (d, $J_{C,P}$ = 9.1 Hz, C_6H_4), 126.0 (q, $^3J_{C,B}$ = 3.2 Hz, *m*-BPh_4), 122.1 (s, *p*-BPh_4), 93.4 (d, $^2J_{C,P}$ = 2.0 Hz, C_7H_6), 90.6 (d, $^2J_{C,P}$ = 1.3 Hz, C_7H_6), 88.3 (s, C_7H_6), 75.6 (s, NBD), 71.3 (s, NBD), 61.1 (s, NBD), 50.5 (d, $J_{C,P}$ = 2.5 Hz, NBD), 47.9 (s, NBD), 28.1 (d, $^1J_{C,P}$ = 18.2 Hz, *i*Pr: CH), 19.0 (d, $^2J_{C,P}$ = 4.2 Hz, *i*Pr: CH_3), 18.2 (s, *i*Pr: CH_3) ppm. ^{31}P NMR (CD_2Cl_2, 81 MHz): δ = 66.5 ppm. MS (ESI): *m*/*z* (%) = 471 (100) $[M - BPh_4]^+$. $C_{50}H_{52}BMoP$ (790.7): calcd. C 75.95, H 6.63; found C 76.30, H 6.24.

[(*o*-*i*Pr$_2$PC$_6$H$_4$-η^7-C$_7$H$_6$)Mo(η^2-HCCPh)(*Mo*−*P*)]BPh$_4$ (7)BPh$_4$: Compound (**7**)BPh_4 could be prepared in a manner similar to that described for (**5**)BPh_4, by treatment of a solution of **3** (397 mg, 1.01 mmol) in THF with $[HNMe_2Ph][BPh_4]$ (532 mg, 1.21 mmol), followed by the addition of phenylacetylene. Yield: 576 mg (72%). ^{1}H NMR (CD_2Cl_2, 600 MHz): δ = 10.41 (d, $^3J_{H,P}$ = 29.4 Hz, 1 H, C≡C), 7.77−7.45 (m, 9 H, C_6H_4 + BPh_4), 7.34 (br. m, 8 H, *o*-BPh_4), 7.01 (t, 8 H, *m*-BPh_4), 6.87 (t, 4 H, *p*-BPh_4), 5.74 (dd, 2 H, C_7H_6), 5.54 (dd, 2 H, C_7H_6), 5.30 (m, 2 H, C_7H_6, 2.83 (m, 2 H, *i*Pr: CH), 1.22 (dd, 6 H, *i*Pr: CH_3), 1.01 (dd, 6 H, *i*Pr: CH_3) ppm. ^{13}C NMR (CD_2Cl_2, 150.9 MHz): δ = 178.5 (d, $^2J_{C,P}$ = 28.4 Hz, ≡CH), 173.2 (d, $^2J_{C,P}$ = 4.5 Hz, ≡CPh), 164.4 (q, $^1J_{C,B}$ = 49.9 Hz, *ipso*-BPh_4), 149.8 (d, $^2J_{C,P}$ = 21.7 Hz, C-8), 136.3 (s, *o*-BPh_4), 132.4 (d, $^4J_{C,P}$ = 2.0 Hz, C-12), 131.7 (d, $^1J_{C,P}$ = 38.2 Hz, C-9), 131.2 (s, C-10), 130.6 (s, *p*-C_6H_5), 130.0 (d, $^3J_{C,P}$ = 5.1 Hz, C-11), 129.6 (s, *m*-C_6H_5), 129.5 (s, *o*-C_6H_5), 127.4 (d, $^3J_{C,P}$ = 8.1 Hz, C-13), 126.0 (q, $^3J_{C,B}$ = 2.6 Hz, *m*-BPh_4), 122.1 (s, *p*-BPh_4), 118.4 (d, $^2J_{C,P}$ = 2.6 Hz, C-1), 95.7 (d, $^2J_{C,P}$ = 2.6 Hz, C-4,5), 94.7 (d, $^2J_{C,P}$ = 2.4 Hz, C-2,7), 82.9 (s, C-3,6), 27.6 (d, 23.0 Hz, *i*Pr: CH), 19.8 (d, $^2J_{C,P}$ = 4.0 Hz, *i*Pr: CH_3), 19.0 (s, *i*Pr: CH_3) ppm. ^{31}P NMR (CD_2Cl_2, 81 MHz): δ = 72.4 ppm. MS (ESI): *m*/*z* (%) = 481 (100) $[M - BPh_4]^+$. $C_{51}H_{50}BMoP$ (800.7): calcd. C 76.50, H 6.29; found C 75.50, H 5.93.

[(*o*-*i*Pr$_2$PC$_6$H$_4$-η^7-C$_7$H$_6$)Mo(η^2-HCC-*t*Bu)(*Mo*−*P*)]BPh$_4$ (8)BPh$_4$: Compound (**8**)BPh_4 could be prepared in a manner similar to that described for (**5**)BPh_4, by treatment of a solution of **3** (235 mg, 0.60 mmol) in THF with $[HNMe_2Ph][BPh_4]$ (315 mg, 0.72 mmol), followed by the addition of *tert*-butylacetylene. Yield: 400 mg (86%). ^{1}H NMR (CD_2Cl_2, 600 MHz): δ = 10.03 (d, $^3J_{H,P}$ = 33.0 Hz, 1 H, C≡CH), 7.70 (m, 1 H, C_6H_4), 7.65 (m, 2 H, C_6H_4), 7.59 (m, 1 H, C_6H_4), 7.33 (br. m, 8 H, *o*-BPh_4), 7.01 (t, 8 H, *m*-BPh_4), 6.88 (t, 4 H, *p*-BPh_4), 6.08 (dd, 2 H, C_7H_6), 5.49 (dd, 2 H, C_7H_6), 5.32 (m, 2 H, C_7H_6), 2.75 (m, 2 H, *i*Pr: CH), 1.44 (s, 9 H, *t*Bu), 1.16 (dd, 6 H, *i*Pr: CH_3), 0.94 (dd, 6 H, *i*Pr: CH_3) ppm. ^{13}C NMR (CD_2Cl_2, 150.9 MHz): δ = 191.2 (s, ≡C*t*Bu), 177.8 (d, $^2J_{C,P}$ = 30.1 Hz, ≡CH), 164.3 (q, $^1J_{C,B}$ = 50.5 Hz, *ipso*-BPh_4), 149.7 (d, $^2J_{C,P}$ = 22.4 Hz, C-8), 136.3 (s, *o*-BPh_4), 132.2 (d, $^4J_{C,P}$ = 1.9 Hz, C-12), 131.8 (d, $^1J_{C,P}$ = 39.0 Hz, C-9), 131.1 (s, C-10), 129.9 (d, $^3J_{C,P}$ = 5.3 Hz, C-11), 127.3 (d, $^3J_{C,P}$ = 7.9 Hz, C-13), 125.9 (q, $^3J_{C,B}$ = 2.6 Hz, *m*-BPh_4), 122.1 (s, *p*-BPh_4), 118.4 (d, $^2J_{C,P}$ = 2.5 Hz, C-1), 94.6 (d, $^2J_{C,P}$ = 2.5 Hz, C-4,5), 94.2 (d, $^2J_{C,P}$ = 1.9 Hz, C-2,7), 81.6 (s, C-3,6), 31.6 (s, *t*Bu), 27.4 (d, 23.6 Hz, *i*Pr: CH), 19.7 (d, $^2J_{C,P}$ = 3.9 Hz, *i*Pr: CH_3), 18.9 (s, *i*Pr: CH_3) ppm. ^{31}P NMR (CD_2Cl_2, 81 MHz): δ = 72.9 ppm. $C_{49}H_{54}BMoP$ (780.7): calcd. C 75.38, H 6.97; found C 75.63, H 6.48.

[(*o*-Ph$_2$PC$_6$H$_4$-η^7-C$_7$H$_6$)Mo(η^2-BH$_4$)(*Mo*−*P*)] (9): A solution of [(*o*-$Ph_2PC_6H_4$-η^7-C_7H_6)$MoBr_2$(*Mo*−*P*)] (500 mg, 0.72 mmol) in ethanol was treated at 0 °C with $NaBH_4$ (250 mg, 6.52 mmol) and stirred for 1 h at ambient temperature. The solvent was removed by evaporation, and the residue was extracted with diethyl ether/hexane (1:1). After evaporation of the solvent, **9** was isolated as a light green compound. Purification by recrystallization from diethyl ether/hexane was possible, affording green crystals of **9**. Yield: 165 mg (36%). ^{1}H NMR ([D$_6$]benzene, 200 MHz): δ = 7.34 (m, 1 H, C_6H_4), 7.12−7.00 (m, 2 H, C_6H_4), 6.86−6.72 (m, 6 H, C_6H_4 + C_6H_5), 6.65 (m, 5 H, C_6H_4+C_6H_5), 5.12 (dd, 2 H, C_7H_6), 4.40 (dd, 2 H, C_7H_6), 4.18 (tm, 2 H, C_7H_6), −5.56 (br. s, 4 H, BH_4) ppm. ^{31}P NMR ([D$_6$]benzene, 81 MHz): δ = 52.6 ppm.

[(*o*-Ph$_2$PC$_6$H$_4$-η^7-C$_7$H$_6$)Mo(η^2-HCCPh)(*Mo*−*P*)]BPh$_4$ (10)BPh$_4$: Compound (**10**)BPh_4 could be prepared in a manner similar to that described for (**5**)BPh_4, by treatment of a solution of **9** (165 mg, 0.36 mmol) in THF with $[HNMe_2Ph][BPh_4]$ (188 mg, 0.43 mmol), followed by the addition of large excess of phenylacetylene. Yield: 186 mg (60%). ^{1}H NMR (CD_2Cl_2, 200 MHz): δ = 10.08 (d, $^3J_{H,P}$ = 34.2 Hz, 1 H, C≡CH), 7.86−7.41 (br. m, 14 H, C_6H_4 + PC_6H_5), 7.31 (br. m, 8 H, *o*-BPh_4), 6.98 (br. t, 8 H, *m*-BPh_4), 6.83 (br. t, 4 H, *p*-BPh_4), 5.86 (m, 2 H, C_7H_6), 5.60 (m, 2 H, C_7H_6), 5.25 (m, 2 H, C_7H_6) ppm.^{31}P NMR ([D$_6$]benzene, 81 MHz): δ = 95.1 ppm.

Catalytic Study: A solution of phenylacetylene (0.2 mL, 3.03 mmol) in THF (10 mL) was treated with (**7**)BPh_4 (128 mg, 0.16 mmol, 5 mol %), and the reaction mixture was stirred at 80 °C for 12 h. The solvent was evaporated, and the residue was transferred to a chromatography column (SiO_2, 4% H_2O). Elution with hexane afforded a yellow oil (245 mg, 65%). GC/MS studies revealed that the mixture contained a linear dimer (12%, *m*/*z* = 204, presumably one regioisomer of diphenyl-1,3-butenyne), 1,3,5-triphenylbenzene (52%, *m*/*z* = 306), a linear trimer (8%, *m*/*z* = 306, presumably one regioisomer of triphenylhex-1-yne-3,5-diene) and 1,2,4-triphenylbenzene (28%, *m*/*z* = 306). Crystals of 1,3,5-triphenylbenzene were isolated from the mixture and characterized by X-ray diffraction analysis.[30] Subjection of these crystals to a GC/MS study confirmed the formation of 1,3,5-triphenylbenzene as the main product.

X-ray Crystallography:[34] Data sets were collected at −75 °C [for **4** and (**5**)BPh_4] with an Enraf−Nonius KappaCCD or at −120 °C [for **3**, (**6**)BPh_4, (**7**)BPh_4, and (**10**)BPh_4] with a Bruker AXS APEX diffractometer, both equipped with a rotating anode and both using Mo-K_α radiation (λ = 0.71073 Å). Empirical absorption correction with SORTAV[35] [for **4** and (**5**)BPh_4] or SADABS[36] [for **3**, (**6**)BPh_4, (**7**)BPh_4, and (**10**)BPh_4] was applied to the raw data. Structure solution in all cases with SHELXS[37] and refinement with SHELXL[38] with anisotropic thermal parameters for all atoms. Hydrogen atoms were added to the structure models on calculated positions and were refined as riding atoms [**4**, (**5**)BPh_4] or are unrefined (for (**10**)BPh_4). Hydrogen atoms for **3**, (**6**)BPh_4, and (**7**)BPh_4 were located in the difference Fourier map and were refined with isotropic thermal parameters. ORTEP[39] was used for all drawings. Additional crystallographic data are listed in Table 3.

Computational Details: All quantum chemical calculations were performed with the TURBOMOLE suite of programs.[40] The phenylacetylene complexes have been fully optimized at the density functional (DFT) level employing the BP86 functional[41] and Gaussian AO basis sets of valence-triple-ξ quality including polarization functions (TZVP, C:[5s3p1d], H:[3s1p], P:[5s4p1d]).[42] For the metals the quasi-relativistic pseudo potentials of the Stuttgart group with a 28 (Mo, Ru) and 60 (Os) electron core, respectively, are used.[43] The corresponding optimized AO basis sets (Mo, Ru: [5s3p3d1f], Os: [6s3p3d1f]) have been taken from the TURBOMOLE library.[44] The calculated dissociation energies have been obtained by freezing the metal fragment without the phenylacetylene ligand in the optimized geometry of the complex (vertical D_e). Comparative calculations have also been performed with the popular B3LYP hybrid functional.[45]

Table 3. Crystallographic data for **3**, **4**, (**5**)$BPh_4 \cdot C_5H_{12}$, (**6**)$BPh_4 \cdot CH_2Cl_2$, (**7**)BPh_4, and (**10**)$BPh_4 \cdot C_6H_{14}$

	3	**4**	(**5**)$BPh_4 \cdot C_5H_{12}$	(**6**)$BPh_4 \cdot CH_2Cl_2$	(**7**)BPh_4	(**10**)$BPh_4 \cdot 3C_4H_8O$
Empirical formula	$C_{19}H_{28}BMoP$	$C_{37}H_{40}MoP_2$	$C_{66}H_{74}BMoN_2P$	$C_{51}H_{54}BCl_2MoP$	$C_{51}H_{50}BMoP$	$C_{69}H_{70}BMoO_3P$
Formula mass, amu	394.13	642.57	1032.99	875.56	800.63	1084.97
a, Å	22.2257(11)	17.635(1)	21.534(1)	10.0047(8)	19.1772(10)	11.1097(5)
b, Å	22.2257(11)	8.681(1)	13.622(1)	14.6763(12)	19.0903(10)	21.2852(10)
c, Å	7.4034(5)	21.649(1)	21.592(1)	14.8010(12)	22.2170(12)	23.4095(11)
α, deg	90.0	90.00	90.0	82.037(2)	90.0	90.00
β, deg	90.0	107.65(1)	118.55(1)	84.542(2)	90.0	96.1750(10)
γ, deg	90.0	90.00	90.0	82.248(2)	90.0	90.00
V, Å^3	3657.1(4)	3158.2(4)	5563.5(5)	2126.2(3)	8133.6(7)	5503.6(4)
$d_{calcd.}$, g cm^{-1}	1.432	1.351	1.233	1.368	1.308	1.309
Crystal system	orthorhombic	monoclinic	monoclinic	triclinic	orthorhombic	monoclinic
Space group	I_{4bar}	$P21/c$	$P2_1/n$	$P\bar{1}$	Pbca	Cc
Z	8	4	4	2	8	4
μ, mm^{-1}	0.799	0.541	0.306	0.507	0.397	0.316
Unique data	11271	7965	9754	5549	5308	12468
observed data $\{I > 2\sigma(I)\}$	10309	6685	5162	4631	4130	11347
*R*1 (obsd. data),%	2.57, *wR*1 = 5.48	3.23, w*R*1 = 7.61	5.98, w*R*1 = 10.42	3.78, w*R*1 = 8.86	2.89, w*R*1 = 6.35	4.43, w*R*1 = 10.97
*R*2 (all data),%	2.88, *wR*2 = 5.53	4.35, *wR*2 = 8.11	14.48, *wR*2 = 12.86	5.00, *wR*2 = 9.48	4.61, *wR*2 = 7.09	4.96, *wR*2 = 11.24
GoF	0.949	1.037	0.990	1.033	1.013	1.045
No. of variables	311	369	650	713	687	650
Res. electron density, e/ Å^3	0.667 /−0.873	0.410 /−0.509	0.560 /−0.430	0.473 /−0.435	0.470/−0.204	1.462/−1.529

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[1] M. I. Bruce, *Chem. Rev.* **1998**, *98*, 2797−2858.
[2] B. M. Trost, F. D. Toste, A. B. Pinkerton, *Chem. Rev.* **2001**, *101*, 2067−2096.
[3] For selected publications, see: [3a] B. M. Trost, A. B. Pinkerton, F. D. Toste, M. Sperrle, *J. Am. Chem. Soc.* **2001**, *123*, 12504−12509. [3b] M. I. Bruce, B. C. Hall, B. W. Skelton, A. H. White, N. N. Zaitseva, *J. Chem. Soc., Dalton Trans.* **2000**, 2279−2286. [3c] E. Rüba, W. Simanko, K. Mauthner, K. M. Soldouzi, C. Slugovc, K. Mereiter, R. Schmid, K. Kirchner, *Organometallics* **1999**, *18*, 3843−3850. [3d] B. M. Tost, B. Vidal, M. Thommen, *Chem. Eur. J.* **1999**, 1055−1069. [3e] C. S. Yi, N. Liu, *Organometallics* **1998**, *17*, 3158−3160. [3f] C. S. Yi, N. Liu, *Organometallics* **1996**, *15*, 3968−3971. [3g] T. Braun, O. Gevert, H. Werner, *J. Am. Chem. Soc.* **1995**, *117*, 7291−7292.
[4] M. L. H. Green, D. K. P. Ng, *Chem. Rev.* **1995**, *95*, 439−473.
[5] [5a] C. E. Davies, I. M. Gardiner, J. C. Green, M. L. H. Green, N. J. Hazel, P. D. Grebenik, V. S. B. Mtetwa, K. Prout, *J. Chem. Soc., Dalton Trans.* **1985**, 669−683. [5b] J. S. Adams, C. Bitcon, J. R. Brown, D. Collison, M. Cunningham, M. W. Whiteley, *J. Chem. Soc., Dalton Trans.* **1987**, 3049−3053. [5c] C. Bitcon, R. Breeze, P. F. Miller, M. W. Whiteley, *J. Organomet. Chem.* **1989**, *364*, 181−193. [5d] R. L. Beddoes, R. W. Grime, Z. I. Hussain, M. W. Whiteley, *J. Chem. Soc., Dalton Trans.* **1996**, 3893−3895.
[6] [6a] J. Okuda, T. Eberle in *Metallocenes* (Eds.: A. Togni, R. L. Halterman), Wiley-VCH, Weinheim, **1998**, Vol. 1, p. 415. [6b] J. Okuda, *Comment, Inorg. Chem.* **1994**, *16*, 185.
[7] P. Jutzi, T. Redeker, *Eur. J. Inorg. Chem.* **1998**, 663−674.
[8] U. Siemeling, *Chem. Rev.* **2000**, *100*, 1495−1526.
[9] H. Butenschön, *Chem. Rev.* **2000**, *100*, 1527−1564.
[10] M. Tamm, T. Bannenberg, B. Dreßel, R. Fröhlich, C. Holst, *Inorg. Chem.* **2002**, *41*, 47−59.
[11] M. Tamm, K. Baum, T. Lügger, R. Fröhlich, K. Bergander, *Eur. J. Inorg. Chem.* **2002**, 918−928.
[12] M. Tamm, B. Dreßel, V. Urban, T. Lügger, *Inorg. Chem. Commun.* **2002**, *5*, 837−840.
[13] M. Tamm, B. Dreßel, K. Baum, T. Lügger, T. Pape, *J. Organomet. Chem.*, submitted.
[14] H. Suzuki, D. H. Lee, N. Oshima, Y. Moro-oka, *Organometallics* **1987**, *6*, 1569−1575.
[15] S. L. J. Conway, L. H. Doerrer, M. L. H. Green, M. A. Leech, *Organometallics* **2000**, *19*, 630−637, and references cited therein.
[16] M. Elian, M. M. L: Chen, D. M. P. Mingos, R. Hoffmann, *Inorg. Chem.* **1976**, *15*, 1148−1155.
[17] [17a] H. Brunner, *Eur. J. Inorg. Chem.* **2001**, 905−912. [17b] H. Brunner, *Angew. Chem.* **1999**, *111*, 1248−1263; *Angew. Chem. Int. Ed.* **1999**, *38*, 1194−1209.
[18] H. Brunner, M. Muschiol, I. Bernal, G. M. Reisner, *J. Organomet. Chem.* **1980**, *198*, 169−178.
[19] For a related chiral ruthenium complex of the type [(η-C_5Me_5)Ru(PPh_3)(PR_3)H] (R = OMe), see: T. Arliguie, B. chaudret, F. A. Jalon, A. Otero, J. A. Lopez, F. J. Lahoz, *Organometallics* **1991**, *10*, 1888−1896.
[20] M. L. H. Green, R. B. A. Pardy, *Polyhedron* **1985**, *4*, 1035−1041.
[21] E. Schwed, H.-U. Hund, H. W. Bosch, H. Berke, *Helv. Chim. Acta* **1991**, *74*, 189−196.
[22] *Comprehensive Organometallic Chemistry II* (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson), vol. 7 (Vol. Eds. D. F. Shriver, M. I. Bruce), Chapman and Hall, Oxford, **1995**.
[23] G. J. P. Britovsek, V. C. Gibson, D. F. Wass, *Angew. Chem.* **1999**, *111*, 448−468; *Angew. Chem. Int. Ed.* **1999**, *38*, 428−447.
[24] J. Chatt, C. M. Elson, A. J. L. Pombeiro, R. L. Richards, G. H. D. Royston, *J. Chem. Soc., Dalton Trans.* **1978**, 165−169.
[25] H. Seino, C. Arita, D. Nonokawa, G. Nakamura, Y. Harada, Y. Mizobe, M. Hidai, *Organometallics* **1999**, *18*, 4165−4173.
[26] R. Usón, L. A. Oro, M. A. Ciriano, M. M. Naval, M. C. Apreda, C. Foces-Foces, F. H. Cano, S. Garcia-Blanco, *J. Organomet. Chem.* **1983**, *256*, 331−347.
[27] J. L. Templeton, *Adv. Organomet. Chem.* **1989**, *29*, 1−100.
[28] J. J. Carbó, P. Crochet, M. A. Esteruelas, Y. Jean, Agustí

Lledós, A. M. López, E. Oñate, *Organometallics* **2002**, *21*, 305−314.
[29] [29a] W. E. Douglas, *J. Chem. Soc., Dalton Trans.* **2000**, 57−62. [29b] M. G. L. Petrucci, A. K. Kakkar, *J. Chem. Soc., Chem. Commun.* **1995**, 1577−1578. [29c] H.-F. Klein, M. Mager, S. Isringhausen-Bley, U. Flörke, H.-J. Haupt, *Organometallics* **1992**, *11*, 3174−3175.
[30] Crystal data for 1,3,5-triphenylbenzene: a = 7.4779(3), b = 19.7314(9), c = 11.2217(5) Å, Z = 4, orthorhombic, space group $Pna2_1$, final R = 3.79% based on 2137 observed structure factors [$I \geq 2\ \sigma(I)$].
[31] L. S. Meriwether, M. F. Leto, E. C. Colthup, G. W. Kennerly, *J. Org. Chem.* **1962**, *27*, 3930−3941.
[32] G. Frenking, N. Fröhlich, *Chem. Rev.* **2000**, *100*, 717−774.
[33] M. Haufe, R. D. Köhn, R. Weimann, G. Seifert, D. Zeigan, *J. Org. Chem.* **1996**, *520*, 121−129.
[34] CCDC-CCDC-183826, -183827, -183828, -183829, -192130, and -192131 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].
[35] SORTAV, R. H. Blessing, *J. Appl. Crystallogr.* **1997**, *30*, 421−426.
[36] SMART, Bruker AXS, **2000**.
[37] SHELXS-97, G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467−473.
[38] SHELXL-97, G. M. Sheldrick, Universität Göttingen, **1997**.
[39] ORTEP-3, L. J. Farrugia, University of Glasgow, **1999**.
[40] R. Ahlrichs, M. Bär, H.-P. Baron, R. Bauernschmitt, S. Böcker, M. Ehrig, K. Eichkorn, S. Elliott, F. Furche, F. Haase, M. Häser, H. Horn, C. Huber, U. Huniar, M. Kattannek, C. Kölmel, M. Kollwitz, K. May, C. Ochsenfeld, H. Öhm, A. Schäfer, U. Schneider, O. Treutler, M. von Arnim, F. Weigend, P. Weis, H. Weiss, TURBOMOLE (vers. 5.3), Universität Karlsruhe, **2000**.
[41] [41a] A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098−3100. [41b] J. P. Perdew, *Phys. Rev. B* **1986**, *33*, 8822−8824.
[42] A. Schäfer, C. Huber, R. Ahlrichs, *J. Chem. Phys.* **1994**, *100*, 5829−5835.
[43] D. Andrae, U. Häussermann, M. Dolg, H. Stoll, H. Preuss, *Theor. Chim. Acta* **1990**, *77*, 123−130.
[44] The AO basis sets used are available at (anonymous) ftp://ftp.chemie.uni-karlsruhe.de/pub/basen
[45] [45a] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648−5652. [45b] P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, *J. Phys. Chem.* **1994**, *98*, 11623−11627.

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