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Journal of Organometallic Chemistry 677 (2003) 1–9

Journal of Organometallic Chemistry

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# Synthesis and structural characterization of molybdenum complexes with linked cycloheptatrienyl–phosphane ligands

Matthias Tamm [a,*], Bernd Dreßel [a], Kim Baum [b], Thomas Lügger [b], Tania Pape [b]

[a] Anorganisch-Chemisches Institut, Lehrstuhl für Anorganische Chemie, Technische Universität München, Lichtenbergstrasse 4, D-85747 Garching, Germany

[b] Institut für Anorganische und Analytische Chemie, Westfälische Wilhelms-Universität, Wilhelm-Klemm-Str. 8, D-48149 Munster, Germany

Received 7 January 2003; received in revised form 11 March 2003; accepted 21 March 2003

## Abstract

The synthesis of *P*-functionalized cycloheptatrienyl chelate complexes incorporating the linked cycloheptatrienyl–phosphane ligand [2-(diisopropylphosphanyl)phenyl]cycloheptatrienyl, $o$-$^{i}Pr_2P–C_6H_4–C_7H_6$, is described. The ligand precursor [2-(cyclohepta-2,4,6-trienyl)phenyl]diisopropylphosphane (**2b**) can be obtained by addition of lithiated $2$-$BrC_6H_4P^{i}Pr_2$ (**1b**) to the tropylium cation $C_7H_7^+$. On reaction with $Mo(CO)_6$, the *P*-functionalized cycloheptatriene **2b** acts as an eight-electron ligand to afford the cycloheptatriene–phosphane chelate complex $[(o\text{-}^{i}Pr_2P–C_6H_4–\eta^6\text{-}C_7H_7)Mo(CO)_2(P–Mo)]$ (**3b**) as a single, chiral regioisomer, which undergoes clean hydride abstraction on treatment with $(Ph_3C)BF_4$. The resulting cationic complex **4b** reacts with sodium bromide to yield the 'chiral-at-metal' complex $[(o\text{-}^{i}Pr_2P–C_6H_4–\eta^7\text{-}C_7H_6)Mo(CO)Br(P–Mo)]$ (**5b**). This 18-electron complex can be oxidized with 0.5 equivalent $Br_2$ to give paramagnetic $[(o\text{-}^{i}Pr_2P–C_6H_4–\eta^7\text{-}C_7H_6)MoBr_2(P–Mo)]$ (**6b**). **6b** is a versatile starting material for the preparation of various cycloheptatrienyl–molybdenum complexes, which is exemplified by the isolation of the dialkyl complex $[(o\text{-}^{i}Pr_2P–C_6H_4–\eta^7\text{-}C_7H_6)Mo(CH_2SiMe_3)_2(P–Mo)]$ (**7b**) upon reaction of **6b** with $Me_3SiCH_2MgCl$. In addition, the X-ray crystal structures of **3b**, **4b**, **5b**, **6b**, and **7b** are reported.

*Keywords:* Cycloheptatrienyl complexes; Ligand functionalization; Molybdenum; Alkyl complexes

## 1. Introduction

η-Cyclopentadienyl complexes, $(\eta\text{-}C_5R_5)M$, as well as η-arene complexes, $(\eta\text{-}C_6R_6)M$, 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 [2]. 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 [3]. Numerous routes to ring-substituted Cp derivatives are known to date, and cyclopentadienyl complexes are nowadays ubiquitous and indispensable in research areas such as homogeneous catalysis [4], organic synthesis [5] and materials science [6]. In contrast, η-cycloheptatrienyl transition metal complexes, $(\eta\text{-}C_7R_7)M$, have been much less thoroughly studied, and with a few exceptions, the use of cycloheptatrienyl ligands had been confined to the parent $C_7H_7$ system [7]. Only recently, we have been able to report on the syntheses of the first complexes with the heptamethylcycloheptatrienyl (CHT*) ligand [8] and of complexes derived from sterically demanding cyclohep-

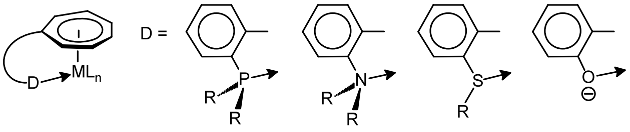

Fig. 1. Cycloheptatrienyl complexes bearing pendant *P*-, *N*-, *S*-, and *O*-donors.

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* Corresponding author. Tel.: +49-89-289-13080; fax: +49-89-289-13473.

*E-mail address:* matthias.tamm@ch.tum.de (M. Tamm).

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doi:10.1016/S0022-328X(03)00318-8

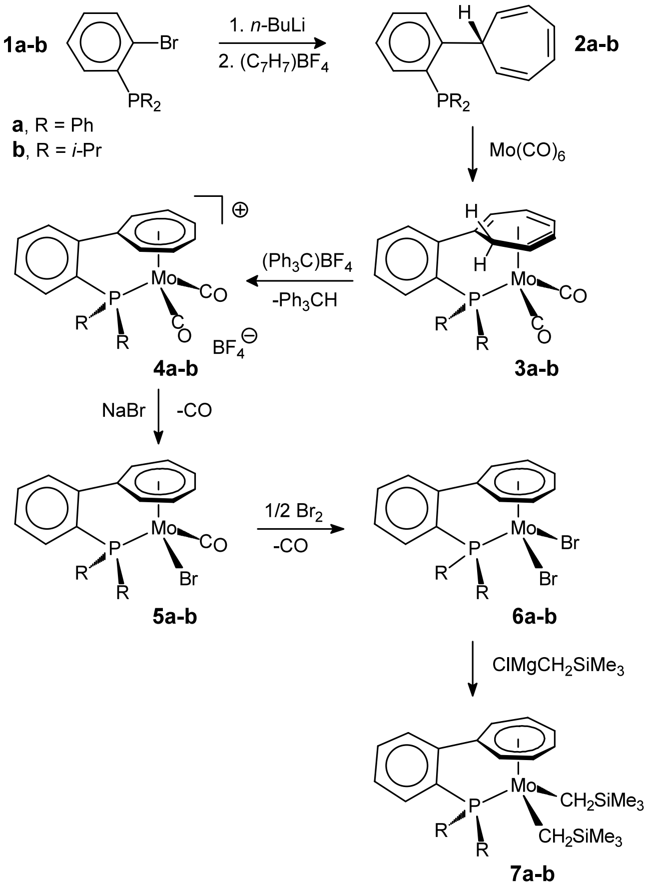
tatrienyl ligands of the type (1,3,5-$C_7H_4R_3$)$BF_4$ (R = $^t$Bu, $SiMe_3$) [9].

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*- [10,11], *O*- [12], *P*-, *As*-, and *S*-donor groups [13]. If properly designed, these ligands can coordinate to a transition metal center in a chelating $\eta^5$:$\eta^1$-fashion, and several of these complexes have played a key role in homogeneous catalysis as so-called constraint-geometry catalyst systems [4]. 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 [14], thioether, amine [15] and phosphane donor groups (Fig. 1) [16,17].

Molybdenum complexes with linked cycloheptatrienyl–phosphane ligands proved to be particularly useful for applications in transition metal catalysis, and we have reported on the syntheses and properties of 17- and 18-electron complexes containing *ortho*-phenylene bridged ligands of the type (2-$R_2PC_6H_4$–$C_7H_6$) (R = Ph, $^i$Pr), which are capable to bind to the metal center in a chelating $\eta^1$:$\eta^7$-fashion [16,17]. For R = Ph, we could demonstrate that the resulting paramagnetic 17-electron complexes of the type [(*o*-$Ph_2PC_6H_4$–$\eta^7$-$C_7H_6$)$MoX_2$(*P–Mo*)] (X = Br, $CH_2SiMe_3$) can be used in the ring-opening metathesis polymerization of norbornene [16]. In order to render the donor moiety more sterically demanding and electron-rich, we aimed towards the replacement of the phenyl substituents for isopropyl groups, and the resulting complexes containing the cationic 14-electron complex fragment [(*o*-$^i Pr_2PC_6H_4$–$\eta^7$-$C_7H_6$)Mo(*P–Mo*)]$^+$ were successfully employed in catalytic alkyne–alkyne coupling reactions [17]. With this contribution, we would like to supply a full account of the preparation and complexation of this new ligand system together with a detailed structural investigation of the resulting 18- and 17-electron molybdenum complexes, which had not been described in our previous publication in this field [17b].

## 2. Results and discussion

The preparation of the cycloheptatriene **2a** with a diphenylphosphanyl donor group has already been described [16]. In a similar manner, (2-bromophenyl)diisopropylphosphane **1b** was obtained in good yield by careful monolithiation of *ortho*-dibromobenzene and reaction with $ClP^iPr_2$. Subsequent treatment of **1b** with $^n$BuLi and addition of the resulting 2-(diisopropylphosphanyl)phenyllithium to the tropylium cation $C_7H_7^+$ [18] furnished **2b** in large quantities. As shown for **2a**, the cycloheptatriene–phosphane ligand **2b** can be used as a multi-dentate ligand, and the reaction of **2b** with $Mo(CO)_6$ in refluxing methylcyclohexane leads to the substitution of four carbonyl ligands and the formation of cycloheptatriene–phosphane complexes of the type [(*o*-$^i Pr_2PC_6H_4$–$\eta^6$-$C_7H_7$)$Mo(CO)_2$(*P–Mo*)]. In comparison to the reaction of cycloheptatriene, $C_7H_8$, with $Mo(CO)_6$, the reaction described here proceeds much faster, and no sublimation of hexacarbonyl 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 **3b** crystallizes as the only detectable regioisomer from the solution upon cooling with dry ice. The formation of **3b** resulted from thermal rearrangement of the coordinated cycloheptatriene ring involving in principle two consecutive 1,5-hydrogen shifts [19]. In its $^1$H-NMR spectrum **3b** exhibits five resonances due to the vinylic protons and two resonances due to the allylic *exo* and *endo* protons (Fig. 2). The $^{31}$P-NMR resonance is shifted from −7.7 ppm in uncoordinated **2b** to 84.5



Scheme 1.

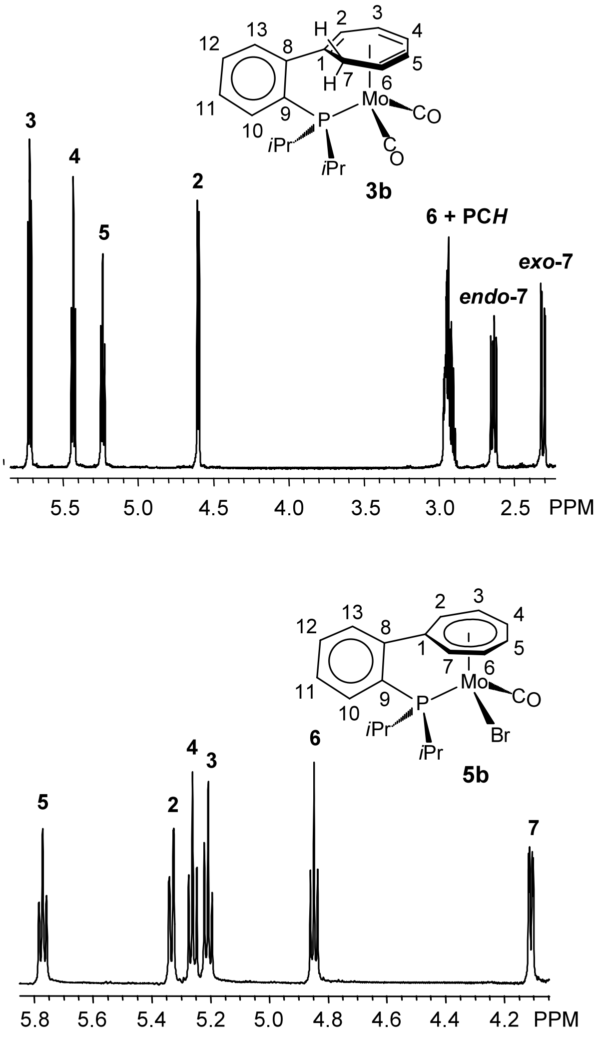


Fig. 2. Selected parts of the $^{1}$H-NMR spectra (600 MHz, $CD_2Cl_2$) of **3b** (top) and **5b** (bottom).

ppm revealing that the phosphorous atom is coordinated to the metal center. As **3b** is obtained as a racemic mixture of two enantiomers, four $CH_3$ and two CH resonances are observed for the diastereotopic isopropyl groups in the $^{13}$C-NMR spectrum. Accordingly, two doublets are found for the $^{13}$CO carbonyl resonances at 227.6 ($^{2}J_{C,P} = 10$ Hz) and 224.4 ppm ($^{2}J_{C,P} = 12$ Hz), which almost perfectly coincides with the resonances found for complex **3a** at 227.2 ($^{2}J_{C,P} = 10$ Hz) and 223.9 ppm ($^{2}J_{C,P} = 12$ Hz).

In order to confirm the spectroscopic results, the molecular structure of **3b** was established by X-ray diffraction analysis, and Fig. 3 (top) shows an ORTEP diagram of one enantiomer. The 2-(diisopropylphosphanyl)phenyl substituent is indeed attached to the vinylic carbon atom C1, which is next to the $CH_2$ (C7) group, and the cycloheptatriene–phosphane ligand is binding to the metal center in a chelating $\eta^6$:$\eta^1$-fashion. If compared to the molecular structures of **3a**, or related cycloheptatriene–molybdenum complexes, e.g. $[(\eta^6\text{-}C_7H_8)Mo(CO)_3]$ [20] and $[(\eta^6\text{-}C_7H_8)Mo(CRR')(CO)_2]$ (R = OEt, R′ = *o*-tolyl) [21], the bond lengths and angles within the seven-membered ring fall in the expected ranges (Table 1).

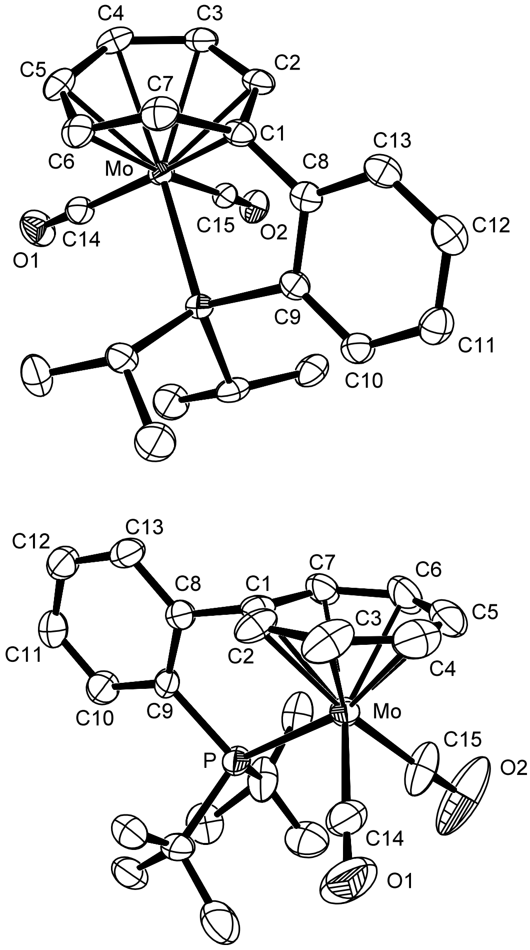


Fig. 3. ORTEP drawings of **3b** (top) and of the cation in **4b** (bottom) with thermal ellipsoids drawn at 50% probability.

In **3b** the *exo*-hydrogen atom is easily accessible to the trityl cation for hydride abstraction, and the cycloheptatrienyl–phosphane complex $[(o\text{-}^{i}Pr_2P\text{–}C_6H_4\text{–}\eta^7\text{-}C_7H_6)Mo(CO)_2(P\text{–}Mo)]BF_4$ (**4b**) is formed almost quantitatively upon treatment with $(Ph_3C)BF_4$ (Scheme 1). With removal of the hydrogen atom from the $CH_2$ group, **4b** becomes $C_s$ symmetric and exhibits only three cycloheptatrienyl resonances in its $^{1}$H-NMR spectrum at 5.90, 5.80 and 5.26 ppm in a 2:2:2 ratio. Accordingly, the $^{13}$C-NMR spectrum displays four resonances for the $C_7H_6$ carbon atoms. The $^{13}$CO resonance for the magnetically equivalent carbonyl groups is observed as a doublet at 216.2 ($^{2}J_{P,C} = 14$ Hz), and the $^{31}$P resonance at 81.8 ppm is only slightly shifted to lower field in comparison with **3b**. To confirm the formation of a cycloheptatrienyl–phosphane chelate complex, a single-crystal of **4b** was subjected to X-ray diffraction analysis. The molecular structure of the cation in **4b** is depicted in Fig. 3 (bottom). It reveals that the ligand does indeed act

Table 1
Selected bond distances (Å) and angles (°) for **3b**, **4b**, **5b**, **6b** and **7b**

| | 3b | 4b | 5b | 6b | 7b |
|---|---|---|---|---|---|
| C1–C2 | 1.392(3) | 1.404(6) | 1.429(3) | 1.421(4) | 1.416(3) |
| C2–C3 | 1.423(3) | 1.398(6) | 1.395(3) | 1.404(4) | 1.409(3) |
| C3–C4 | 1.417(3) | 1.400(7) | 1.423(3) | 1.419(4) | 1.415(3) |
| C4–C5 | 1.424(3) | 1.377(7) | 1.390(3) | 1.396(4) | 1.394(4) |
| C5–C6 | 1.382(3) | 1.407(6) | 1.420(3) | 1.407(4) | 1.403(3) |
| C6–C7 | 1.505(3) | 1.420(6) | 1.410(3) | 1.396(4) | 1.403(3) |
| C1–C7 | 1.523(3) | 1.394(5) | 1.413(3) | 1.425(4) | 1.430(3) |
| C1–C8 | 1.491(3) | 1.509(5) | 1.509(3) | 1.495(4) | 1.498(3) |
| Mo–C1 | 2.369(2) | 2.253(3) | 2.237(2) | 2.244(2) | 2.268(3) |
| Mo–C2 | 2.315(2) | 2.313(4) | 2.329(2) | 2.278(3) | 2.339(2) |
| Mo–C3 | 2.287(2) | 2.292(4) | 2.306(2) | 2.260(3) | 2.323(2) |
| Mo–C4 | 2.306(2) | 2.295(4) | 2.291(2) | 2.295(3) | 2.311(2) |
| Mo–C5 | 2.338(2) | 2.292(4) | 2.320(2) | 2.316(3) | 2.282(2) |
| Mo–C6 | 2.454(2) | 2.315(4) | 2.286(2) | 2.287(3) | 2.305(2) |
| Mo–C7 | | 2.314(4) | 2.280(2) | 2.282(3) | 2.337(2) |
| Mo–C14/C20 | 1.987(2) | 2.003(5) | 2.020(3) | | 2.236(2) |
| Mo–C15/C24 | 1.952(2) | 2.003(5) | | | 2.231(2) |
| Mo–P | 2.4618(5) | 2.4915(11) | 2.4861(5) | 2.5658(8) | 2.5753(7) |
| Mo–Br1 | | | 2.6465(3) | 2.5861(5) | |
| Mo–Br2 | | | | 2.5884(5) | |
| Mean/max deviation [a] | | 0.033/−0.061 (at C1) | 0.062/−0.059 (at C1) | 0.033/−0.024 (at C1) | 0.055/−0.043 (at C7) |
| P–Mo–C14/C20 | 99.45(6) | 91.74(16) | 89.36(6) | | 94.29(6) |
| P–Mo–C15/C24 | 91.63(6) | 90.08(13) | | | 82.75(6) |
| P–Mo–Br1 | | | 88.22(2) | 93.65(2) | |
| P–Mo–Br2 | | | | 86.11(2) | |
| (C1–C7)–(C8–C13) [b] | | 102.0 | 106.4 | 107.2 | 96.5 |

[a] Minimum and maximum deviation from the least-squares plane containing C1–C7.

[b] Interplanar angles.

as a chelate ligand in a $\eta^7$:$\eta^1$-fashion with a slightly distorted perpendicular orientation of the six- and seven-membered rings (interplanar angle of 78.0°). The molybdenum atom is symmetrically bound to the seven ring-carbon atoms with the shortest bond to C1 [2.253(3) Å] and the longest bond to C6 [2.315(4) Å] (Table 1). These distances fall in the range observed for the cation in **4a** (Mo–C1 = 2.262(3) Å; Mo–C6 = 2.323(4) Å). Additionally, no significant deviation from planarity can be observed for the seven-membered ring in **4b**, and the mean and maximum deviations from the least-squares plane (C1–C7) are 0.033 and −0.061 Å (for C1).

For the preparation of catalytically active cycloheptatrienyl–molybdenum complexes containing the $[(o\text{-}{}^i\text{Pr}_2\text{PC}_6\text{H}_4\text{–}\eta^7\text{-C}_7\text{H}_6)\text{Mo}(\mathit{P{-}Mo})]$ moiety [16,17], we sought for the removal of the two CO ligands in **4b**. As described for **4a**, this can be achieved stepwise by subsequent substitution and oxidation reactions. The first CO is easily substituted upon treatment of **4b** with an excess of NaBr in acetone at elevated temperature leading to the high-yield formation of $[(o\text{-}{}^i\text{Pr}_2\text{PC}_6\text{H}_4\text{–}\eta^7\text{-C}_7\text{H}_6)\text{Mo(CO)Br}(\mathit{Mo{-}P})]$ (**5b**). In **5b**, the pseudotetrahedrally coordinated molybdenum center has four different ligands, and the complex is thus obtained as a racemic mixture of two enantiomers. As this representative of so-called ‘chiral-at-metal’, half-sandwich compounds [22,23] is configurationally stable, the diastereotopic cycloheptatrienyl hydrogen atoms give rise to six different $^1$H-NMR resonances. This portion of the 600 MHz spectrum is shown in Fig. 2 (bottom). Accordingly, seven $^{13}$C-NMR resonances are observed for the $C_7H_6$ carbon atoms together with six resonances each for the phenylene-bridge as well as for the for the isopropyl groups. The assignment of all $^1$H- and $^{13}$C-NMR resonances in **5b** is supported by two-dimensional NMR spectroscopy (COSY and NOE experiments). The $^{13}$CO carbonyl resonance in **5b** is observed as a doublet at 237.0 ppm ($^2J_{C,P} = 17$ Hz), and one single $^{31}$P-NMR resonance is found at 65.5 ppm. As expected, the IR spectrum of **5b** exhibits one CO absorption at 1941 cm$^{-1}$, which is in good agreement with the stretching frequencies observed for **5a** at 1946 cm$^{-1}$ and for the closely related, unbridged analogue $[(\eta\text{-C}_7\text{H}_7)\text{Mo(CO)Br(PPh}_3)]$ at 1944 cm$^{-1}$ [24].

Removal of the remaining CO group in **5b** requires an oxidative decarbonylation, and the addition of 0.5 equivalent of bromine to a solution of **5b** in THF results in a rapid color change from green to red–brown and simultaneous gas evolution. After stirring for 1 h at ambient temperature, paramagnetic $[(o\text{-}{}^i\text{Pr}_2\text{P–C}_6\text{H}_4\text{–}\eta^7\text{-C}_7\text{H}_6)\text{MoBr}_2(\mathit{Mo{-}P})]$ (**6b**) can be isolated as an air-stable, microcrystalline brown solid after precipitation with hexane (Scheme 1). The formation of **6b** can be explained by oxidation of **5b** with (1/2) eq. $Br_2$ to give the labile odd-electron intermediate $[(o\text{-}^iPr_2P\text{–}C_6H_4\text{–}\eta^7\text{-}C_7H_6)Mo(CO)Br(\mathit{Mo-P})]Br$, which rapidly undergoes carbonyl substitution by bromide to afford the dibromo complex **6b** in high-yield. Due to the unpaired electron in **6b**, the compound was only characterized by mass spectrometry, and the purity was additionally checked by elemental analysis.

Single crystals of both **5b** and **6b** could be obtained by recrystallization from dichloromethane/hexane allowing to establish their molecular structures by X-ray crystal structure determinations (Fig. 4). The Mo–C(ring) distances (Table 1) in both complexes do not differ significantly and range from 2.2237(2) to 2.320(2) Å (mean 2.29 Å) in **5b** and from 2.244(2) to 2.316(3) Å (mean 2.28 Å) in **6b**. In contrast, the Mo–P bond length of 2.5658(8) Å in **6b** is significantly longer than that in **5b** [2.4861(5) Å], whereas the reverse trend is observed for the Mo–Br distances (Table 1). It should be noted that the positions of all hydrogen atoms could be refined for **5b** and **6b**. Therefore, it is possible to establish in each case the angles between the centroid of the cycloheptatrienyl ring, the $C_7$ carbon atoms and the adjacent hydrogen atoms revealing a significant out-of-plane displacement for the $C_7$ hydrogen atoms. The average bending is about 9–10° 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 [7,25].

We had previously shown that the dibromide **6a** forms mono- and dialkyl complexes on reaction with an etheral solution of $Me_3SiCH_2MgCl$ [16]. Similarly, treatment of **6b** with a large excess of the Grignard reagent furnished the dialkyl complex $[(o\text{-}^iPr_2P\text{–}C_6H_4\text{–}\eta^7\text{-}C_7H_6)Mo(CH_2SiMe_3)_2(\mathit{Mo-P})]$ (**7b**). Extraction with hexane, transfer of the mother liquor to a chromatography column ($SiO_2$) and elution with diethyl ether/petroleum ether (1:1) led to the collection of an orange fraction, from which air-stable **7b** could be isolated in quantitative yield. The purity of the paramagnetic complex was only checked by mass spectrometry and by elemental analysis. The molecular structure of **7b** could additionally be established by means of X-ray diffraction analysis, and Fig. 5 shows an ORTEP presentation of **7b**. The substitution of the two bromine atoms in **6b** 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 **7b**. Thus, the Mo–C distances range from 2.281(2) to 2.339(2) Å (mean 2.31 Å), and they are only slightly enlongated in comparison to those in **6b** [2.244(2)–2.316(3) Å (mean 2.280 Å)] (Table 1), and the Mo–P bond lengths of 2.5658(8) Å (**6b**) and 2.5753(7) Å (**7b**) are almost identical. The cycloheptatrienyl ring in **7b** remains 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 **7b** [2.231(2),

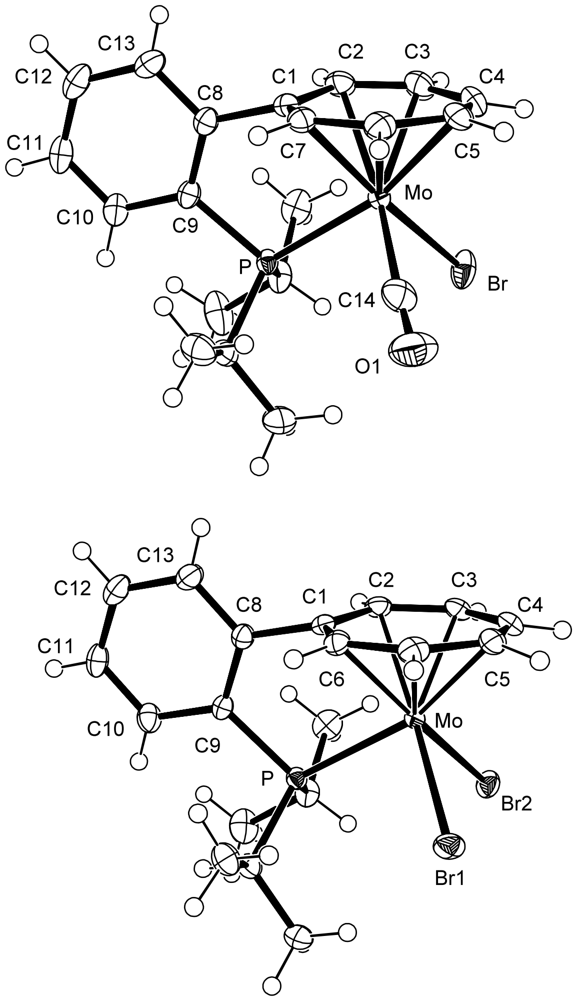


Fig. 4. ORTEP drawings of **5b** (top) and **6b** (bottom) with thermal ellipsoids drawn at 50% probability.

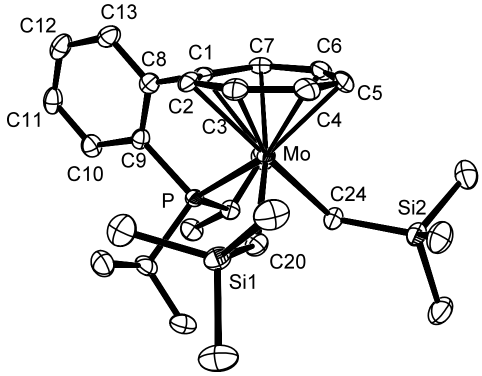


Fig. 5. ORTEP drawing of **7b** with thermal ellipsoids drawn at 50% probability.

2.236(2) Å] are rather large but still comparable to those found in other molybdenum alkyl complexes, which lie in the range 2.08–2.20 Å [26]. The bond angles Mo–C–Si of 124.34(12) and 130.52(11)° in **7b** are significantly larger than expected for sp$^3$-hybridized carbon atoms, although similar bond angles have also been found in molybdenum(VI) and tungsten(VI) neosilyl complexes [16,26].

## 3. Conclusion

With this contribution, we have presented a full account of the preparation of 18- and 17-electron molybdenum complexes containing a chelating [2-(diisopropylphosphanyl)phenyl]cycloheptatrienyl ligand together with a comparative structural investigation of complexes containing the [($o$-$R_2PC_6H_4$–$\eta^7$-$C_7H_6$)Mo($P$–$Mo$)] moieties (R = Ph, **3a**–**7a**; R = $^i$Pr, **3b**–**7b**). It can be concluded that rendering the phosphane donor group more sterically demanding and electron-rich by replacing the phenyl substituents for isopropyl groups does generally lead to an increased stability and solubility of the resulting complexes, which will be useful for further exploration and exploitation of the applicability of these systems in homogeneous transition metal catalysis. Both dibromides **6a** and **6b** have already proven to be versatile starting materials for the generation of catalytically active molybdenum complexes [16,17], which indicates that cycloheptatrienyl complexes can indeed be potentially useful for applications in homogeneous transition metal catalysis. 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 that of cyclopentadienyl and benzene complexes.

## 4. Experimental

All operations were performed in an atmosphere of dry argon by using Schlenk and vacuum techniques. Solvents were dried by standard methods and distilled prior to use. Tropylium tetrafluoroborate [27] and triphenylcarbenium tetrafluoroborate [28], were prepared according to published procedures. Elemental analyses (C, H, N) were performed on a Heraeus CHNO-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 using the solvent as internal standard, whereas $^{31}$P-NMR measurements were run on a Bruker AC 200 spectrometer using 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 has been supported by two-dimensional NMR spectroscopy (COSY and NOE experiments). For the atomic numbering schemes used in Section 4, see Figs. 2–5.

### *4.1. [2-(Cyclohepta-2,4,6-trienyl)phenyl]diisopropylphosphane (**2b**)*

A solution of **1b** (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 ($C_7H_7$)$BF_4$ (5.01 g, 28.16 mmol) was added at −78 °C, and the resulting reaction mixture was slowly warmed to room temperature (3 h). Extraction with hexane (100 ml) and evaporation of the solvent afforded **2b** as a colorless, viscous liquid. Yield: 5.12 g (64 %). $^1$H-NMR ($CDCl_3$, 200 MHz): $\delta$ 7.42 (m, 1H, $C_6H_4$), 7.32–7.16 (m, 2H, $C_6H_4$), 7.10 (td, 1H, $C_6H_4$), 6.57 (t, 2H, $C_7$ ring: CH), 6.07 (m, 2H, $C_7$ ring: CH), 5.13 (dd, 2H, $C_7$ ring: CH), 3.87 (m, 1H, $C_7$ ring: *tert*-CH), 1.88 (sep., 2H, $^i$Pr: CH), 0.86 (dd, 6H, $^i$Pr: $CH_3$), 0.71 (m, 6H, $^i$Pr: $CH_3$). $^{31}$P-NMR ($CDCl_3$, 81 MHz): $\delta$ −7.7. MS (EI): $m/z$ (%) 284 (78) [$M^+$], 269 (8) [$M-CH_3$]$^+$, 241 (56) [M−$^i$Pr]$^+$. Anal. Calc. for $C_{19}H_{25}P$ (284.38): C, 80.25; H, 8.86. Found: C, 80.23; H, 8.59%.

### *4.2. [($o$-$^i$$Pr_2P$–$C_6H_4$–$\eta^6$-$C_7H_7$)Mo(CO)$_2$($P$–$Mo$)] (**3b**)*

The phosphane **2b** (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 with stirring for 10 h. The solvent and unreacted Mo(CO)$_6$ were removed in vacuo, and the residue was recrystallized from dichloromethane/hexane at −78 °C. After 12 h, **3b** was isolated as a red, crystalline solid by filtration. Yield: 8.84 g (64 %) $^1$H-NMR ($CDCl_3$, 600 MHz): $\delta$ 7.48–7.45 (m, 1H, $C_6H_4$), 7.29 (m, 3H, $C_6H_4$), 5.73 (t, 1H, 3-H), 5.44 (t, 1H, 4-H), 5.24 (t, 1H, 5-H), 4.61 (d, 1H, 2-H), 2.98–2.90 (m, 2H, 6-H + $^i$Pr: CH), 2.65 (dd, 1H, 7-*endo*-$CH_2$), 2.32 (dd, 1H, 7-*exo*-$CH_2$), 2.18 (sep., 1H, $^i$Pr: CH), 1.42 (dd, 3H, $^i$Pr: $CH_3$), 1.38 (dd, 3H, $^i$Pr: $CH_3$), 1.25 (dd, 3H, $^i$Pr: $CH_3$), 0.99 (dd, 3H, $^i$Pr: $CH_3$). $^{13}$C-NMR ($CDCl_3$, 150.7 MHz): $\delta$ 227.6 (d, $^2J$(C,P) = 9.8 Hz, CO), 224.4 (d, $^2J$(C,P) = 12.2 Hz, CO), 152.7 (d, $^2J$(C,P) = 25.1 Hz, C-8), 149.7 (d, $^1J$(C,P) = 32.7 Hz, C-9), 131.4 (s, $C_6H_4$), 129.4 (d, $J$(C,P) = 2.2 Hz, $C_6H_4$), 127.1 (d, $J$(C,P) = 11.1 Hz, $C_6H_4$), 126.5 (d, $J$(C,P) = 5.2 Hz, $C_6H_4$), 103.7 (d, $^2J$(C,P) = 1.2 Hz, C-5), 97.3 (s, C-2), 88.0 (d, $^2J$(C,P) = 2.0 Hz, C-3), 85.8 (d, $^2J$(C,P) = 2.5 Hz, C-4), 85.1 (s, C-1), 44.9 (d, $^2J$(C,P) = 4.7 Hz, C-6), 36.1 (d, $^1J$(C,P) = 18.7 Hz, $^i$Pr: CH), 34.0 (d, $^2J$(C,P) = 1.3 Hz, C-7), 27.6 (d, $^1J$(C,P) = 22.6 Hz, $^i$Pr: CH), 21.4 (d, $^2J$(C,P) = 6.3 Hz, $^i$Pr: $CH_3$), 19.9 (d,

$^2J$(C,P) = 8.8 Hz, $^i$Pr: CH$_3$), 19.5 (d, $^2J$(C,P) = 2.5 Hz, $^i$Pr: CH$_3$), 19.4 (m, 2C, $^i$Pr: CH$_3$). $^{31}$P-NMR (CDCl$_3$, 81 MHz): $\delta$ 84.5. MS (EI): $m/z$ (%) = 436 (52) [M$^+$], 408 (8) [M−CO]$^+$, 380 (100) [M−2CO]$^+$. IR (CH$_2$Cl$_2$): $\tilde{\nu}$ (CO) 1908, 1826 cm$^{-1}$. Anal. Calc. for C$_{27}$H$_{21}$MoO$_2$P (436.22): C, 57.94; H, 5.56. Found: C, 57.32; H, 5.58%.

### 4.3. *[(o-$^i$Pr$_2$P–C$_6$H$_4$–$\eta^7$-C$_7$H$_6$)Mo(CO)$_2$(Mo–P)]BF$_4$* (**4b**)

A solution of **3b** (8.84 g, 17.53 mmol) in dichloromethane (200 ml) was treated with (Ph$_3$C)BF$_4$ (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 **4b**, which was isolated as an orange, crystalline solid by filtration, washing with diethyl ether and drying in vacuo. Yield: 8.34 g (90 %). $^1$H-NMR (CD$_3$CN, 400 MHz): $\delta$ 7.64 (dt, 1H, C$_6$H$_4$), 7.60–7.48 (m, 2H, C$_6$H$_4$), 7.57 (dd, 1H, C$_6$H$_4$), 5.90 (m, 2H, 3, 6-H), 5.80 (dd, 2H, 4,5-H), 5.26 (dd, 2H, 2,7-H), 2.47 (sep., 1H, $^i$Pr: CH), 2.45 (sep., 1H, $^i$Pr: CH), 0.96 (d, 3H, $^i$Pr: CH$_3$), 0.91 (dd, 6H, $^i$Pr: CH$_3$), 0.86 (d, 3H, $^i$Pr: CH$_3$). $^{13}$C-NMR (CD$_3$CN, 100.6 MHz): $\delta$ 216.2 (d, $^2J$(C,P) = 14.4 Hz, CO), 148.4 (d, $^2J$(C,P) = 20.9 Hz, C-8), 139.3 (d, $^1J$(C,P) = 37.3 Hz, C-9), 133.0 (d; $J$(C,P) = 2.5 Hz, C$_6$H$_4$), 132.2 (s, C$_6$H$_4$), 130.7 (d, $J$(C,P) = 5.5 Hz, C$_6$H$_4$), 128.6 (d, $^3J$(C,P) = 3.1 Hz, C-1), 127.8 (d, $J$(C,P) = 10.4 Hz, C$_6$H$_4$), 97.8 (s, C-2,7), 97.1 (s, C-3,6), 94.6 (d, $^2J$(C,P) = 4.0 Hz, C-4,5), 27.6 (d, $^1J$(C,P) = 24.3 Hz, $^i$Pr: CH), 18.4 (d, $^2J$(C,P) = 4.1 Hz, $^i$Pr: CH$_3$), 18.3 (s, $^i$Pr: CH$_3$). $^{31}$P-NMR (CD$_3$CN, 81 MHz): $\delta$ 81.8. MS (ESI): $m/z$ (%) = 435 (100) [M−BF$_4$]$^+$. IR (CH$_2$Cl$_2$) $\tilde{\nu}$ (CO) = 2024, 1983 cm$^{-1}$. Anal. Calc. for C$_{21}$H$_{24}$BF$_4$MoO$_2$P (522.13): C, 48.31; H, 4.63. Found: C, 48.07; H, 4.52%.

### 4.4. *[(o-$^i$Pr$_2$P–C$_6$H$_4$–$\eta^7$-C$_7$H$_6$)Mo(CO)Br(Mo–P)]* (**5b**)

A solution of **4b** (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 **5b** as a green, crystalline solid. Yield: 0.72 g (35 %). $^1$H-NMR (CD$_2$Cl$_2$, 600 MHz): $\delta$ 7.68 (dt, 1H, C$_6$H$_4$), 7.55 (t, 1H, C$_6$H$_4$), 7.53–7.47 (m, 2H, C$_6$H$_4$), 7.20 (dd, 2H, $o$-C$_6$H$_5$), 5.80 (t, 1H, H-5), 5.35 (d, 1H, H-2), 5.28 (t, 1H, H-4), 5.23 (t, 1H, H-3), 4.87 (t, 1H, H-6), 4.12 (d, 1H, H-7), 2.57 (sep., 1H, $^i$Pr: CH), 2.56 (sep., 1H, $^i$Pr: CH), 1.31 (dd, 3H, $^i$Pr: CH$_3$), 1.07 (dd, 3H, $^i$Pr: CH$_3$), 1.02 (dd, 3H, $^i$Pr: CH$_3$), 0.82 (dd, 3H, $^i$Pr: CH$_3$). $^{13}$C-NMR (CD$_2$Cl$_2$, 150.7 MHz): $\delta$ 237.0 (d, $^2J$(C,P) = 16.5 Hz, CO), 151.2 (d, $^2J$(C,P) = 25.0 Hz, C-8), 138.5 (d, $^1J$(C,P) = 34.4 Hz, C-9), 130.2 (d, $J$(C,P) = 2.3 Hz, C$_6$H$_4$), 130.0 (s, C-12), 128.2 (d, $J$(C,P) = 4.5 Hz, C$_6$H$_4$), 127.2 (d, $J$(C,P) = 8.3 Hz, C$_6$H$_4$), 109.2 (s, C-1), 100.9 (s, C-3), 95.9 (d, $^2J$(C,P) = 1.3 Hz, C-2), 95.5 (d, $^2J$(C,P) = 5.1 Hz, C-4), 94.4 (d, $^2J$(C,P) = 4.5 Hz, C-5), 87.5 (s, C-7), 79.1 (s, C-6), 24.6 (d, $^1J$(C,P) = 18.4 Hz, $^i$Pr: CH), 24.5 (d, $^1J$(C,P) = 14.1 Hz, $^i$Pr: CH), 19.1 ($^2J$(C,P) = 4.3 Hz, $^i$Pr: CH$_3$), 17.8 ($^2J$(C,P) = 3.3 Hz, $^i$Pr: CH$_3$), 17.0 ($^2J$(C,P) = 4.4 Hz, $^i$Pr: CH$_3$), 16.8 ($^2J$(C,P) = 5.2 Hz, $^i$Pr: CH$_3$). $^{31}$P-NMR (CD$_2$Cl$_2$, 81 MHz): $\delta$ 66.5. MS (EI): $m/z$ (%) = 459 (100) [M−CO]$^+$, 379 (8) [M−CO–Br]$^+$ 336 (10) [M−CO–Br–C$_3$H$_7$]$^+$. IR (CH$_2$Cl$_2$) $\tilde{\nu}$ (CO) = 1941 cm$^{-1}$. Anal. Calc. for C$_{20}$H$_{24}$BrMoOP (487.22): C, 49.30; H, 4.96. Found: C, 49.83; H, 4.95%.

### 4.5. *[(o-$^i$Pr$_2$P–C$_6$H$_4$–$\eta^7$-C$_7$H$_6$)MoBr$_2$(Mo–P)]* (**6b**)

A solution of **5b** (4.92 g, 8.86 mmol) in tetrahydrofurane (120 ml) was treated with a solution of bromine (0.24 ml, 4.68 mmol) in tetrahydrofurane (10 ml) at 0 °C, and the resulting mixture was subsequently stirred for 12 h at ambient temperature. The solution was reduced in volume to about 50 ml and added dropwise to rapidly stirred hexane to precipitate **6b**, which was isolated as a crystalline solid by filtration, washing with hexane and drying in vacuo. Purification was possible by recrystallization from dichloromethane to afford brown crystals of **6b**. Yield: 5.30 g (86 %). MS (EI): $m/z$ (%) = 539 (51) [M$^+$], 459 (68) [M−Br]$^+$, 379 (1) [M−2Br]$^+$ 293 (9) [M−2Br–2$^i$Pr]$^+$. Anal. Calc. for C$_{19}$H$_{24}$Br$_2$MoP (539.12): C, 42.33; H, 4.48. Found: C, 41.73; H, 4.48%.

### 4.6. *[(o-$^i$Pr$_2$P–C$_6$H$_4$–$\eta^7$-C$_7$H$_6$)Mo(CH$_2$SiMe$_3$)$_2$(Mo–P)]* (**7b**)

A solution of **6b** (500 mg, 0.93 mmol) in THF (20 ml) was treated with a large excess of Me$_3$SiCH$_2$MgCl (9.3 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 **7b** as an orange, crystalline solid. Yield: 445 mg (90%). MS (EI): $m/z$ (%) = 554 ( < 1) [M$^+$], 467 (1) [M−CH$_2$SiMe$_3$]$^+$, 379 (2) [M−2CH$_2$SiMe$_3$]$^+$. Anal. Calc. for C$_{27}$H$_{46}$MoPSi$_2$ (553.74): C, 58.56; H, 8.37. Found: C, 59.30; H, 8.99%.

Table 2
Crystallographic data for **3b**, **4b**, **5b**, **6b**, and **7b**

| | **3b** | **4b** | **5b** | **6b** | **7b** |
|---|---|---|---|---|---|
| Formula | $C_{21}H_{25}MoO_2P$ | $C_{21}H_{24}BF_4MoO_2P$ | $C_{20}H_{24}BrMoOP$ | $C_{19}H_{24}Br_2MoP$ | $C_{27}H_{46}MoPSi_2$ |
| Formula weight (amu) | 436.32 | 522.13 | 487.21 | 539.11 | 553.73 |
| Crystal system | tetragonal | monoclinic | monoclinic | triclinic | orthorhombic |
| Space group | $I4_1/a$ (no. 88) | $C2$ (no. 5) | $P2_1/n$ (no. 11) | $P\bar{1}$ (no. 2) | $P2_12_12_1$ (no. 19) |
| Unit cell | | | | | |
| $a$ (Å) | 29.8475(11) | 14.1728(18) | 7.3399(3) | 7.4390(12) | 10.0229(14) |
| $b$ (Å) | 29.8475(11) | 10.1940(13) | 17.3379(7) | 8.4097(13) | 13.3649(19) |
| $c$ (Å) | 8.7098(5) | 15.613(2) | 15.2786(6) | 16.236(3) | 21.519(3) |
| $\alpha$ (°) | 90 | 90 | 90 | 77.982(3) | 90 |
| $\beta$ (°) | 90 | 104.198(2) | 98.674(1) | 80.976(3) | 90 |
| $\gamma$ (°) | 90 | 90 | 90 | 75.498(3) | 90 |
| $V$ (Å$^3$) | 7759.3(6) | 2186.8(5) | 1922.1(1) | 955.9(3) | 2882.5(7) |
| $D_{calc}$ (g cm$^{-1}$) | 1.494 | 1.580 | 1.684 | 1.873 | 1.276 |
| $Z$ | 16 | 4 | 4 | 2 | 4 |
| $\mu$ (mm$^{-1}$) | 0.770 | 0.721 | 2.848 | 4.947 | 0.606 |
| Unique data | 3407 | 5003 | 4418 | 5474 | 6950 |
| Observed data $\{I > 2\sigma(I)\}$ | 3138 | 4273 | 4017 | 4915 | 6631 |
| $R_1$ (observed data) (%) | 2.22, $wR_1 = 5.30$ | 3.74, $wR_1 = 7.24$ | 2.28, $wR_1 = 5.26$ | 3.29, $wR_1 = 7.66$ | 2.81, $wR_1 = 6.11$ |
| $R_2$ (all data) (%) | 2.50, $wR_2 = 5.42$ | 4.71, $wR_2 = 7.54$ | 2.63, $wR_2 = 5.39$ | 3.79, $wR_2 = 7.88$ | 3.02, $wR_2 = 6.17$ |
| Goodness-of-fit | 1.075 | 0.958 | 1.046 | 1.053 | 1.057 |
| No. of variables | 326 | 312 | 319 | 304 | 280 |
| Res. electr. dens. (e Å$^{-3}$) | 0.37/−0.20 | 0.67/−0.33 | 0.65/−0.34 | 1.22/−1.08 | 0.87/−0.35 |

### 4.7. *X-ray crystallography*

All data sets were collected at −120 °C with a Bruker AXS APEX diffractometer equipped with a rotating anode using Mo–$K_\alpha$ radiation ($\lambda = 0.71073$ Å). Empirical absorption correction with SADABS [29] (for **4b**, **6b** and **7b**) was applied to the raw data. Structure solution in all cases with SHELXS [30] and refinement with SHELXL [31] with anisotropic thermal parameters for all atoms. Hydrogen atoms were added to the structure models on calculated positions are unrefined. Hydrogen atoms for **3b**, **5b** and **6b** were located in the difference Fourier map and were refined with isotropic thermal parameters. ORTEP [32] was used for all drawings. Additional crystallographic data are listed in Table 2.

## 5. Supplementary material

Crystallographic data (excluding structure factors) for the structures **3b**–**7b** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 194077–194081. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

## Acknowledgements

This work was financially supported by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie and the government of North Rhine-Westphalia (Bennigsen-Foerder-Preis 2000 to M.T.). M.T. is grateful to Prof. W.A. Herrmann (Munich) for the appointment to temporarily represent the Chair of Inorganic Chemistry at the Technische Universität München.

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